A STUDY OF KINETICS AND MECHANISM OF ADSORPTION ON ACTIVATED CARBON

AND

MECHANISM OF ACTIVATION

A Thesis
Presented for the degree of
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JAHAN ARA BEGUM

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In memory of my
departed parents

Jahan Ara Begum.

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This thesis which is submitted for the consideration of an award of the degree of Doctor of Philosophy is a record of work carried out by the author in the laboratory of the Institute of Fuel Research and Development, BCSIR, Dhaka. The work described here is wholly original except where due reference has been made.

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ABSTRACT

Massive literature is available on adsorption equilibria but only few studies had been directed towards adsorption kinetics and mechanism, particularly, in solution.

The present investigation was thus undertaken to gain a better insight into the mechanism of adsorption by studying kinetics of adsorption from solution on activated carbon (from cocoanut shell).

For the purpose iodine and acetic acid were choosen as adsorbate for this study considering their general use in evaluating activated carbon. This study included study of isotherms, isobars, isosteres and kinetics of adsorption.

The adsorption isotherms in the temperature range $303^{o}k$ - $363^{o}k$ were found to be of type V (for acetic acid) and type III (for iodine) of Brunauer's classification. An attempt was made to analyse iodine adsorption data by using Langmuir equation as modified by Kipling and it was found that both the solvent and solute were adsorbed on the carbon surface.

A semi-empirical equation developed by Liszi was used to explain the kinetic data of iodine and acetic acid adsorption on activated carbon. The equation was represented as

$$v = \frac{t}{\gamma + \delta t}$$

where, v = quantity adsorbed by a unit mass of the adsorbent during the time t.

γ, δ = constants depending on pressure/concentration

t = time.

The kinetics of adsorption were studied in the temperature ranges $303^{o}k$ - $363^{o}k$. The kinetic data showed that the results were in agreement with the Liszi equation. The order of adsorption varied from 0.66 to 1.2 for iodine and from 1.48 to 2.00 for acetic acid except at $323^{o}k$ when the order was found to be low (1.07). The rate constant values were used to get an idea of the magnitude of the activation energy of adsorption which varied from 0.4358 Kcal/mole to 2.74 Kcal/mole for iodine. The activation energy for acetic acid showed a constant value of 5.36 Kcal/mole. Heats of adsorption were determined by isosteric method. The value obtained for acetic acid varied from .44 Kcal/mole to 7.45 Kcal/mole in the temperature ranges $303^{o}k$ - $363^{o}k$ and for iodine from 0.4919 Kcal/mole to 3.0926 Kcal/mole in the temperature ranges $303^{o}k$ - $363^{o}k$. These low values of activation energies and heats of adsorption indicated that the adsorption of acetic acid and iodine on activated carbon was Vander Waals' type i.e. physical adsorption.

The mechanism by which activated carbon functions are yet to be explained clearly. A thorough understanding of the sorptive mechanism was therefore essential for accomplishing the most effective use of active carbon. It was found that both particle diffusion and mass action contribute to the kinetics of iodine and acetic acid adsorption on carbon. A mechanism for adsorption consistent with the experimental results is suggested. Mathematical expression for the phenomena were formulated for both iodine and acetic acid.

The specificity of zinc chloride treated activated carbon was explained. It was found that very minute quantities of zinc were held strongly by active carbon on certain areas of carbon surface or internal pores. This perhaps was responsible for specificity though it was not possible unequivocally to assign a mechanism for the activation of carbon.

The measurements of the surface areas was undertaken as it was a highly significant parameter in nearly all physical and chemical processes of adsorption involving powdered solids. Iodine adsorption and BET (Brunauer, Emmett and Teller) methods were used to measure the surface areas of different carbons. A value of $41.14A^{o2}$ was used for the molecular area of iodine. This value gave surface areas of different adsorbents (carbon) consistent with those obtained by the BET method. The iodine adsorption method was simple, and determination of the surface areas were made fairly quickly. The method was free of lengthy and complicated calculations involved in the BET method.

Symbols and Abbreviations used

q = Amount adsorbed at certain time t (in g.).

p = Equilibrium pressure.

t = time.

q_m = Monolayer volume.

q_a = Heat of adsorption.

T = Temperature (°K).

q_d = Differential heat of adsorption.

q_{st} = Isosteric heat of adsorption.

E_a = Activation energy of adsorption.

R = Gas constant.

K = Specific rate constant.

A = The frequency factor.

K_a = Rate constant for adsorption.

K_d = Rate constant for desorption.

θ = Fraction of the surface covered (surface coverage) i.e.
amount adsorbed in g.

δR = radius.

S = Surface area.

W = The surface concentration.

D = Diffusion co-efficient.

C = Concentration of the solution at equilibrium.

C_o = Initial concentration of the solution.

CONTENTS

Chapter I. INTRODUCTION.

Chapter 2. Experimental.

Chapter 3. Results and Discussion.

CHAPTER I. INTRODUCTION.

1.1 ACTIVATED CARBON:

The term 'activated carbon' comprises a family of substances which is a porous carbonaceous material having a strongly developed internal surface . But no definite structural formula can be assigned to activated carbon nor its identity can be proved by any chemical analysis. It is stated that, 'carbon has a memory' and the adsorption characteristics of an activated carbon are dependent on the history of its preparation. The characteristics of activated carbons are known to vary with the raw materials used, the conditions of activation and the nature of the activating agents. The same raw materials can be transformed into different members of the family by giving appropriate treatments during preparation.

The only way of identifying an activated carbon is by its adsorptive and catalytic properties. Various modifications of the same process of activation are found to alter the adsorption characteristics of carbon for different types of adsorbates in different ways i.e. each method of activation leaves a characteristic imprint on the adsorptive powers. The activation of carbon is generally considered to consist in one or more of the following processes: (i) increasing the active surface area, eg by increasing the porosity (it is to the highly porous structure that the extensive specific surface area of active carbon, amounting to hundreds of square metres per gramme is due) ; (ii) removal of any substances, inorganic or organic which might poison the active centres ; (iii) producing fresh active centres, which might consist of unoriented carbon atoms of higher energy potential on the surface or the fixation of other polar atoms or groups on the surface.

The physical structure, the porosity, and the accessibility of the internal surface of active carbons to the molecules in the liquid or solution or gas phase exert fundamental influence on their specificity and selectivity. The selectivity of activated carbon makes it suitable for a wide variety of its use, such as decolourisation, vapour adsorption, solvent recovery, purification of industrial gases, catalyst carrier etc. The mechanism by which activated carbon functions to remove the undesirable impurities from solutions have never been clearly explained. A thorough understanding of these sorptive mechanism is essential for accomplishing the most effective use of active carbon in the above mentioned fields.

1.2 GENERAL METHODS OF PREPARATION:

The methods of preparation of activated carbon are summarised in Fig. 1.1

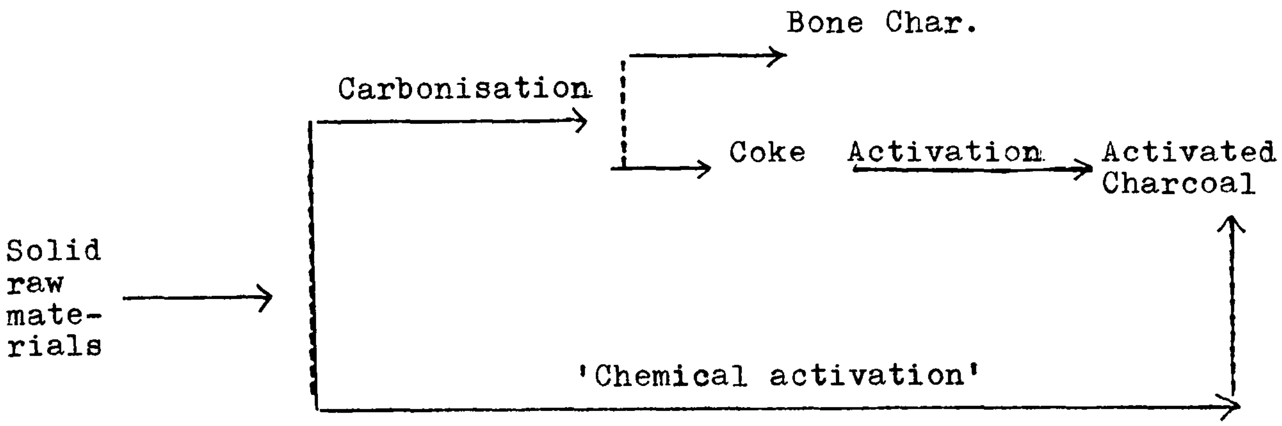


Fig. 1.1 Schematic representation of different methods for the preparation of active charcoal.

Details of the manufacture of commercial charcoals [1-6] are relevant here only in so far as they are related to the properties of the products. The raw materials are always organic, and nearly always of biological origin, though a few experimental products have been made from synthetic polymers, eg polyvinylidene chloride (Saran charcoals) [7-8] and divinylbenzene copolymer[9]. Charcoals having the finest pores have been made from hardwoods[10], nutshells and in recent years, from various grades of coal. The suitability of coal varies with the rank, and in order to achieve satisfactory mechanical as well as adsorptive properties, it is usual to blend a caking with a non-caking coal. These are ground to fine powder, briquetted under high pressures without a binder, and carbonised at a low temperature [11-13] (600°C). The open pore structure of gas coke shows the need for preliminary treatment. A remarkable variety of other substances has been investigated [3,4].

Two stages, viz., carbonisation and oxidation are recognised in the production of an activated charcoal. In 'carbonisation' the original material is pyrolysed in the absence of air to remove most of the elements other than carbon as volatile compounds[14]. For a given material the fundamental structure of the carbon residue, in particular its potential pore-structure, is determined by the precise conditions used in the carbonisation process, especially in the case of coal [11,12,15]. In the oxidation stage the reagents used are mostly gaseous (air, oxygen, chlorine, sulphur vapour, CO_2 etc.) and most of them give rise to an exothermic process.

The reaction with steam, however, is endothermic, which makes control of temperature easier (especially in the industrial scale) and hence the reproducibility of the product, a factor to which little attention seems to have been paid in most early work. Deitz[4] gives extensive reference to early work in his book.

Both the activating agent and the temperature of activation affect the properties of the product. The endothermic processes usually need a higher working temperature than the exothermic processes ; air[6] and sulphur[16] vapour react readily at 300°-600°C, whereas steam and CO_2 need a temperature of 700°-1000°C, depending on the type of charcoal being activated [17,18]. Lower temperatures are possible if the reaction is catalysed, and some catalysts such as potassium carbonate may occur in the charcoal as ash. On this subject there is a considerable amount of literature of which only a few references may be cited [10,119-132]. The kinetics and reaction mechanisms of these processes have been discussed[131] and reviewed recently.

Several processes in which carbonisation and activation are carried out in one operation have been devised. They are sometimes termed rather unsatisfactorily, 'chemical activation'. The raw material is intimately mixed with a dehydrating and / or oxidising agent such as $ZnCl_2$, phosphoric acid, or potassium sulphide, and heated in the absence of air. In many cases, the activating agent liberates a gas which assists the development of an extensive pore system. The advantage of an one-stage process is somewhat offset by the need (in most cases) to remove the inorganic materials left in the charcoal.

This is not always completely successful ; a typical $ZnCl_2$ - activated wood charcoal was found to contain 6.38% of ZnO (Zinc oxide)[19]. As with raw materials, a considerable number of activating agents have been investigated, but only a few have found wide acceptance[3].

1.3 DEFINITION AND TYPES OF ADSORPTION :

Adsorption is one of the most fundamental properties of surfaces, being the essential underlying cause for a wide variety of interfacial and colloidal phenomena. Surface of a substance is the exterior of a material body. However, a surface is actually a boundary because where the mass of one body ends the mass of another begins. When a solid is immersed in a liquid, the surface of the solid faces a corresponding surface of the liquid ; the region enclosed by these two surface are known as interface, and it is within this interfacial region accumulation of a substance i.e. adsorption occurs. So adsorption is a surface phenomenon.

When two immicsible phases are brought into contact, it is usually found that the concentration of one phase is greater at the inter-face than in its bulk resulting from inelastic collision suffered by the molecules on the surface. Negative adsorption results in a lower concentration of the species in the interface than in the bulk. Although there is no chemical distinction between the molecules or atoms on the surface and the molecules or atoms in the bulk, energy consideration lead to quite dissimilar properties.

It is considered that atoms in any surface are subject to unbalanced forces of attraction perpendicular to the surface plane, and therefore possess certain unsaturation. Adsorption occurs due to this unsaturation of the surface. The valency requirements of the atoms or molecules on the surface are not fully satisfied by bonding with nearby atoms, and thus they possess certain unsaturation. The two immiscible phases in which the adsorption phenomena are observed may be of various types eg gas-solid, solid-solid, gas-liquid, solid-liquid, and liquid-liquid.

An interfacial phenomenon, whether at gas/solid or liquid/solid interface, is exciting in the sense that we are taken to a new world of two dimensions. Of these again, the gas-solid systems are fascinating because of the diverse nature of the phenomenon at such interface. A gaseous system consists of an assembly of a large number of particles swiftly flying at random in all possible directions, with wide range of translational velocities. When such molecules strike a solid surface, a few things may happen. The gas molecules may undergo reflection like a perfectly elastic body, but this is rarely the case. Although the molecules are moving constantly, they tend to spend sometime on the solid surfaces as if the tired molecules want to take some rest in a sitting place. Some mysterious forces operate and these forces may be termed in a non-committal form as 'residual field of forces'. The gas molecules impinging against any solid or liquid surface, condense on the surface being held by the field of force of the surface atoms. These molecules may subsequently evaporate from the surface.

The length of time that elapses between the condensation of a molecule and its subsequent evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this time lag. This time lag or the resting time of the gas molecules may vary over a wide range, from 10^{-13} sec. to any large period one can imagine.

In the case of adsorption from solutions, differences found between the adsorptive behaviour of vapours and that of solutes can be traced to a different character of the interface. In solid/gas interface, the gas space serves primarily as a reservoir from which molecules are delivered to, or received from the interface.

The solid/liquid interface presents a definite contrast ; here the liquid side of the interface exerts a number of positiv influences as for example, (i) attraction of sorbent surface for solute, (ii) attraction of sorbent for solvent, (iii) solubilizing power of solvent for solute, (iv) association, (v) effect of solvent on orientation at interface, (vi) ionization, (vii) competition for interface in presence of multiple solutes, (viii) interactions of multiple solutes, (ix) Co-adsorption, (x) molecular size of molecules in the system, (xi) Pore size distribution in the adsorbent, and (xii) surface area of the adsorbent. The intensity, magnitude, and direction of influence will vary according to the specific assortment of solutes and solvents ; the resultant can serve to augment, modify or nullify the attractive forces exerted by the adsorbent side of the interface.

Differences in adsorption characteristics of solutes and gases including vapours are revealed by studying temperature. An elevation in temperature increases the escaping tendency of a vapour or gas from the interface and invariably diminishes the adsorption especially in the case of physical adsorption. Similar action operates at the carbon/liquid interface, but here it is often dwarfed by the influence of temperature on solvent affinities. This should not be taken to mean that temperature is without influence on adsorption from solution ;certainly temperature can have much influence on the magnitude and direction of many factors mentioned above [i.e. from (i) to (xii)] and thereby alter the course of an adsorption. But the resulting action is quite specific ; instances are known in which a change in temperature increased the adsorption of one ingredient and simultaneously decreased the adsorption of another ingredient in the same system. Some substances, after becoming adsorbed, undergo a change so that they are no longer soluble and such changes may be accelerated by a rise in temperature.

The extent of adsorption from solution increases with concentration; but it is probable that a limit is attained in adsorption by a solid surface from solution, just as is the case in the adsorption of gas by a solid or a gas-liquid interface. It is certain that whatever the mechanism of adsorption from solution, the extent depends mainly on the available surface of the adsorbent, although specific factors are sometimes evident, especially with colloidal particles. The order in which a series of solutes are taken up from the solution is therefore, in general, very much the same for different forms of charcoal, silica, and other finely divided adsorbents. The process of adsorption is almost invariably reversible and a definite equilibrium is reached in a short time dependent on the concentration of the solution and the quantity of the adsorbent.

Adsorption generally takes place with a decrease in free energy and entropy. The extent of adsorption depends on the amount of free surface exposed and the pressure or concentration, the nature and kind of adsorbent and that of the adsorbed substance and on the temperature of the system. Adsorption when involves the condensation of several layers is termed as multimolecular.

Long experience has revealed that there are mainly two types of adsorption, depending on the nature and the extent of forces acting between the adsorbent and the adsorbate. If the surface is saturated, i.e. if the valency requirements of the atoms on the surface is satisfied, adsorption tends to take place only through the forces of physical attraction. This type of adsorption is called physical or Vander Waals' adsorption. The nature and mechanism of physical adsorption is similar to that of condensation of vapour on the surface of its own liquid. Second type of adsorption is chemisorption, which results due to the unsaturation of the surface. In chemisorption such a surface will tend to form chemical bonds with a nearby phase.

Though physical adsorption and chemisorption has been differentiated in various ways, in a surface phenomenon where there is a transition from one process to another it is not always possible to separate them with exactness. Even then there are few features distinguishing these two processes.

In considering the nature of bonding it may be stated that in physical adsorption no chemical bonds are broken or made and the chemical nature of the adsorbate is therefore unchanged as there is no electron transfer between the adsorbate and the adsorbent.

In chemisorption, adsorbate may undergo chemical changes and may be dissociated into independent fragments i.e. electron transfer takes place in chemisorption. Radicals and atoms are thus the units of which adsorbed layers are made.

Two separate problems are involved in the consideration of the mechanism of chemisorption — the nature of the surface bond and the nature of the surface radicals. There is evidence that each of the three main types of chemical bond — the ionic, covalent and co-ordinate, may be formed in chemisorption. For ionic bond, the ease of passage of electrons across the surface plane, that is the magnitude of the work function may decide both the ease of formation and strength of the bond. Covalent bonds can only be formed if the adsorbent possess orbitals with unpaired electron capable of entering into covalence. Co-ordination by donation of electrons to the adsorbent requires the latter to have a vacant orbital capable of receiving the pair of electrons. These considerations suggest that the nature of the surface bonds formed in the adsorption of particular molecules depend largely on the electronic structure of the adsorbent and therefore specificity in chemisorption and catalytic reactions also arise mainly from this factor. The presence of defects in the crystal lattice of the adsorbent is one of the important factors which govern the process of chemisorption.

Physical adsorption which involves only the Vander Waals' types of forces is found to occur at relatively low temperature. Since chemisorption involves forces of chemical nature, it occurs specially at relatively high temperature and it is indicated by

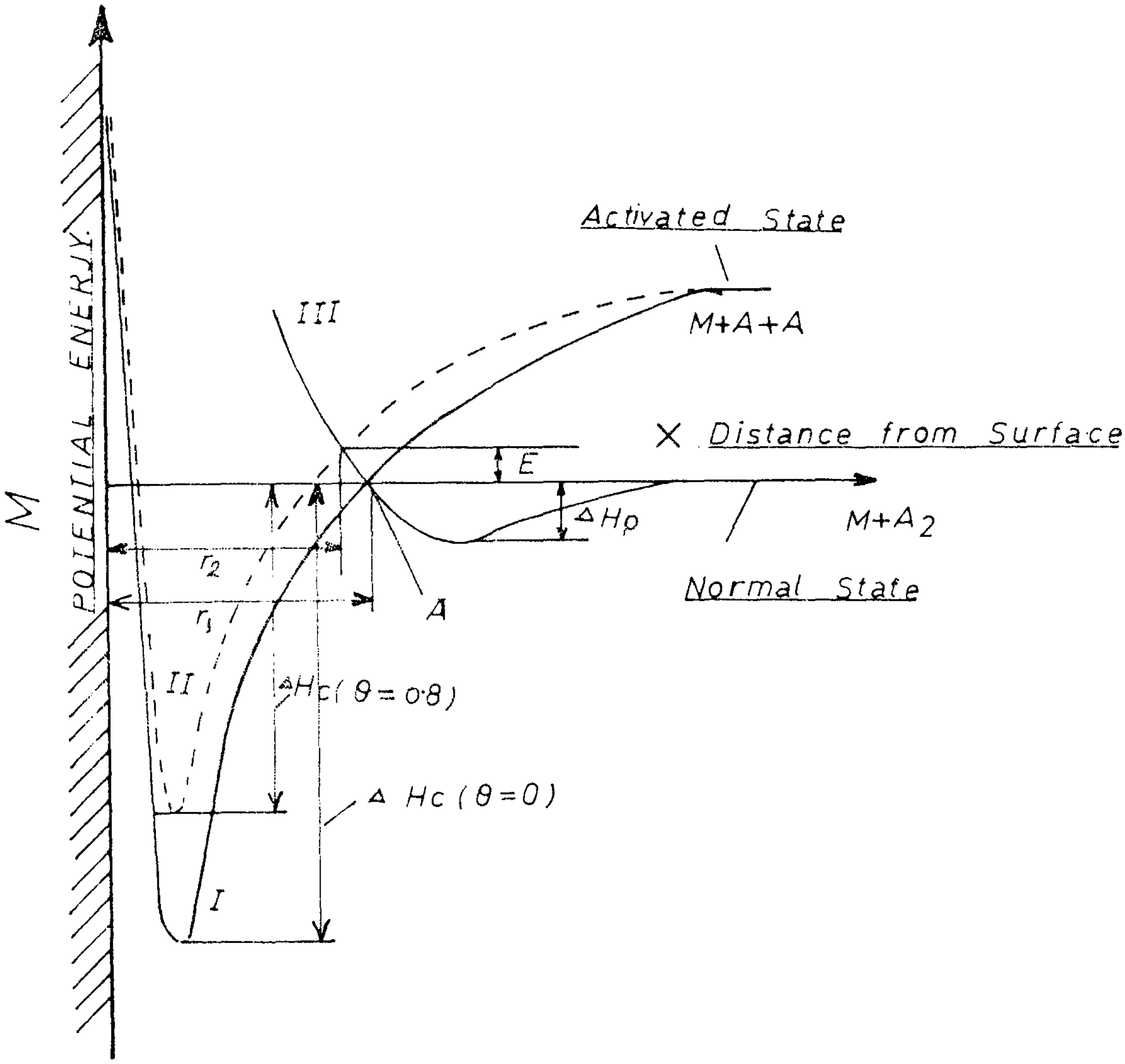


Figure - 1.2 : Schematic representation of the local course of the energy for the physiosorption and chemisorption processes for a hypothetical system, composed initially of a molecule A_2 and a solid surface M. Curves (I) and (II) are the potential curves for the chemisorbed state at coverages of $\theta \to 0$, and $\theta = 0{\cdot}8$ respectively. Curve (III) is the potential energy curve for the molecule x_2, with reference to the surface M. ΔH_p is the heat of physiosorption; ΔH_c is the heat of chemisorption and E is the energy of activation when $\theta = 0.8$.

SOURCE : Ref. 20.

high heat of adsorption and activation energy.

Both physical adsorption and chemisorption processes are accompanied by changes of some potential energy. It may sometimes happen that chemisorption is initially unactivated and that as coverages increase it becomes activated. This kind of behaviour can be understood by reference to the potential energy diagram as shown in Fig. 1.2, which refers to a hypothetical system[20].

Two potential curves (i) and (ii) are drawn for the chemisorption process ; the first (which corresponds to a coverage of $\theta \approx 0$) is lower than the second, (which refers to a relatively high coverage $\theta \approx 0.5$ — 0.8) because at low coverages the more active sites will be occupied preferentially while at higher coverages only the less active sites will be available. As the molecule A_2 approaches the solid surface M, it is first physically adsorbed (curve (iii)) with a heat of adsorption Δ Hp. When the molecule has reached within a distance r_1 it is in a position to cross over to curve (i) if the surface is virtually bare ; no energy of activation is needed because the crossing point A is located below the line of zero potential. If however, the coverage is already high, an energy of activation E will be necessary to bring about a transfer from the physisorbed to the chemisorbed state because the point of intersection of curves (iii) and (ii) is located above the line of zero potential i.e. they cross in a region where the repulsive forces predominate. Thus a fast and non activated chemisorption will take place at low coverages followed by a slow and activated chemisorption taking place at high coverages. This model as described here is too simple to apply to all cases[21].

One of the most important criterion to distinguish between physical adsorption and chemisorption is the measurement of the heat of adsorption. Chemical bonds are normally stronger than physical forces of attractions ; so heat of chemisorption should therefore be large while heats of physical adsorption should be low. Chemisorption processes are usually accompanied by high enthalpy changes, usually in the range of 10-150 kcals/ mole, while that for physical adsorption is comparable with the heat of liquifaction having values in the range of 2 - 10 kcals/ mole. Measurements of heat of adsorption therefore often provide a useful but not always decisive method (because more recent work has shown that the heats of chemisorption can be far smaller than was previously believed) to determine the extent of the surface interaction and hence the type of adsorption. In making comparisons it should be noted that in both types of adsorption, because of surface heterogeneity and lateral interaction effects, the heats of adsorption may vary considerably with surface coverage. This effect is particularly marked in chemisorption where the lateral interaction forces, being invariably repulsive, reinforce the effects of heterogeneity.

Adsorption processes are generally exothermic, therefore it is expected that the extent of adsorption of gases on solid surfaces at a definite pressure should decrease with increase in temperature in accordance with the principle of Le Chatelier. In case of physical adsorption, the amount of substance adsorbed decrease with rise of temperature. But the process of chemisorption, which involves forces of chemical nature, mostly shows a positive temperature co-efficient i.e. the amount of adsorption increases with rise of temperature.

Physical adsorption is generally a reversible process but the process of chemisorption is usually characterized by irreversibility.

Physical adsorption and chemisorption may sometimes be distinguished by their different rates of approach to equilibrium. Physical adsorption is instantaneous but, with highly porous or finely powdered adsorbents, diffusion of the adsorbate molecule into the adsorbent mass is often slow, particularly at low pressures. Chemisorption may be instantaneous but there are many systems where chemisorption involves an activation energy. In both physical and chemical adsorption, precise measurements may be hampered by the establishment of a pseudo - equilibrium. Thus the outer strata of adsorbent are more heavily covered with adsorbate than the centre of the solid mass ; subsequent redistribution of the adsorbed film to give uniform coverage at all points in the solid mass is sometimes an extremely slow process. Clearly, the use of a rate criterion to distinguish physical from chemical adsorption is associated with complications.

Other important criteria to distinguish physical adsorption and chemisorption are changes in the optical property, magnetic susceptibility and magnetic anisotropy of the adsorbed molecules. The change of electrical and magnetic properties are associated with chemisorption and they characterize the type mechanism operated in chemisorption of a particular system. The nature of the surface radicals is of interest because they decide the mechanism of catalytic reactions. Dipole moment measurements are also useful for identifying the type of adsorption. Now a days, infrared spectroscopy, NMR spectroscopy and field emission microscopy have been successfully employed for investigation of adsorption of gases on solids.

Chemisorption is more specific in its chemical nature than physical adsorption. In the case of chemisorption the maximum extent of adsorption will be the formation of a monolayer of adsorbed species on the adsorbent. However, a monolayer of adsorbed species is seldom realised, as in chemisorption the adsorbed species became electrically charged and form a barrier for further exchange of electrons between the adsorbent and the adsorbate. In case of physical adsorption such electrostatic interactions are absent and formation of several layers of adsorbed species on the adsorbent is possible, particularly at low temperature.

Under certain conditions two types of adsorption take place simultaneously and a sharp differentiation is impossible.

1.4. GENERAL APPROACH TO ADSORPTION STUDIES :

When an adsorbate is adsorbed on the surface of an adsorbent, the following informations are of interest.

(i) Nature of adsorption viz physical or chemical,

(ii) Conditions (temperature, pressure, state of the adsorbent) under which physical or chemical adsorption takes place.

(iii) Thermodynamic data regarding the adsorption process. These include the amount of adsorbate adsorbed under various equilibrium pressures at definite temperatures, the isosteric heat of adsorption etc.

(iv) The fate of the adsorbed molecule ; whether it is adsorbed chemically unchanged or is dissociated. How is it bonded to the adsorbent ? ; the nature of the bond between the adsorbent and the adsorbate eg ionic, covalent etc ; the strength of the bond between the adsorbed species and the adsorbent.

(v) The rate of a particular types of adsorption and the factors influencing the rate ; whether it is fast and non-activated or is slow and activated or is so slow as to be undetectable in a reasonable period of times;if it is an activated process then the magnitude of the energy of activation of the process.

The most significant and resourceful information in the study of any surface phenomena is obtained from the adsorption equilibria expressed as isotherms, isobars and isosteres.

1.4.1 ADSORPTION EQUILIBRIA :

The process of adsorption of an adsorbate molecule 'X_2' on the surface sites 'S' of a solid adsorbent may be expressed as[22]

$$X_2 + S \rightleftharpoons S - X_2\ (\text{ads})$$

Then the equilibrium constant K of the process is

$$K = \frac{[(S - X_2)\text{ads}]}{[X_2][S]}\ , \quad [\ ]\ \text{denotes concentration}$$

$$\text{Therefore,}\quad [(S - X_2)\text{ads}] = K[X_2][S]$$

If $[S - X_2]_{\text{ads}}$ is measured as a function of the equilibrium pressures or concentrations of X_2 (that is, the pressure or concentration of the adsorbate after the adsorption process has reached equilibrium) at a definite temperature, then an isotherm is obtained.

1.4.1.1. Adsorption isotherms:

An isotherm can be viewed as a map of the way in which an adsorbable solute distributes itself between the adsorbent and the solvent. Isotherms can convey an overall picture of many data more clearly than could be derived directly from numbers. Experimental measurements of the amount adsorbed, q, as a function of pressure (or concentration) and temperature may conveniently be plotted in the form of adsorption isotherms[22].

$$q = f(p)_T$$

Isotherms are essentially plots of the free energy change as a function of amount adsorbed. Their shape can also yield qualitative information about the adsorption process and semiquantitative measure of the fraction of the surface covered by adsorbate (and hence, with assumption, the surface area of the adsorbent). For these reasons and because they can be measured directly, isotherms are the most commonly used p-q-T plots in the adsorption studies.

Although adsorption isotherms with shapes ranging from the monotonous to the very complicated types have been reported in the literature, the classification introduced by Brunauer et al.[23], for systems at temperatures below the critical temperatures of the gas, is nonetheless valuable. Five principal forms of adsorption isotherms encountered by them in adsorption studies are illustrated in Fig. 1.3. Type I is characterized by the formation of a complete monolayer. Type II is very common in the case of physical adsorption and undoubtedly corresponds to multilayer formation. Type III is relatively rare, an example is the adsorption of bromine on silica

Gel and characterized by a heat of adsorption equal to or less than the heat of liquifaction of the pure adsorbate. Type IV and V are characteristic of multilayer adsorption on highly porous adsorbents, the flattening of the isotherms at the highest pressure being attributed to capillary condensation phenomena and may show hysteresis effects. A number of equations each with a definite theoretical model have been developed to relate the dependence of the amount adsorbed with the equilibrium pressure or concentration of the adsorbate and if there is an agreement between the experimental isotherm and the theoretical isotherms, some insight into adsorption process may be gained.

Of the several proposed theoretical and empirical isotherms, the Langmuir[19,24], the Freundlich[25], the Gibbs'[26], the Tempkin[27], and the BET[28] isotherms are important. Each of these isotherms is characterized by certain assumptions and each applicable to certain experimental systems.

Langmuir isotherm: The Langmuir isotherm is the best known of all the isotherm equations, mentioned above, partly because of the simplicity of the equation itself and the physical picture behind it, and partly because a great many experimental isotherms fit the equation reasonably well. The isotherm is represented mathematically in the following way:

$$\frac{p}{q} = \frac{1}{aq_m} + \frac{p}{q_m} \qquad \ldots\ldots\ldots\ldots \qquad (1.1)$$

where, 'p' is a definite equilibrium pressure and 'q' is the amount of substance adsorbed at that pressure. 'q_m' is the volume of gas adsorbed to form a complete monolayer and 'a' is a constant. This equation is the most ideal form of the equation for adsorption isotherm, and is based on certain fundamental assumptions as follows:

(i) The energy of adsorption is constant, and independent of the extent of surface coverage, which, in turn, implies that the surface is entirely uniform in nature.

(ii) Adsorption is localised and takes place only through collision of gas molecules with vacant sites and interaction among the adsorbate molecules is negligible.

(iii) Each site can accommodate one and only one adsorbed particle and forms the so called adsorption complex.

(iv) Adsorption is confined to unimolecular layer where the concentration of the adsorbate can attain a limiting maximum value.

Thus the Brunauer[23] type I isotherm as shown in Fig. 1.3 is the Langmuir type, which is characterized by a monotonic approach to a limiting adsorption which corresponds to a complete monolayer. For an adsorption where the adsorbate molecule dissociates into two radicals each occupying one site, the Langmuir equation be rearranged to the form[23]

$$\frac{\sqrt{p}}{q} = \frac{1}{\sqrt{a}\,.qm} + \frac{\sqrt{p}}{qm} \qquad .... \qquad .... \qquad .... \qquad (1.2)$$

where the symbols have the same meaning as before. Thus Langmuir isotherm besides enabling us to calculate the surface area of the adsorbent from the amount of gas required to obtain monolayer coverage, indicates whether a gas molecule is dissociatively chemisorbed. It is not irrelevant to mention here that the best method to calculate the surface area of the adsorbent is by the BET method.

<u>Freundlich isotherm</u>: Many experimental isotherms fit the empirical isotherm of Freundlich which may be expressed in the form,

$$q = cp^{1/n} \quad \ldots \quad \ldots \quad \ldots \qquad (1.3)$$

Or, the logarithmic form,

$$\log q = \log c + 1/n \log p \ldots (1.4).$$

where p and q have the same meaning as before 'c' and 'n' are temperature dependent parameters. The quantity 'n' which is generally greater than one, is characteristic of a particular system. Although the Freundlich isotherm was developed empirically, it can be derived theoretically by assuming that the surface of the adsorbent is heterogeneous, and the heat of adsorption falls logarithmically with coverage.

Gibb's isotherm: Gibb's derived an equation for adsorption isotherm based on thermodynamic principles and can be represented as

$$\Gamma = - \frac{d\gamma}{dc} \cdot \frac{c}{RT} \quad \ldots \quad \ldots \quad \ldots \qquad (1.5)$$

where, 'γ' is the surface tension of the solution, 'Γ', the excess concentration (i.e. concentration in excess of the concentration in the bulk) of the solute on the surface, 'c', the concentration of the solute, 'R', the gas constant and T, the absolute temperature. Gibb's method however gives approximate values.

Tempkin isotherm: Tempkin isotherm is applicable to chemisorption processes showing linear dependence of the heat of adsorption on the extent of surface coverage. The equation for Tempkin isotherm is

$$\log p = A + Bq_a \quad \ldots \quad \ldots. \qquad (1.6)$$

where, 'A' and 'B' are constants, 'p' is the pressure and 'q' is the heat of adsorption.

<u>BET isotherm</u>: Brunauer, Emmett and Teller have developed from kinetic considerations, a very important isotherm where provision is made for the formation of multilayer. They actually showed how to extend Langmuir's approach to multilayer adsorption, and their equation has come to be known as the BET equation, which can be represented in the following way:

$$\frac{p}{q(p_o - p)} = \frac{1}{q_m c} + \frac{c - 1}{q_m c} \cdot \frac{p}{p_o} \quad \ldots\ldots \quad \ldots\ldots \quad (1.7).$$

where, 'q', 'p', 'q_m' have the same significance as in the Langmuir equation and 'c' is a constant which is related only to the heat of adsorption, heat of liquefaction of the adsorbate and temperature of the experiment and 'p_o' is the saturation vapor pressure of the adsorbate at the particular temperature. This sort of isotherm is found only in the case of physical adsorption, and it is widely used for determining the surface area of solids.

1.4.1.2 <u>ADSORPTION ISOBARS</u>: The function $q = f(T)_p$ at a constant pressure (or concentration) i.e. the variation of the amount of substance (adsorbate) adsorbed with temperature at a constant equilibrium pressure or concentration is called the adsorption isobar. A study of the adsorption isobar can often furnish useful information about the nature of adsorption. If one type of adsorption operates, the quantity adsorbed at constant pressure will fall monotonically with increasing temperature ; if two or more kinds operate in different temperature ranges the uptake of adsorbate may increase with temperature between these ranges and the isobar shows maxima and minima.

1.4.1.3 ADSORPTION ISOSTERES: Further information can be secured from a study of adsorption isosteres,

$$P = f(T)_q$$

i.e. isosteres represent the pressure required to bring about a definite extent of adsorption in equilibrium at different temperatures. These cannot be measured directly because it is impractical to hold 'q' constant. Instead, values of P and T corresponding to fixed values of 'q' are interpolated from a family of adsorption isotherms. Provided the heat of adsorption does not vary significantly over the temperature range studied, plotting the isosteres in the familiar form log P vs 1/T will yield a family of straight lines, each corresponding to a fixed value of the amount adsorbed. The linearity of the isosteres, incidentally provides a useful check on the internal consistency of the isotherms. So the most significant application of isosteres is in determing the isosteric heat of adsorption.

1.4.2. HEAT OF ADSORPTION:

It has already been mentioned that the magnitude of the heat of adsorption often indicates whether adsorption is physical or chemical. Heat of adsorption is also dependent on the coverage. It is usually found to decrease with coverage. Two important reasons for this decrease are:

(i) The surface of the adsorbent is heterogeneous. The more active sites are covered first, so that heat of adsorption is high at low coverages.

(ii) The adsorbed species interact with one another, so that when the coverage is high, such interaction is also high and so the heat of adsorption is low.

Measurement of the heat of adsorption:-

Heats of adsorption may be determined from isosteres, from desorption rates or measured calorimetrically. The integral heat of adsorption can be calculated directly by the calorimetric method. From the integral heat of adsorption, the differential heat of adsorption q_d can be calculated by operation suggested by the equation

$$q_d = \left[\frac{dQ}{d\theta}\right]_{\Sigma,T} \quad \dots \quad \dots \quad (1.8)$$

where, Q is the integral heat of adsorption, Σ the surface area of the adsorbent and T is the temperature in ^oK at which the heat of adsorption is measured, θ is the surface coverage.

In a system where calorimetric method is impracticable the isosteric method is the only alternative. The basis for the determination of the heat of adsorption by the isosteric method is the application of the clausius - Clapeyron equation,

$$\left(\frac{\partial \ln P}{\partial T}\right)_\theta = \frac{q_{st}}{RT^2} \quad \dots \quad \dots \quad (1.9)$$

where for a particular coverage θ , P is the equilibrium pressure at temperature T and q_{st} is the isosteric heat of adsorption. By the application of this equation to the adsorption data at different temperatures, the isosteric heat of adsorption q_{st} can be obtained. From thermodynamic consideration q_{st} may be correlated with q_d by the equation,

$$q_{st} = q_d + RT \quad \ldots \quad \ldots . \quad (1.10)$$

Thus the isosteric method, to all intents and purposes, can be looked upon as a substitute for the calorimetric method in obtaining the relevant information.

Equation (1.9) itself cannot be used to determine the heat of adsorption. It is the integral form of (1.9) which is useful. Equation (1.9) can be expressed either in definite integral form

$$q_{st} = 2.303\ R \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1} \quad \ldots \quad \ldots \quad (1.11).$$

or, in the indefinite form,

$$\log p = \frac{-q_{st}}{2.303\ RT} + \text{Const.} \quad \ldots . \quad \ldots . \quad (1.12)$$

and the value of q_{st} can be evaluated by carrying out the operation, specified by each of the above forms. In using equation (1.11) data can be derived from any two isotherms ; in using equation (1.12) the requisite data are to be derived from the adsorption isosteres. A linear isostere is then constructed by plotting $\log P$ vs $1/T$, whose slope gives the isosteric heat of adsorption.

The definite integral form given by equation (1.11) is highly useful in determining the value of q_{st} over the selected ranges of temperature corresponding to various regions of isobars. This procedure gives average heat of adsorption between the two temperatures used in this calculation.

Determination of heat of adsorption by equation (1.12) is useful to show how q_{st} values vary with temperature. By determining the q_{st} values at various coverages prediction can be made about the heterogeneity of the surface and the mobility of the adsorbed layers.

1.4.3 KINETICS OF REACTION WITH SPECIAL REFERENCE TO KINETICS OF ADSORPTION :

Chemical reactions involve the forming and breaking of chemical bonds. As a result, the products have properties and geometrical structure different from that of the reactants. All chemical reactions take place at a definite rate. It is the study of the rates at which such reactions occur, and the influence of certain conditions on the rates, which are included in the subject of chemical kinetics. In the study of reaction kinetics, reactions are divided into classes determined either by molecularity, that is, by the number of atoms or molecules whose concentrations determine the velocity, or kinetics of the process.

Chemical kinetics is concerned fundamentally with the details of the process whereby a system goes from one state to another and with the time required for the transition. Equilibrium can also be treated in principle on the basis of kinetics. The experimental study of the various factors such as concentration, pressure, temperature etc, which influence the rate of the reactions are included in chemical kinetics. Finally, the kinetic data are used to explain the rate in terms of the reaction mechanism.

1.4.3.1 Methods of Kinetic study of reactions:

In a kinetic study of a reaction there is no way of measuring the rate directly in a simple manner ; normally the rate of a chemical reaction is expressed as the variation in concentration of either reactants or products with time at constant temperature. Thus the rate of the reaction,

$$A + B \longrightarrow C$$

is given by

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{d[C]}{dt} \qquad \text{concentration/time.}$$

where, $[A]$, $[B]$, $[C]$ denote the concentration of A, B and C and 't' the time. Plotting a curve with concentration vs time the slope of the curve at any time gives the rate of the reaction at that time. Therefore, the determination of reaction rates by conventional methods reduces to a study of concentration as a function of time.

In general, analytical procedures may be divided into two broad categories, chemical and physical. Chemical analysis involves a direct determination of the concentration of one of the reactants or products by volumetric or gravimetric procedures, the former being preferred because of rapidity. Chemical methods of analysis have the advantage of giving an absolute value of the concentration. But since the rates of a reaction are very sensitive to temperature, the reaction temperature must be carefully maintained constant by the thermostatic control during the kinetic investigation of the reaction system.

On the otherhand, physical methods of analysis are usually much more convenient than the chemical methods. A physical method is one which measures some physical property of the reaction mixture, the property changing appreciably as the reaction proceeds. So, there must be a substantial difference in the contribution of the reactants and products to the particular physical property choosen. This is one requirement of any physical measurements as a criterion of the extent of reaction. Another requirement is that the physical property will be preferably a linear function of concentration that is the property varies in a simple manner with the concentration of reactants and products. Such a relationship exists, for example, between concentration and electrical conductance, optical density, rotation of polarized light and pressure of gases. In dilute solutions many other physical properties such as the specific volume, refractive index, vapour pressure, and fluidity become linear functions of the concentration. In practice, of course, many of these linear relationships will break down if applied over too wide range of concentration, due to the deviations from the ideal behaviour and also nonlinearities in the mathematical forms of the ideal laws relating the properties to concentration.

1.4.3.2 Adsorption Kinetics: The study of adsorption kinetics gives very interesting information about the type and mechanism of the adsorption process concerned. The adsorption process may be treated as a chemical reaction following some definite order and the measurement of the temperature co-efficient of the specific adsorption rate shows whether the process is activated or not. The rate will appear to be independent of temperature in non-activated chemisorption processes.

For kinetic studies, the fall of pressure with time due to adsorption, volumetric method of adsorption measurements can be used. Treating the adsorption process as a chemical reaction between the adsorbate molecules and the adsorbent sites, the usual rate equations for chemical reactions may be tested. However, the adsorption data seldom fit the conventional rate equations. This is not surprising, as the adsorbent sites are almost always heterogeneous in nature, and there is interaction between adsorbed species.

From the rate measurements, information regarding the type of adsorption can be obtained. Rate data also reveal distinction between the following types of adsorption:

(i) Activated adsorption without the participation of a precursor:- This type of adsorption is characterized by exponential increase in the rate with increasing temperature, continuous fall in the rate with increasing coverage, direct propertionality of rate to the pressure of the adsorbate.

(ii) Non-activated adsorption: This is characterized by zero or negative temperature co-efficient of rate, proportionality of rate to the pressure.

(iii) Activated adsorption with participation of a precursor:- This type is characterized by an exponential increase in the rate with temperature, continuous fall in the rate with increasing coverage, no simple dependence of the rate on the adsorbate pressure.

1.4.4. <u>ACTIVATION ENERGY</u>: The effects of temperature on homogeneous and heterogeneous reactions are generally described in terms of the Arrhenions equation.

$$\frac{d \ln K}{dt} = Ea/RT^2 \quad \dots \quad \dots \qquad (1.13)$$

where, K is the specific rate constant, R the gas constant and Ea the energy of activation for homogeneous reactions. Ea is taken as the energy with which molecules must be supplied, by collision or otherwise, before they can react. In general, E_a is related to the magnitude of the energy barrier which must be surmounted by the reactants. A similar significance is frequently assigned to E_a for the case of chemisorption, E_a being taken as a measure of the excess energy required by the adsorbate to permit the formation of a chemical bond between the adsorbate and the surface. The integrated Arrhenious equation

$$\ln K = \frac{-E_a}{RT} + \text{constant} \quad \ldots \quad \ldots \qquad (1.14)$$

is used and, by graphical procedures or suitable algebraic manipulation, a value of E_a results from kinetic data obtained at two or more temperatures. However, in view of certain as yet unresolved complexities, the significance of E_a for adsorption cannot be analogous to that for homogeneous reactions.

Equation (1.14) may be written as follows:

$$K = A.e^{-E_a/RT} \quad \ldots \quad \ldots. \qquad (1.15)$$

where, 'A' is a constant which is usually known as the frequency factor for the reaction. The factor $e^{-E_a/RT}$ is recognised as the Boltzman expression for the fraction of systems having energy in excess of the value of E_a and this fraction correspond to the activated complex. Hence, according to the above equation (1.15), a plot of log K against 1/T should be linear with a "-"ive slope having the value $^{-E}/2.303$ R and intercept being equal to log A. Thus the constants 'A' and 'E_a' may be evaluated.

1.5 REVIEW ON ADSORPTION OF GASES ON SOLID ADSORBENTS OTHER THAN CARBON AND DIFFERENT RATE EQUATIONS:

The adsorption of gases on solids proceeding at a measurable rate has been the subject of numerous investigations. The influence of varying experimental conditions on adsorption kinetics has been studied by various means, but the individual investigations are mainly incomplete, at times fragmentory, and are scattered through the literature of four decades. Comparison of data is further hindered by lack of uniformity in representation of rate data. Attempts to represent the experimental data by algebraic mass-action functions involving integral or fractional powers of concentration, or by partial pressure of gas and a constant rate parameter of definite order, have not been successful. Various empirical formulations for adsorption kinetics were often unconvincing and limited to the particular adsorbate-adsorbent system under consideration.

Most of the rate equations for adsorption that have been used originate from the concepts of Langmuir's mechanism[19,24]. The observed rate of adsorption is considered as the difference between the rate of adsorption and the rate of desorption.

$$\frac{dq}{dt} = K_aP(1-\theta) - K_d\theta$$

where, θ is the fraction of the surface that is covered, and K_a and K_d are the rate constants for adsorption and desorption respectively. Approximations are necessary to apply this relation. At conditions far removed from the steady-state condition, $(1-\theta) \approx 1$, and desorption can be neglected. An expression for "driving force" in terms of distance from equilibrium coverage or pressure may be added.

Thus Kobukowa[29] considered the expression

$$\frac{dq}{dt} = K_a (P - P_e)$$

where Pe is the equilibrium pressure. Integrating with $\frac{dq}{dt} \approx -\frac{dP}{dt}$ yields

$\ln (P - P_e)/ P_s - P_e = kt$, where Ps is the initial pressure. For adsorption of methane on nickel at about 10^{-} cm of Hg, Kobukowa obtained straight lines on plotting log(P - Pe) vs t. However, only five or six points were obtained for experiments for 60 minutes duration. Barrer[30] similarly expressed the adsorption of hydrogen on graphite and diamond. For hydrogen-charcoal Kingman[31] assumed that $K_d = 0$ and that $\theta \approx q \approx (P_s - P)$, obtaining

$$dq/dt = K_1 P(K_2 + P).$$

Equations are elaborated by Troesch[32] for constant volume and constant pressure systems. Classical equations are given elsewhere[33,34] in detail for cases such as adsorption of more than one gas, or dissociation.

Ward[35] considered gas uptake to be partly a solution process with diffusion of gas from the surface to the interior as the rate-controlling step. The equation

$q = 2 SW \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}}$ was proposed, where 'S' is the surface area, W the surface concentration of gas, and D the diffusion co-efficient. Plots of q versus $t^{\frac{1}{2}}$ for the hydrogen-copper system were linear at low coverages, but deviations from linearity occured and increased with increasing coverage. This equation was also used by Morozov[36] for the adsorption of hydrogen on iron.

To correct for deviations Ward[35] assumed that the copper adsorbent was in the form of spheres of radius σ_R and that A was constant. The corrected general equation was,

$$q = A\left[4/3\,\pi\sigma_R^3 - \frac{8\sigma_R^3}{\pi} \sum_{1}^{\infty} 1/n^2 \, \exp\left(-kn^2\pi^2 t/\sigma_R^2\right)\right]$$

where k and n are constants. The fit of the last equation to hydrogen-copper data extends to higher coverages than that of the first, but seems still inadequate. Wards[35] mechanism of solution is obsolete.

Burwell and Taylor[37] observed that data for different experiments on chemisorption of hydrogen on Cr_2O_3 gel would approximate a common curve when 'q' was plotted against 'bt', 'b' is a constant whose value is characteristic of temperature and pressure. Putting $b = P^n A \exp\left(-E/RT\right)$ improved the approximation which, however, still remained inadequate. These data were examined by Clarke, Kassel, and Storch[38], who note that, when a smooth curve is drawn through the points of one experiment on a q-t plot, extrapolation to the starting time would indicate an appreciable amount of adsorption coincident with the beginning of the experiment. This amount is 0.2 + 1.1 ml [and is equivalent to the amount qo mentioned by Taylor and Thon[39]] and was subtracted from q values to give corrected values, q_c, which were applied to a derived equation. The latter was obtained from a simple model involving a primary adsorption process followed by diffusion to secondary adsorption sites. The equation,

$$tP = (k_1 + k_2P)q_c + (k_3 + k_4P)q_c^2$$

gave reasonable results, plots of $\frac{tP}{q_c}$ vs q_c being linear except at initial conditions. Howard and Taylor[40] used the equation,

$$\frac{dq}{dt} = k_1 q^{k_2}$$

to express the rate of adsorption of hydrogen and ethylene on Cr_2O_3 gel. The constants k_1 and k_2 are stated to be independent of q over wide intervals and are characteristic of the surface and the gas. The integrated equation is

$$\log q = k_3 + k_4 \log t$$

On plotting log q against log t, line showing a slight curvature are obtained. A general equation of the form $q = k_1 t^{k_2}$ is used by Bangham and Burt[41,42] to describe the adsorption of carbondioxide and ammonia by glass. This is later used in different corrected form. Thus Maxted and Moon[43,44] used an equation

$$dq/dt = nk(q_e - q)t^{n-1}$$ which on integration

becomes $\frac{q_e}{q_e - q} = kt^n$

where q_e is the amount adsorbed at the end of the process and k and n are constants. Data for the adsorption of hydrogen and deuterium on platinum, plotted as log log $\frac{q_e}{q_e - q}$ vs log t, yield straight lines upto about 0.4 q. Maxted and Hassid[45] expressed data for the adsorption of oxygen on platinum in similar fashion.

Ijima used a similar equation,

$\log \frac{p}{p - p_e} = k_1 + k_2 t$, to express the adsorption of hydrogen, deuterium, and ethylene on nickel[46-49]. Kwan[50] has deduced a power rate law, expressed as

$$-\frac{dp}{dt} = k_1 p\,\theta^{-k_2} - k_3\theta^{k_4}$$

where, θ is the fractional coverage. The constants are obtained by evaluating $-\frac{dp}{dt}$ graphically from the p-t curve. $\log\left[\left(\frac{-dp}{p\,dt}\right)\Big/\frac{1-p}{p}\right]$ is then plotted against $\log\theta$. Here p is the pressure of gas which would be in equilibrium with the amount of gas chemisorbed at time 't' and may be estimated from the isotherm. If the reverse rate is negligible it is sufficient to plot $-\frac{dp}{p\,dt}$ vs $\log\theta$ i.e. the $k_3\theta^{k_4}$ term is neglected. A simpler equation was proposed earlier by Ghosh, Sastri and Kini[51,52,53].

According to a table of Kwan[54] the power rate law is applicable to the adsorption of hydrogen on nickel[46], carbon[55], ZnO[56], and Cr_2O_3[57], oxygen on $CuO.Cr_2O_3$[58] ; of nitrogen on promoted iron[59] and tungsten[60,61], and of hydrogen and carbonmonoxide on Fischer-Tropsch catalyst.[51,52]

The common characteristics of such empirical or derived equations is that they frequently fail to represent rate data over considerable portions of an experiment. Even when 'straight lines' are obtained for some part of a rate plot, the representation of data is imprecise and at times improper and incompatible with the equation tested because of simplication or of approximations of values of 'qe' or 'pe' or 'p'. Also, scatter of data over 'linear' portions sometimes is not random. For example, for Howard and Taylor's[40] data on the adsorption of hydrogen on Cr_2O_3 at 383°C, q changes from 4.0 ml at t = 2 min to q = 28.1 ml at t = 120 min.

In view of uncertainty in representing rate data, above equations are almost useless from the mechanistic point of view. Most of the kinetic data (for gas-solid system) obtained so far have been attempted to explain by the well known Elovich equation[39,62-66] which can be represented as

$$\frac{dq}{dt} = ae^{-\alpha q}$$

The integrated form of the equation is expressed as

$$q = \frac{2.3}{\alpha}\log(t + t_o) - \frac{2.3}{\alpha}\log t_o$$

where,

q = amount of gas chemisorbed at time 't' and

t_o = a constant, which is defined as $t_o = \frac{1}{a\alpha}$, 'a' and 'α' are also constants whose values are dependent on the pressure and temperature of the particular run. The value of the constants 't_o' is chosen to linearize the plot of q against log(t + to). The elovich equation, however, has general application to chemisorption kinetics. Ritchie[67] developed an alternative to Elovich equation

$$\frac{d\theta}{dt} = \alpha(1 - \theta)^n$$

which on integration gives

$$\frac{1}{(1-\theta)^{n-1}} = (n - 1)\alpha t + 1, \text{ for } n \neq 1 \quad .... \quad (A)$$

or $\theta = 1-e^{-\alpha t}$, for n = 1 .... (B), where,

θ = fraction of the surface sites which are occupied by adsorbed gas.

n = number of surface sites occupied by each molecule of adsorbed gas.

α = the rate constants, and t = time.

It is assumed that no site is occupied at $t = o$. If we introduce the amount of adsorption, "q" at a time 't' ; equation (A) becomes

$$\frac{q_{\alpha}^{\,n-1}}{(q_{\alpha} - q)^{n-1}} = (n-1)\,\alpha t + 1$$ and similarly

equation (B) becomes

$$q = q_{\alpha}\left(1 - e^{-\alpha t}\right),$$ where q_{α} is the amount of adsorption after infinite time.

Jaroniec[68,69] derived the equation of A.G. Ritchie (1977) for the kinetic adsorption isotherm on the basis of the theory describing the kinetics of adsorption of gases on energetically heterogeneous solid surfaces. This equation was also generalized to the kinetics of adsorption of multicomponent gas mixtures. Balasubramanian[70] introduced a small correction due to initial rapid chemisorption on some favoured surface sites in the equation of A.G. Ritchie for the analysis of kinetics of chemisorption of gases on solid surfaces. The correction factor can be computed by a successive approximation procedure, and use of the equation then yields consistent values for the various kinetic parameters.

D.S. Javanovic (1969) derived an equation[71] for physical adsorption isotherm. But the equation is based on an erroneous assumptions concerning the rate of adsorption. When the correct formulation is used, the resultant isotherm is that due to Langmuir.

1.6 REVIEW ON ADSORPTION OF GASES ON CARBON ADSORBENTS :

Adsorption on carbons merits individual attention. Although voluminous literature[3,4,72] is available on adsorption, the actual knowledge of the properties of carbon adsorbents is rather limited. Few data on chemisorption kinetics are available and their meaning is obscured by inadequacy of knowledge[73] of the physical and chemical properties of the adsorbent and by the frequent occurence of surface interactions other than simple chemisorption. Some recent work indicates that charcoals contain significant amounts of hydrogen, that the surface is acid[22,74] and that it contains free radicals[75-77] and surface complexes[19,74,78-81]. An electron resonance study[76] suggests the existence of two types of oxygen interactions with the surface. The structure and properties of coals are similarly unknown[82] and there is some indication that with some uptake of organic vapors under conditions of physical adsorption there are irreversible changes in the adsorbent structure[83]. Some recent literature on sorption by coals is reviewed[84,85]. Oxidation phenomena are not pertinent.

Lendle[86] expressed oxygen adsorption on sugar charcoal in the range 0-350°C by the empirical formula :

$$q = k_1 - k_1 \exp(-k_2 t) = k_1 (1 + e^{-k_2 t}).$$

Data are given in a graph, and a table gives q values at times of 10,30,50,70 and 90 min. The nature of the q-t curves (the latter being given as continuous curves without experimental points) reflects a rapid adsorption in the first 10 - 20 min, followed by a relatively slow uptake for the remainder of the experiment. Elovich plots of the data, as well as the shapes of the q-t plots, suggest the presence of two kinetic stages. However, the data are too sparse to permit precise curve fitting and can be used only qualitatively.

Kingman[55] measured the kinetics of hydrogen adsorption on a Norit G.R. charcoal, degassing at 950°C between runs. The rate at 420 - 530° was proportional to the pressure p and to the extent available surface, i.e.

$$-\frac{dp}{dt} = k_1 p(c-q)$$

where q is the amount adsorbed and k_1 and c are constants. Some change in k_1 was noted and attributed to a change in the surface due to the high-temperature degassing. Kingman noted that in the first few minutes the rate was always greater than that calculated and suggested the presence of a few very active carbon atoms with which reaction occurs with great rapidity. Elovich plots of the data of the two sample runs given show no such deviation in the early stages of the reaction ; eg, in one case the Δp-logtplot was linear from 0.1 to 2 hr. and curved sharply towards the t-axis over the next 4 hr, thus showing the general characteristics of a reaction which was desirable by the Elovich equation over about 90 percent of its course and which then decelerated markedly as an end-point was approach. These characteristics are those which may be predicted from the experimental method, a much smaller volume of gas than that required to saturate the surface.

Barrer[87] studied the interaction of hydrogen with charcoal over a large temperature range. The kinetics were expressed by

$$\frac{-dp}{dt} = k\,(p - pe)$$

where, pe is the pressure at equilibrium. No q-t data are given. The temperature dependence of the kinetics complex, shown by the plots of the rate constant k versus T°C. Between 300°C and 600°C, k is exponentially dependent on T, while above 600°C there is proportionality with $t^{\frac{1}{2}}$. Such latter dependence is characteristic of diffusion and has been taken to indicate penetration of gas into the interior of the adsorbent. The kinetics of chemisorption of methane and methane-d_4 have been expressed by the same rate equation as for hydrogen[88].

Barrer[30] found a small but strong chemisorption of hydrogen on diamond. That adsorption, and that of hydrogen on graphite were characterized by an initially rapid adsorption rate which was followed by a steady decrease in speed. When log $(p-p_e)$ is plotted as a function of t, the graphs showed curvature, and for not too great degrees of surface coverages, θ, the equation

$$d \log (p-p_e)/dt = k(1-\theta)\exp\left(-E/RT\right)$$

can be used. No q-t values are given. Plots of the apparent activation energy E versus θ for graphite, two charcoals, and diamond reflects a difference in behaviour of the adsorbents. The diamond curve is concave to the q-axis, not convex as for the other carbons, and it does not commence with a small E value at small q as do the plots for the other carbons. Barrer attributed these differences to variations in the carbon - carbon distances of the adsorbents.

For the adsorption of oxygen on diamond, there are four effects[30]. (A) At $-78^\circ C$ predominantly physical adsorption occured. There was a slight chemisorption (B) From 0° to $199^\circ C$ physical adsorption was slight in comparison with chemisorption. On successive addition of oxygen, adsorption proceeded more and more slowly. The residual gas atmosphere is pure oxygen (C) From $244^\circ C$ to $370^\circ C$ a burst of carbondioxide occured at each admission of oxygen until, when all the oxygen is consumed, nearby pure carbondioxide remained. The amount of the carbondioxide is very much smaller than the amount of oxygen originally taken up. (D) At higher temperatures the oxide surface film itself decomposed, the supernatant gas consisting of carbon monoxide and carbondioxide. The rate of sorption was given as

$$-\frac{dp}{dt} = k(1 - \theta)p$$

but was of limited applicability because k was a function of coverage. No q-t data ha been given.

An analysis of kinetic data of the adsorption of oxygen, hydrogen, and carbonmonoxide on charcoal has been made by Keyer and Roginsky[89], who have compared four kinetic expressions of Rhead and Wheeler[90,91]. The kinetic expressions are shown below:

1. $\ln \frac{p_o}{p_o -} = kt$

2. $q_s = A \ln(t + t_0)$

3. $q_s = A_1 t^{1/n}$.

4. $\frac{dq}{dt} = k(p_o - q_s)(s_o - q_s)$, where '$q_s$' being expressed in percent of initial amount of gas s_o. Of these, the linear log q - log t plot being preferred, this bilogarithmic law

being related to the statistical theory of a nonhomogeneous surface having an exponential distribution of site energies. Plots of log q versus log t for the three runs of Rhead and wheeler are roughly linear, but there is considerable scatter of points, as there is also for Elovich plots of the same data. Those plots, however, indicate a discontinuity at about 8 min. The q - log t plots of Keyer and Roginsky's data on the adsorption of oxygen on charcoals containing potassium carbonate or copper (II) acetate, given in a small graph, are S-shaped and show some scatter of points. The authors preferred log q vs log t plots, which are linear but also show scatter. The data are inadequate for precise curve fitting. Again, the Elovich plots have the characteristics of plots showing more than one kinetic stage. For Burstein's data[92] on the adsorption of hydrogen on platinized charcoal, Keyer and Roginsky similarly prefer linear log q - log t plots to slightly curved q - log t plots. Again, there is considerable scatter of data. The q - log t plots could be discontinuous or could be linearized by replotting as log (t + k), but the number of points is not abundant. Similar remarks apply to the treatment of Burstein's data for the adsorption of carbon monoxide on charcoal.

Jonas and Svirbely[93] studied the adsorption kinetics of CCI_4 and $CHCl_3$ vapor on activated carbon and tried to fit their data into the equation,

$$t_b = \left[\left(\rho_B We/c_0 v_L\right)\right] \times \left[\lambda - \frac{V_L}{K_V} \ln \left\{K\left(c_0/c_b\right)\right\}\right] \qquad \ldots\ldots \qquad (1.16)$$

Where,

k_V = rate constants for the adsorption process.

c_b = break through concentration.

k = a factor depending on the shape of the adsorption isotherm obtained mathematically in the derivation as an integration constant.

v_L = the superficial velocity of gas-air mix

C_0 = the inlet concentration (g/cm^3).

λ = bed depth (cm)

t_b = time

w_e = the weight of the adsorbed substances in equilibrium with C_0 .

ρ_β = the bulk density (g/cm^3) of the adsorbed bed.

This equation (1.16) is too involved to be of general use. J. Liszi[94] studied and measured the rate of adsorption and desorption of carbondioxide on charcoal Nuxit BO in an isothermal, isobaric system. He developed a semi-empirieal rate equation,

$$\vartheta = \frac{t}{\gamma + \delta t} \qquad \ldots\ldots \quad \ldots \quad (1.17)$$

where 'ϑ' is the amount adsorbed. This equation (1·17) contains two constants γ and δ dependent on the pressure. From an examination of the equation, conclusion can be drawn that this equation is suitable to describe the time dependence of most sorption processes when the adsorbed mass is plotted against time, the resulting curves are first linear, but later on they approach limit values. The kinetic curves measured in different systems have similar shapes. They differ only in the slope of the initial, nearly linear region, in the sharpness of the 'bent', and in the magnitude of the saturation values. If the constants are suitably selected, equation (1.17) gives the sorption rates for different systems under different conditions. Müller[95] determined the rate of sorption of uranium hexafluoride on a copper catalyst, Wicke[96] on the system activated charcoal carbondioxide and Bergter[97] applied this equation to describe the rate of adsorption of steam on activated charcoal.

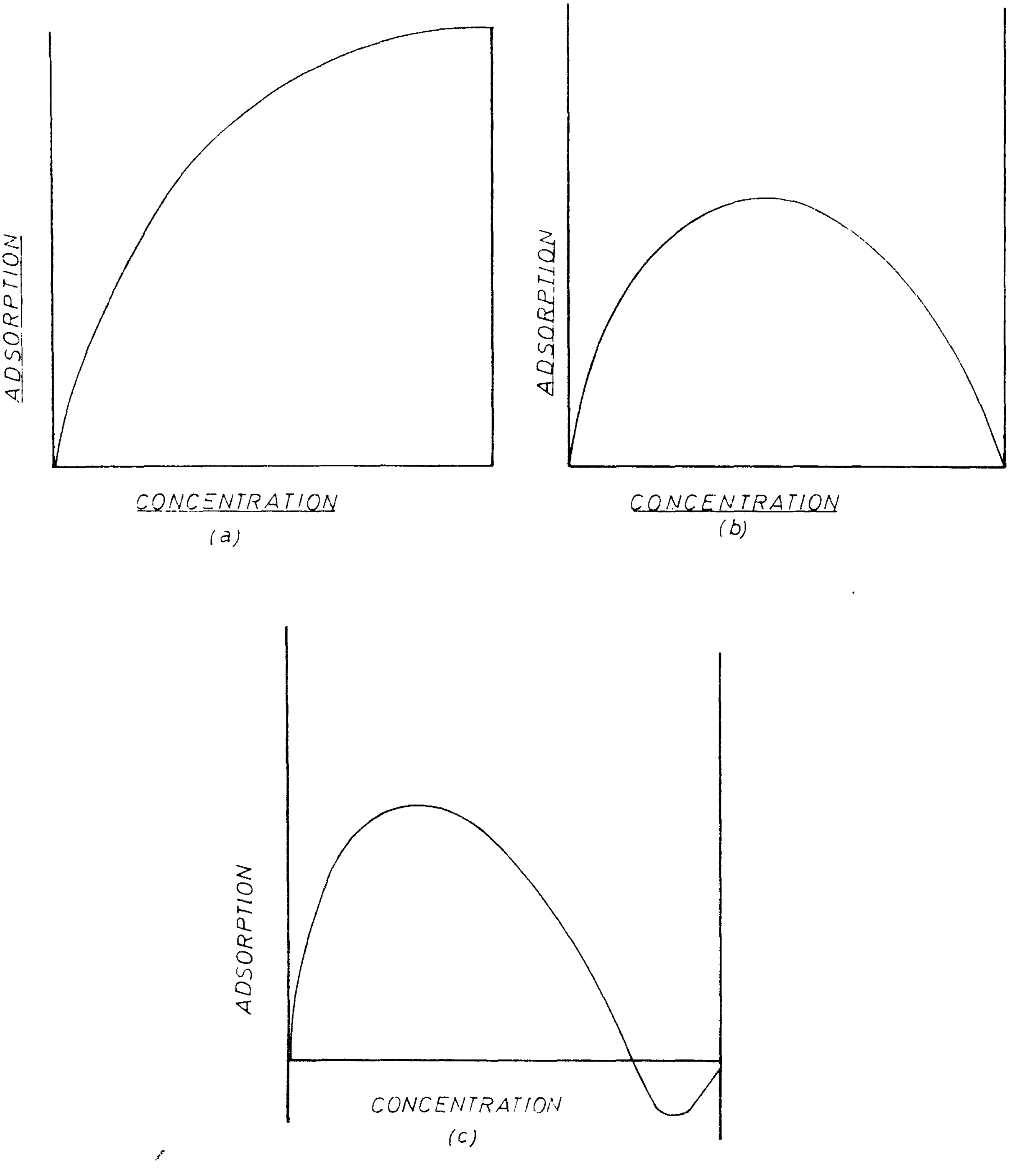
In résumé, several kinetic expressions have been more or less satisfactorily applied to gas-carbon kinetic data. Careful scrutiny suggests, however, that any claim for acceptance of a particular equation is definitely unwarranted. The state of knowledge of adsorption kinetics on carbons can be summarized as follows: (A) There are very few rate experiments (B) for those few experiments, not enough detailed q - t data exist. (C) Experimental precision is poor. There is too much scatter and too few points to permit precise curve fitting. (D) For the adsorption of oxygen, atleast, there is evidence for more than one gas-solid interaction. Probably all adsorption measurements should be accompanied by analysis of supernatant gas. (E) There are some crude and qualitative indications that more than one kinetic process is involved. (F) The lack of adequate data suggests that not only are adsorptions on carbon surfaces complex, but that their kinetics are unknown.

1.7. REVIEW ON ADSORPTION OF LIQUIDS FROM SOLUTION ON SOLIDS WITH REFERENCE TO CARBON.

A cursory study of the literature will reveal that the theory of adsorption of liquids on solids is very much less completely worked out than is the theory for adsorption of gases and vapours by solids. This is doubtlessly due to many factors that make the study of such phenomena in solution much more difficult to interpret with certainty than similar adsorption from the gas phase. To mention only one of these, adsorption from solution always involves a competition between atleast two adsorbates, the solvent and one or more solutes. Like the adsorption of gaseous mixtures, it is not very well understood.

In view of the incompleteness of the theoretical treatment that has been given, adsorption from solution upto the present time, it seems worthwhile merely to enumerate a few generalizations relative to the characteristics of such systems. Much of the original work on adsorption from solutions of solids (as on adsorption from solution generally) is described by Freundlich and summarised in his book[25], who carried out a great deal of the experimental work. In considering adsorption from dilute solutions, he has not made any distinction between solid and liquid solutes. Also, no distinction is made between systems of limited miscibility or solubility (eg aqueous solutions of phenol or benzoic acid) and those of complete miscibility (eg aqueous solutions of acetone or acetic acid). The early experiments have been almost entirely confined to dilute aqueous solution, the isotherm is assumed to represent the adsorption of the 'solute' and it is usually represented by the Freundlich equation. At low concentrations of dissolved materials, it is usually found that the amount of adsorption varies with the concentration of the dissolved substance according to the Freundlich equation[25] for solutions.

$$\frac{x}{m} = kc^{1/n} \quad \ldots \quad \ldots \quad (1.18)$$



(a)

(b)

(c)

FIGURE-14. TYPES OF ADSORPTION ISOTHERM (SOLID-SOLUTION SYSTEM)

SOURCE : Quart Rev 1951, 5, 60. J.J. KIPLING.

where, 'x' is the amount of solute adsorbed on 'm' grams of the adsorbent, 'c' is the concentration of the solution at equilibrium, k and n are constants, the form 1/n being used to emphasize that 'c' is raised to a power less than unity.

Later the Langmuir equation was used in a form thought to be appropriate for adsorption from solutions, the pressure terms being replaced by concentration terms. This has led to the use of adsorption from solution for evaluating surface areas of solids, although no justification is given for this application of the Langmuir equation to a type of systems for which it has not been derived.

The common shape of isotherm for adsorption of a solid from solution is shown in Fig. 1.4(a) both for solutions of solid (eg benzoic acid in water or stearic acid in benzene) and for solutions of liquid (eg acetic acid in water). This isotherm (Fig. 1.4(a)) can usually be fitted by Freundlich equation at low concentrations. If adsorption is examined upto the solubility limit, however, it is usually found that the curve becomes asymptotic to a limiting value of adsorption. It cannot, therefore, be fitted accurately by the Freundlich equation over the whole of the available range of concentration.

At higher concentrations, this equation (1.18) no longer applies. As a matter of fact, frequently the adsorption of the solute goes through a maximum and then decreases and becomes negative [98]. The manner in which the amount of adsorption varies with concentrations is well illustrated by the adsorption isotherms shown in Fig. 1.4 (a,b,c). It is probable that many of the examples that have been studied would have followed this course if they had been carried over sufficiently large ranges of concentrations.

Although the majority of the isotherms for adsorption of solids from solution have the shape shown in Fig. 1.4(a), several other shapes for adsorption from solution have been observed and recorded, but each is found for a few systems only. The isotherms have been classified by Giles et al.[98] according to the scheme shown in Fig.1.5. The main classification is based on the initial slope of the isotherm ; and the subclassification on the shape at higher concentrations.

The main classes are : (a) S curves which is obtained if (i) the solvent is strongly adsorbed, (ii) there is strong intermolecular attraction within the adsorbed layer, (iii) the adsorbate is mono-functional. The second condition is most likely to obtain if the major axis of the adsorbed molecules is perpendicular to the surface. By "mono-functional" is meant that the molecule has a single point of strong attachment in an aromatic system, or an aliphatic system of more than five carbon atoms; the adsorbate is moreover, not micellar. An example is a monohydric phenol, especially if adsorbed on a polar substrate from polar solvent. (b) L curves, the normal or Langmuir type isotherms. It may be found when there is no strong competition from the solvent for sites on the surface. Another possibility is that, if the adsorbate has linear or planer molecules, the major axis is paralled to the surface (c) H curves occur when there is high affinity between the adsorbate and adsorbent which is shown even in very dilute solutions. Thus it can result from chemisorption or from the adsorption of polymers or ionic micelles.

(d) C curves indicate constant partition of the adsorbate between the solution and the adsorbent. Linear curves are given by solutes which penetrate into the solid more readily than does the solvent. It appears mainly with textile fibres, into which the solute penetrates to further extents as its concentration in the solution is increased.

A number of isotherms show steps, the steps, in general, appear to mark a phase-change in the adsorbed layer or the onset of the formation of a second layer after completion of the first. A less common shape involves a wave rather than a step. The change in slope occurs at too small a value of adsorption to be due to the formation of a second layer of molecules, and there is no obvious phase-change which can occur. It is therefore thought that it indicates a form of co-operative adsorption[99]. Sometimes the deformation of adsorbate molecule may occur in the adsorbed film, the lateral interactions increasing the ease of adsorption[98]. This effect can occur only at relatively high surface coverages, and may therefore account for the position of the break between the two halves of the isotherm.

Several attempts have been made to derive a general equation for the adsorption isotherm for solution /solid system. The early attempts are summarized by Swan and Urquhart[100]. As yet, no simple equation has been put forward which can be applied universally. This undoubtedly arises from the wide range of complexity found in solutions.

The adsorption at the solid-solution interface is influenced by the nature of the substance to be adsorbed, the nature of the solid adsorbent, and the nature of the liquid medium. Many equations that have been derived, proved inadequate because the role of the solvent has been neglected. Advances in treating the solid-solution interface have depended on the recognition that the liquid phase contains at least two components. The nature of the adsorption isotherm has had to be reconsidered in the light of this.

It is formerly assumed that the change in concentration is a measure of the extent to which one component (the 'solute') has been adsorbed. The extent of adsorption is given by multiplying the change in concentration by the weight of solution used. It is tacitly assumed that the second component (the 'solvent') is not involved in the adsorption process, and can be regarded merely as a "space" in which the solute has played[101]. This concept may prove to be approximately valid for systems in which the 'solute' has very limited solubility in the "solvent". For systems in which the two components are completely miscible, however (eg. ethyl alcohol and benzene), neither can be regarded as solvent or as solute over the whole range of concentration. It thus becomes important to recognize that each component of the mixture may be adsorbed. The realisation that each component in a binary system (solvent and solute in a solution) is likely to be adsorbed brought forward many attempts to measure the adsorption values. The degree of "adsorption" of a solute is usually determined by comparing its concentration in a known volume (or weight) of solution before and after adsorption. It has then usually been taken that x g. of solute are adsorbed per g. of adsorbent, where,

$$x = v(c_0 - c)/1000\ m \quad \dots \quad \dots \qquad (1.19)$$

Where, Co = initial concentration of solution in g./l.

C = final concentration of solution in g./l.

v = volume of solution used in ml, and

m = weight of adsorbent in g.

Alternatively, a similar expression based on weight instead of volume, of solution has been used. There are two reasons for which this equation is unsatisfactory. First, it has been pointed out by Williams[101], and soon afterwards by Schmidt-Walter[102], that the equation ignores the change in total volume of the solution which is caused by the removal of the adsorbed material. Hence x, does not measure the true amount of solute adsorbed, it is based immediately on the difference between the initial and final concentrations of the solution, and is therefore referred to as the 'apparent adsorption' of the solute. Williams[101] developed an equation taking into account the change of volume which takes place on adsorption,

$$x' = M\,(Co - C)/\,m(1 - C) \qquad \ldots \qquad \ldots \qquad (1.20)$$

where concentrations are expressed in g. of solute per g. of solution and M,g. of solution. An alternative method of obtaining true adsorption values as been put forward by Ostwald & de Izaguirre[103]. This is a theory of adsorption which embodies an equation relating the true adsorption of each component to the concentration of the equilibrium solution. If x, and y g. are the actual amounts of solute and solvent adsorbed from M g. of solution, the concentration being initially Co and finally Cg. of solute per g. of solution, we have,

$$C = (MCo - x)\ /\ (M - x - y) \qquad \ldots \qquad \ldots. \qquad (1.21)$$

This is an equation which allows for change in volume due to adsorption.

Kipling[104] applied this equation which have been put forward by Ostwald and de Izaguirre. They have considered that both solvent and solute is being adsorbed, assuming that the adsorption of the solute follows the Langmuir's equation. The Kipling's modified form of equation can be put forward as

$$M(c_0-c) = x(1-c) - yc \qquad \ldots\ldots \qquad (1.22)$$

It is assumed that adsorption of the solvent as well as of the solute follows the exponential law, so that, $x = k_1c^{\alpha}$ and $y=mk_2(1-c)^{\beta}$ then

$$M(c_0-c)/m = k_1c^{\alpha}(1-c) - k_2(1-c)^{\beta}c \qquad \ldots\ldots \qquad (1.23)$$

This equation agrees in form with an equation derived by Williams[180] to relate apparent adsorption to true adsorption. Williams[101], however, only relates (c_0-c) to x and y, without making further assumption about the relation between x,y, and c. The constant of Kipling's equation can be obtained as follows:

At low c, the term $k_2(1-c)^{\beta}c$ is neglected, when equation (1.23) becomes

$$\frac{M(c_0-c)}{m} = k_1c^{\alpha}(1-c)$$

or $$\frac{M(c_0-c)}{m(1-c)} = k_1c^{\alpha}$$

or $$x = k_1c^{\alpha} \qquad \left\{ \text{when } x = \frac{M(c_0-c)}{m(1-c)} \right\}$$

or $$\log x = \log k_1 + \alpha \log c \qquad \ldots \qquad \ldots \qquad (1.24)$$

So, a plot of log x vs log c will give a straight line the value of 'α' and k_1 are obtained respectively from the slope and the intercept.

At higher concentration c,

$$\frac{M(c_0 - c)}{m} = k_1 c^{\alpha}(1 - c) - k_2(1 - c)^{\beta} c.$$

or $$\frac{M(c_0 - c)}{m} - k_1 c^{\alpha}(1 - c) = - k_2(1 - c)^{\beta} c.$$

or $$\Delta = - k_2(1 - c)^{\beta} c$$

[when Δ = the difference between $k_1 c^{\alpha}(1 - c)$ and the observed value $M(c_0 - c)/m$.]

or $$\left|\frac{\Delta}{c}\right| = k_2(1 - c)^{\beta}$$

or $$\log \left|\frac{\Delta}{c}\right| = \log \left\{k_2(1 - c)^{\beta}\right\}$$

or $$\log \left|\frac{\Delta}{c}\right| = \log k_2 + \beta \log(1 - c) \qquad \ldots \qquad (1.25)$$

Thus a plot of log $\left|\frac{\Delta}{c}\right|$ against log $(1 - c)$ will give a straight line. The value of 'k_2' and β are obtained from the intercept and slope respectively.

This cardinal feature of adsorption from solution seems first to have been clearly understood by Williams in 1913, and was later emphasized by Heymann and Boye[105]. It has, however, even now not been recognized by all text books. It is now possible to understand, qualitatively, the significance of isotherms of the type shown in Fig. 4(C). Over the first part of the concentration range, one component is adsorbed preferentially with respect to the first. This means that, at equilibrium, it is present in the adsorbed layer in greater proportion than in the bulk liquid. "Negative" adsorption of component 1 (i.e. solute) thus means preferential adsorption of component 2 (solvent). For completely miscible liquids, the isotherm must fall to zero at each end of the concentration range, as no change in composition at these points (i.e. of the pure liquids) is possible. This point has been emphasized by Patrick and Jones[106].

For solvents of approximately the same adsorbabilities, the concentrations of solutes required to cause a given amount of adsorption will, according to Freundlich[25], be in the same ratio as the solubilities of the solutes. He quotes experiments of Lundelius[107] to illustrate the rule. The adsorption of iodine on charcoal from carbondisulfide, chloroform, and carbon tetrachloride were the same in amount when the concentrations were in the ratio 4.5 : 2 :1, whereas the corresponding solubilities were in the ratio 4.8 : 1.8 : 1 . The value of the exponential term, l/n has been found to be the same for all three systems.

Another well-known relation dealing with the influence of the solute is Traube's rule[108]. It states that "the adsorption of organic substances from aqueous solutions increases strongly and regularly as we ascend on the homologons series". This behaviour is illustrated by Table - 1.1. As is evident, the ratio of the concentration of a given number of the homologous series to that of the next higher member required to give the same amount of adsorption on charcoal is approximately constant, and equal to a value between 2 and 3. This behaviour is

Table - 1.1 TRAUBE'S Rule for the adsorption of fatty acids by Blood-charcoal (t = 25°C).

Adsorbed Substance	Gram-mole per litre in solution for 1.26 mg. mole per gram adsorbed on charcoal.
Formic acid	0.251
Acetic acid	0.169
Propionic acid	0.056
Butyric acid	0.016

Source : Reference (25).

strikingly similar to the influence of these same solutes on the surface tension of water, and serve as an illustration of the importance of interfacial tension in adsorption from solution.

The conclusion must not be drawn, however, that the relative power of adsorption of different solutes can always be judged by their effect on the surface tension of the solvent. Some substances such as benzoic acid and succinic acid are adsorbed strongly even though they have only slight effect on the surface tension of water[25]. Furthermore, the sugars are fairly well adsorbed in spite of the fact that they actually raise the surface tension of the solvent, water.

The adsorption of electrolytes on solids is, in general, very much smaller than the adsorption of nonelectrolytes. Furthermore, the adsorption of acids is usually greater than the adsorption of salts. One ion of an electrolyte is frequently adsorbed more strongly than the other ion on certain adsorbents. Thus, in some cases, the cations in solution will be adsorbed more strongly than the anions ; in other instances, the anions are adsorbed more strongly. This preferential ion adsorption is believed to be practically always an exchange adsorption in which either one of the ions of the adsorbent is displaced into the solution or an ion from some impurity on the adsorbent is displaced into the solution[25]. Kaolin and the Zeolites[109], for example undergo base exchange in the course of which some of their own positive ions may be displaced by cations from solution. Charcoal permits this same preferential adsorption of cations, in some instances, but probably does so by virtue of some impurity on its surface giving an equivalent amount of cation to the solution.

In many of the classical studies of adsorption from solution on carbon, the monocarboxylic acid have been used[22]. These studies are limited, in so far as they are confined to aqueous solutions, both by the complexity of the solutions (that of acetic acid has been extensively investigated[110]) which makes interpretation difficult, and by the small number of acids which can be investigated. In some cases, moreover, difficulties in interpreting the results arise because the adsorbents, though known to be porous, has not been characterized further.

The adsorption of long chain fatty acids (notably stearic acid) from solutions in organic solvents has been studied by Kipling and Wright[111], and Madan and Sandle[112] for evaluating surface characteristics of active carbons. Surface area, surface acidity, particle size and conductivity measurements[113] and also solid state studies[114] have been done to characterize the surface of active carbon. It as been thought useful to extend the investigation to further selected members of the homologons series. It has become evident that no simple pattern of adsorption be described for the series as a whole because a variety of factors are involved.

To evaluate the chemical and physical parameters associated with the adsorption of aromatic hydroxy compounds (for example phenol) by activated carbon, investigation have been carried out by many workers[115,116]. The overriding theme has been directed towards improving the understanding of activated carbon adsorption processes. Both the kinetics of adsorption and the extent of adsorption at equilibrium are dependent on the physical and chemical characteristics of the adsorbent, adsorbate and experimental systems. Parameters evaluated include temperature, hydronium ion concentration, concentration of buffer, type of adsorbate, initial adsorbate concentration, competitive adsorption, and carbon particle size. In addition, the nature of the rate limiting step in the adsorption is described.

Sen, Bhattacharyya and Naidu[117] have attempted to correlate pore size distribution, and other physical characteristics with the adsorption capacities of active carbon (four samples) with respect to methylene blue, iodine and hydrogen sulphide. A comparison of the data shows that the specific surface and total pore volume do not have any relation with the specificity of the active carbon.

The characteristics of the uptake of phenol and nitrophenols by active carbon have been investigated by Mattson et al.[118]. The measurement of solution equilibrium parameters as well as surface structural characteristics determined by infrared internal reflection spectroscopy (IRS) are presented[119]. This technique permits direct spectrophotometric observation of solid surfaces, and therefore provides a direct means for the identification of the organic functional group characteristics at the surface, both before and after adsorption.

There has been a considerable amount of indirect study on the nature of the oxygen containing functional groups present on the surfaces of carbons[119,120-126]. It has been observed that oxidation and reduction of active carbon markedly influences the nature of the phenol and nitrobenzene isotherm[120]. Coughlin and Ezra[120] have showed that oxidation of active carbon considerably lowers the capacity of both active carbon and carbon black for adsorption of phenol and nitrobenzene in the low solute concentration regions of the isotherms. They also observed that reduction of the carbon resulted in the opposite effect. It is suggested[120] that adsorption of phenol takes place with the pi-electron system of the graphatic rings of the carbon basal planes[113], and that the presence of additional acidic surface oxygen groups produced by ecidification of the carbon, at the basal plane edges, serves to withdraw electrons from t-he pi-system of the basal planes[120]. This does not explain[120] how such an electron withdrawal effect makes itself felt over the large distances of the basal ring system, nor does it explain the nature of interaction of the sorbates on the basal planes.

Giles et al.[98] pointed out that the adsorption isotherm for phenol on carbon usually shows a two-step process, resulting in two plateaus. The oxidation-reduction studies of Caughlin and Ezra[120] have showed that this second plateau is apparently independent of the oxidation state of the carbon surface. Giles[98] suggested that the second step of the isotherm involve an uncovering of part of the surface and readsorption of the phenol molecules in a different orientation. It has been suggested[98] that this reorientation involved a change from a flat configuration to an end-on configuration where the hydroxyl group is directed away from the carbon surface.

Nagy et al.[127] showed that solid-liquid interfacial phenomenon can be used to study surface properties of porous activated carbon. The surface area of active carbon is determined by equilibrium adsorption of liq MeOH - C_6H_6 , EtOH - C_6H_6, AcoH - C_6H_6, and AcoH - H_2O. An isotope mol. exchange method (with liq EtoH - labelled with 14C) is given for study of the kinetic properties of active C solid-liquid interfaces, especially in relation to pore structure study and adsorption.

1.8 Review on Mechanism of adsorption and activation:

To elucidate the rate-controlling mechanism, Nachod and Wood[128] studied the rates of ion-exchange reactions. They studied the rates of exchange of the pairs of ions hydrogen-calcium and sodium-calcium with a number of commercial cation-exchange resins in dilute solutions. They concluded that the "rate of bringing dissolved ions upto and away from the surface of the exchange granules" is rate determining. Kurin & Myers[129] studied the kinetics of anion-exchange on four weak base resins using a number of anion-pairs and concluded that "diffusion" is the rate-controlling process in all cases. Boyd et al.[130] developed equations for evaluating rate-controlling process in heterogeneous ion-exchange reactions of the type

$$A^+ + BR \rightleftarrows AR + B^+$$

where A^+ is the ingoing ion ; BR the ion-exchanger, B^+, the displaced ion.

The kinetics of this process have been interpreted in terms of the three rate processes as below :

(i) When the process is controlled by diffusion in and through the adsorbent particle, the kinetics of exchange process obeys the equation

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 Bt} \qquad \ldots\ldots\ldots \qquad (1.26)$$

in which $F = Q_t/Q_\infty$, the fractional attainment of equilibrium of an ingoing (or outgoing) ion where Q_t , the amount of exchange after time t, and Q , the amount of exchange after infinite time ;
$B = \bar{D}\pi^2/r_0^2$; $\bar{D}$ being the effective diffusion co-efficient of the exchanging ions in the solid, and r_0 = radi of the particle. According to the equation (1.26) F is a function of B and t only and is thus independent of the concentration of the ingoing ion, since there is no concentration term in the equation. For every value of F a value of Bt can be calculated and vice versa and values of Bt for various values of F have been tabulated[131]. The plots of Bt vs t should be linear and pass through the origin if particle diffusion is rate controlling i.e. B value is independent of t in case of particle diffusion.

(ii) When the process is controlled by diffusion through a thin liquid film surrounding the particle, the equation is represented as

$$\log(1 - F) = -\left(R/2.303 \right) \cdot t \qquad \ldots\ldots\ldots \qquad (1.27)$$

where R = $\frac{3D^{l}}{r_0 \Delta r_0 \chi}$, D^{l} is the film diffusion constant r_0 , the particle radius, Δr_0 , the film thickness, and χ, the distribution constant, defined by the ratio of the concentration of the adsorbing ion A^+ in the adsorbent to that in the solution i.e. $\chi = K_c\rho(n_{\beta R}/m_{\beta^+})$ where K_c is the mass law equilibrium constant, ρ the particle density. With time value of m_{β^+} increases and $n_{\beta R}$ decreases i.e. with the progress of exchange R increases.

(iii) when the process is a chemical action, the kinetics of adsorption is given by

$$\log(1 - F) = -\left(\frac{S}{2.303}\right)\cdot t \qquad \ldots\ldots\ldots \qquad (1.28)$$

where S = $k_1 m_A^+ + k_2 m_B^+$, m_A^+ and m_B^+ denote the concentration of the ions $\overset{+}{A}$ + and $\overset{+}{B}$ in solution and k_1 and k_2 are the forward and reverse specific rate constants. The value of S depends on the relative values of k_1 and k_2 and the concentration change of A^+ and B^+. So, with time S decreases.

Mechanism of activation:

A survey reveals that an active adsorptive charcoal must contain a network of capillaries, some large and some small. This seems essential in order to provide avenues by which the molecules that are to be adsorbed can gain entrance to the interior of the charcoal particles and the large surface area that must necessarily be located in small pores. When, however, we come to a discussion of the pore shape and ask whether we consider charcoal as a honeycomb structure of approximately cylindrical pores, or as a collection of platelets more or less parallel to each other and forming box-like capillaries of rectangular cross section, or some combination of these , or some arrangement involving pores of still different shapes, we find ourselves in the realm of speculation and are unable to speak with certainty. Perhaps the best procedure to follow in summarizing the evidences is to consider the results obtained from each of the principal tools and types of measurement from which information as to the pore shape and general structure of charcoal can be obtained. The various tools include X-ray diffraction studies, microscopic studies, electron microscope studies, measurements and calculations of area and pore volume, chemical behaviour of charcoal, expansion of charcoal during adsorption, and measurements of the true density of the carbon in charcoal.

Cokes, chars, and activated carbons are frequently termed amorphous carbon. X-ray studies have shown that many so-called amorphous substances have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with the crystalline state. An amorphous looking powder may be composed of crystals of submicroscopic dimensions, so-called crystallites. This is true of chars and cokes.

Studies by Riley[132-135], Warren[136], Berl[137], Hofmann[138], and others, have shed much light on the structure of these carbon crystallites. Although interpretation of the x-ray diffraction patterns is not free from ambiguities, there is general agreement that amorphous carbons consists of flat plates in which the carbon atoms are arranged in a hexagonal lattice (Fig. - 1.8), each atom,

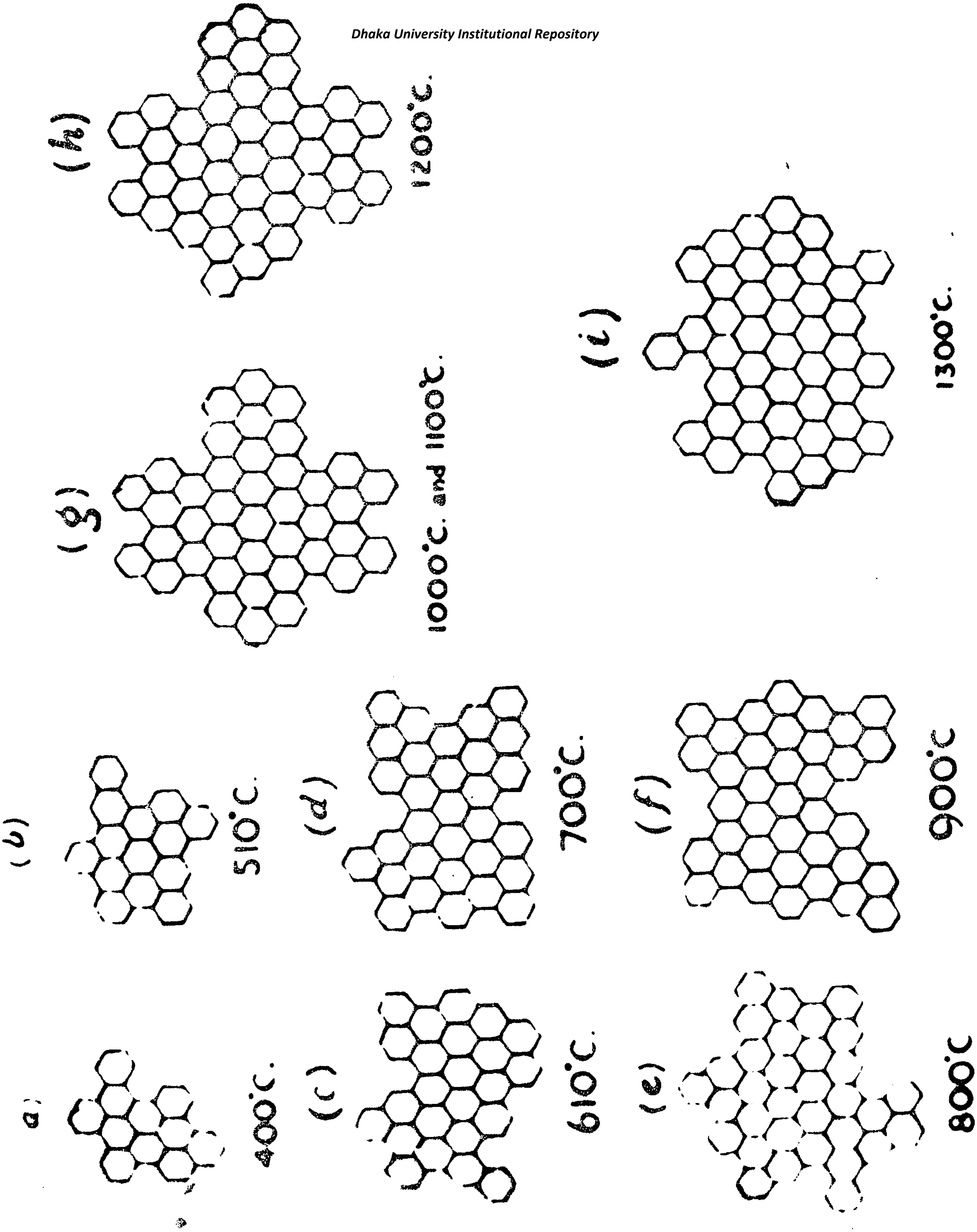


Figure - 1.8 : Arrangement of carbon atoms in a single-layer plane of crystallites formed at different temperatures.

SOURCE: H.L. Riley : Chemistry and Industry, 58 No.17, 391(1939).

except those at the edge, being held by covalent linkages to three other carbon atoms. The crystallites are formed by two or more of these plates being stacked one above the other. Although these crystallites have some structural resemblance to a larger graphite crystal, differences other than size exist. In graphite, the plates are more closely together; moreover, the manner in which the plates are stacked above one another follows a definite crystalline pattern in graphite, a feature that is absent in the carbon crystallites. Johnstone and Clark[139a,139b] conclude that "the data obtained from the x-ray study evidently give credence to the ideas that activation is essentially a process of cleaning out capillaries, in changing their size and perhaps their shape, without greatly affecting the matrix structure of carbon." The presence of large capillaries in the surface of charcoal particles has been shown by the photomicrographs[203,204]. These reports however show nothing about the shape or distribution of the fine pores.

In addition to the evidence provided by x-ray and microscopic examinations, differences between chars and graphite have been shown by chemical methods[140,141]. Chars and cokes react with gaseous oxygen at lower temperatures than does graphite ; however graphite is oxidised much more readily than char by a mixture of chromic and phosphoric acids at a temperature of 100°C[134,135]. It is also well known that standard charcoals can all be converted by proper chemical treatment into compounds that appear to have a central nucleus of carbon atoms arranged much as though they were in a plane of graphite. Thus mellitic acid has been reported[142] to be formed in good yield by controlled oxidation with nitric acid.

This certainly indicated that much of the carbon is arranged in two - dimensional graphite-like sheets or platelets and again is consistent with the x-ray picture of the structure of charcoals. At least five different observers[143-148] have noted that when charcoal picks up water vapor in the higher relative pressure ranges it expands[149]. It should be noted, as pointed out by Kummer[150], that it is much easier to imagine the expansion of charcoals if they are made up of platelets[151]. If the pore structure consists of a honeycomb of cylinders, the possibility of expansion seems much more limited.

The size of the crystallites is influenced by the temperature of carbonization and to some extent, by the composition and structure of the raw material. In chars prepared from such substances as cellulose, the 'c' dimension (height of the crystal) shows little change until a temperature of 1300°C is reached, whereas the 'a' dimension (diameter of each layer) shows a continuous growth upto 700°C[133]. This latter fact is of interest because many properties such as electrical conductivity and ease of subsequent activation show a change at this temperature.

The crystallites may be formed through several mechanisms[133,152-154]. During pyrolysis, the original organic substance may be split into fragments which regroup to form the thermostable aromatic structure existing in the hexagon. It is also possible that suitable nuclei initiate a transformation in which the hexagonal lattice grows gradually at the expense of the original substance. The transformation is seldom complete and residual hydrocarbon chains and rings remain.

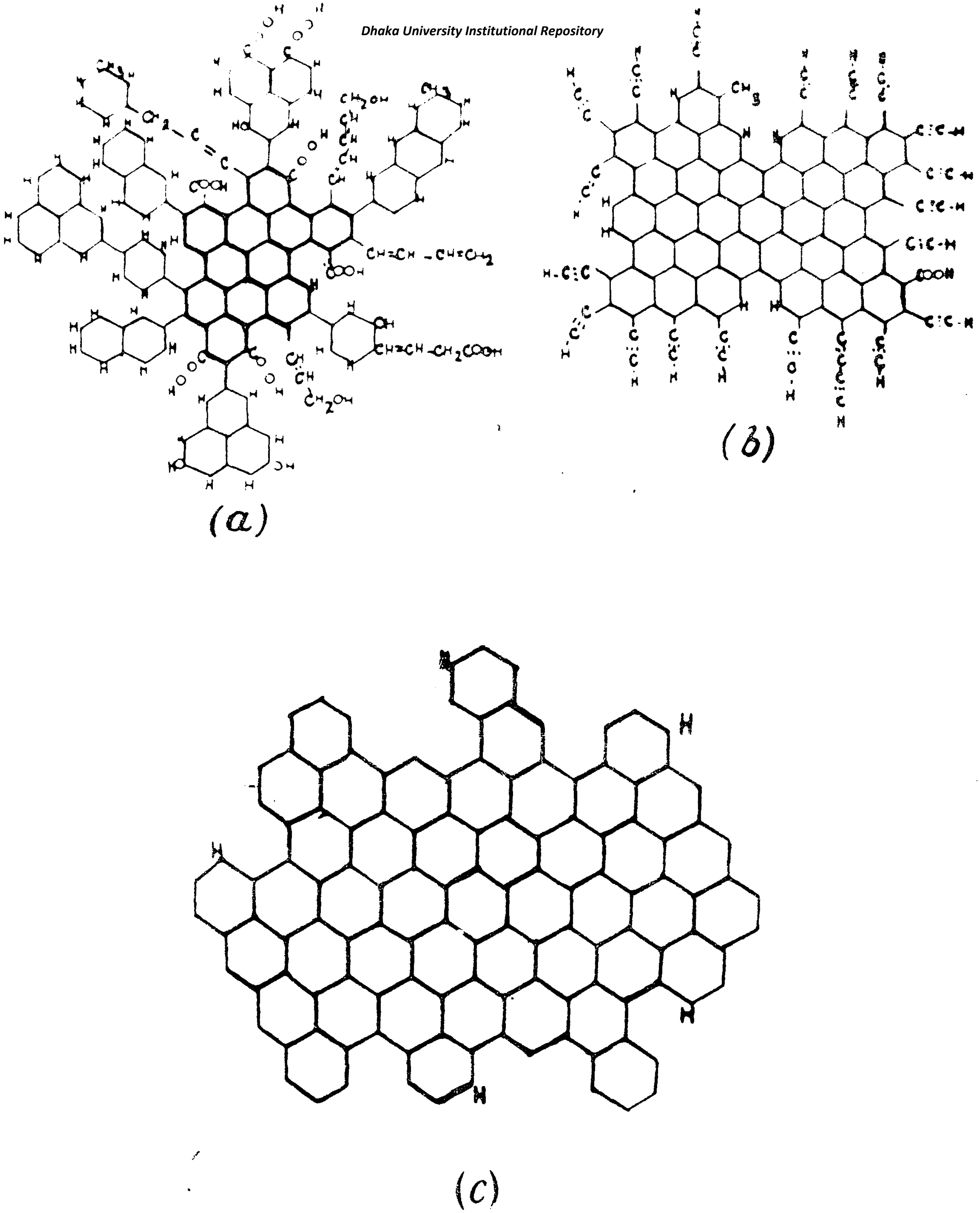


Figure - 1.9 : Hypothetical structures of crystallites.
SOURCE: H.L. Riley, Chemistry and Industry, 58 No.17,391(1939).

As these residual hydrocarbons cannot be extracted with solvents or removed by degassing they are presented to be attached by chemical bonds to the border atoms of the crystallites. A hypothetical structure is shown in Fig. 1.9 . It is to be noted that the term hydrocarbon, usually applied to the cementing substances, may also cover compounds containing other elements in addition to hydrogen and carbon, such as oxygen[3]. It is believed by some that the hydrocarbon may cement the crystallites into clusters to form secondary structures. Differences in the size, shape, and arrangement of the crystallites in the secondary structures [illegible] affect the adsorptive power and other properties of the char[136].

While studying the nature of the carbon surface, a number of workers observed capillary action in the numerous micropores in carbon to be the cause of certain adsorptive properties. Other adsorptive properties are traced (as stated earlier) to the large surface area of carbon. Since carbon is porous, its surface area cannot be measured directly ; hence, it is calculated indirectly either from adsorption data or thermal effects. Data obtained by these methods indicate that the total surface area of active carbons ranges between 2×10^4 and 6×10^4 sq. cm per g . The total surface area is measured under special conditions that seldom can be provided in routine experimental work.

Under the conditions that exist in many experimental studies, only part of the surface participates in an adsorption. This limited availability of the surface can be conveniently explained by assuming the surface to be heterogeneous and by assuming that some substances are adsorbed only by the more active areas, the "active centres". According to this theory, an increase in the adsorptive power of a carbon during activation is associated with the formation of additional centres. We have no knowledge of the chemical structure of 'active centres'. X-ray diffraction patterns do not disclose differences between active and inactive carbons, but this does not disprove the existence of active centres since they are probably not of sufficient thickness to produce interference of x-rays. Until more is knownof the mechanism whereby an adsorbed molecule is attached to the carbon surface, there are advantages in broadly defining an active centres as the sum of the forces that hold an adsorbed molecule.

However, quantitative distinctions are not sufficient to explain all differences between carbons; qualitative variations also exist. Methylene blue may be preferentially adsorbed by one carbon, and phenol by another carbon. To interpret such variations in behaviour, it becomes necessary to assume the existence of different types of active centres, each types having characteristic adsorptive powers, or, in otherwards, that two carbons can differ both in kind and quantity of active centres. Active centres possibly correspond to specific geometric arrangement of surface atoms - patterns that may include noncarbon atoms. The substance called 'active carbon' is not pure carbon; many noncarbon elements are present and are attached to the carbon atoms by chemical bonds[155]. The influence of the noncarbon ingredient has been traced to the manner in which they alter the mechanism of an activating process. Apart from being a ladder to achieve a more effective spacing and structural arrangement of the carbon atoms, some noncarbon elements become part of the molecular architecture of the activated carbon. This is indicated by the tenacity with which many foreign elements are held by carbon[156-159]. These strongly held foreign elements provide adsorptive bonds. There is considerable evidence that oxygen can be attached by covalent bonds to the carbon structure to form stable surface oxides, and specific adsorptive and catalytic properties are traced to their presence similar observations have been made as to the effect of other elements, such as nitrogen, sulfur, iron and hydrogen. The influence of noncarbon atoms may extend to adjacent carbon atoms in a manner analogous to the way in which a polar group introduced into an organic compound affects the chemical properties of remote atoms.

When sulfur is heated with carbon, only part of the sulfur can be separated subsequently by extraction with toluene, by oxidation with bromine, or by heating to 900°C in a stream of nitrogen; but heating in a stream of hydrogen will remove the sulfur as hydrogen sulfide. All these indicate a chemical union between the carbon and sulfur atoms, a union which Wibaut[160] suggested to be similar to the surface oxides. Ley and Wibaut[161] found evidence that nitrogen is combined with carbon in a form suggestive of nitrile groups. Miller[162] studied a commercial carbon from which repeated boiling with acid failed to extract appreciable quantities of the mineral ingredients, but when the carbon was ashed, the ash dissolved readily.

At one time, the adsorptive powers of animal char re believed to reside in chemically held nitrogen[156,163], later when very active carbons re produced from nitrogen-free source materials, the importance of nitrogen s discredited[164]. In this connection, however, some workers have observed that carbon from nitrogen-free sources may contain appreciable quantities of combined nitrogen[165], indicating that carbon can fix nitrogen during the activation process.

Carbon, prior to activation, contains hydrogen in the form of hydrocarbon chains and rings attached to border atoms of the hexagon plates. Much of this hydrogen is removed during activation at temperatures below 950°C, but some hydrogen is still held after activation and is not released unless much higher temperatures are reached[166]. It is to be noted that the evolution of this latter portion of hydrogen at very high temperatures is paralleled by a simultaneous decrease in adsorptive power.

We can return to a consideration of the changes produced in carbon during the activation processes. In attempting to understand the influence of the noncarbon constituents on activation, one must distinguish between effects produced during the carbonization or pyrolysis and those produced during the subsequent ignition or oxidation[167]. Some chemicals such as zinc chloride or calcium chloride exert an influence only during the carbonization stages, whereas others, such as potassium carbonate and phosphoric acid, can affect the properties when present during the oxidation stage.

One view of the action of mineral ingredients during the carbonization is that they provide a skeleton on which the carbon is deposited[137], the freshly formed carbon becoming bounded by adsorption forces to the mineral elements. Evidence of such bonding is available when carbonaceous substances burn on cooking utensils or on the valves of gasoline engines. Such carbon is difficult to remove by mechanical means. As expressed by Alexander and McBain[168]: "It seems as if the naccent bonds, appearing as the more or less profound chemical changes occur, tend to be satisfied by whatever is nearest." When the mineral ingredients are subsequently removed by dissolving in acid or water, the exposed carbon surface becomes free to attract and adsorb other substances.

At one time, the action of oxidizing gases such as air and steam, is believed to involve preferential oxidation of hydrocarbons that has been deposited on the surface during the carbonization stage. Oxidation increases the surface area and enlarges the pore volume by (i) burning awaycarbon atoms from the walls of open pores and (ii) perforating closed pores and thereby providing access to pores formed initially without an inlet. No doubt all this action explains much improvement in adsorptive power, but it fails to explain specific effects. Thus oxidation with steam at 800°C provides specific powers unlike those produced with activation by air at 500°C. An understanding of the phenomena involved in the combustion of carbon is veiled by the complexities surrounding chemical reactions that include a solid phase. The equilibrium conditions that govern the final composition of products are known, but this sheds little light as to the path of the reaction. That such knowledge would shed much light on the development of adsorptive power is questionable but the inability to obtain information shows why it is difficult to interpret the relation between conditions of activation and the specific types of adsorptive powers that are formed.

Many noncarbon ingredients exert specific influences during oxidation with steam or air[4,169-170]. Some of these effects may be due to an influence on the temperature at which the activation occurs. We can only guess as to the mechanism of the influence of chemicals that are added after carbonization but before activation proper. Thus, carbon will burn at lower temperatures when potassium carbonate and NaOH is present, whereas orthophosphoric acid raises the ignition point. Such an influence may determine which carbon atoms will be selectively etched away during activation, and in turn, set the pattern for the atomic spacing on the final product. That noncarbon atoms are held or adsorbed on certain areas of the surface and activation involves oxidation at the point of bond between the carbon and the inorganic ingredients is illustrated[4] by processes in which a normally soluble inorganic substance becomes bonded to the carbon during carbonization and cannot be extracted with water until after activation.

The presence of certain inorganic substances increases the yield of char[171]. This suggests that they remain with the carbon and perhaps alter the course of the reactions in pyrolysis. Chemicals that are of value during carbonization are characterized by dehydrating properties. Apart from swelling or solubilizing action, they cause hydrogen and oxygen atoms in the source material to be stripped away as water, rather than as hydrocarbons or as oxygenated organic compounds, and thereby leave less of the objectionable tarry material on the carbon. Although the mechanisms that have been mentioned indicate how noncarbon ingredients could enhance adsorptive power in general, they fail to explain specific effects. Something more than this (increase of adsorptive power) is involved, because certain adsorptive properties of a carbon produced by the zincchloride process are unlike those of a carbon produced by the calcium chloride process. A convenient interpretation is that each chemical exerts a specific influence on the molecular architecture of the surface of the resulting carbon. Another interpretation is that the presence of inorganic ingredients alter the size of the pores formed during activation[172]. Another possible mechanism is suggested by the work of Berl[137] who found evidence that some elements, such as potassium, can penetrate between the hexagon plates of the crystallites and spread them apart, enabling erosion to occur at surfaces otherwise unexposed.

1.9 THE USE OF ADSORPTION FROM SOLUTION IN MEASUREMENT OF SURFACE AREA:

One of the most important application of Vander Waals adsorption is the use of adsorption measurements to determine the surface areas of finely divided and porous solids. The specific surface area, $\sum$, of a solid is defined as the surface area per unit mass. It is usually expressed in square meters per gram. The monolayer capacity, Vm, is defined as the quantity of adsorbate which would be required to cover the adsorbent with a monomolecular layer only. The measurement of the specific surface areas of solids is becoming increasingly important, for it is a highly significant parameter in nearly all physical and chemical process of adsorption involving powdered solids.

It is not surprising, therefore, that much research on the problem of measuring surface area has been conducted, and many methods devised. Most of these are, however, open to criticism.

Methods based on physical adsorption of gases (nitrogen, orgon, krypton) at low temperatures (together with electron microscopy for non-porous solids) are standard methods. It can atleast be claimed that the B.E.T. equation provides a standard procedure for determining empirically the point at which monolayer adsorption is complete on non-porous solids. Moreover, interest both in the adsorption of gases by solids and in the determination of surface areas is such that this method is likely to remain of primary importance. Simplified experimental procedures are being developed and the theoretical background is being continually examined. Other methods, for example, the permeability methods of Rigden[173], and of Lea and Nurse[174], can be criticized on the grounds that the mathematics of the method are largely empirical, and also that the methods are, completely unreliable for areas greater than 2 sq. m/g. Light extinction methods, such as the Wagner[175] turbidimeter and Heywood[176] method, are unsatisfactory because the laws governing their usage are different depending on whether the particles are larger or smaller than the wavelength of light. This leads to obvious difficulties where, as is generally the case, one is examining a mixture of such particle. Sedimentation methods of Hinkley[177], are dependent on achieving a high degree of dispersion of the powder in the working fluid, which is generally extremely difficult ; and in these methods, too large errors in sampling can arise. Moreover, none of the above methods is capable of measuring internal surface area, which is often very important ; the socalled "heat of wetting" method, however, does measure internal as well as external area. Unfortunately, this method only measures the heat evolved when the powder is wetted by a liquid ; to arrive at the surface area from the heat evolved, one multiplies the heat evolved by a factor. This factor varies from family of substances to family of substances, and can, infact only be correctly arrived at if one knows the area of one or more members of the family concerned accurately. This latter obviously must be determined by some other method. However, once the constant for a particular family is known, surface areas can be determined with fair accuracy by this method. But it must be emphasized that the calorimetric method of determining heat evolved is not easy, and hardly suitable, if accurate results are required, for routine measurements.

There remains only electron microscopic and adsorption from solution methods. The electron microscope, whilst of course extremely accurate, is expensive, needs careful operation, and the particle count and subsequent construction of the particle size distribution curve is extremely laborious and time consuming.

The gas adsorption method[178] are comparatively simple. The operations may be performed easily and determinations are made fairly quickly, and the method is accurate to ± 5% ; the surface measured being the sum of the internal and external areas. They involve no assumptions as to the particle shape, pore size and shape, and porosity, and their results show a fairly high degree of consistency. Other advantages are that only a small sample, which can be recovered intact, is needed and that there is no personal factor to consider. It is clear therefore, that this method offers the greatest of advantages over all others described above.

The gas adsorption methods are based upon BET theory or Langmuirs' theory of adsorption and many workers measured the surface area of solids using these two theories and we will mention a few of them. Joyner et al.[179] have used the Langmuir method to calculate 'Vm' values from their isotherms for nitrogen adsorption at - 195°C on six different charcoals. The equation fitted upto relative pressures of 0.3 to 0.4 but the points in fact lay on a slight curve Accurately linear plots were reported by Fireman et al.[180] for nitrogen at - 195°C and butane at 0°C on six different charcoals. Acceptable linear plots have also been obtained for nitrogen and a variety of simple hydrocarbon vapours on charcoal by Nay and Morrison[181] Nitrogen isotherms at - 195°C and -183°C on a number of charcoals have been tabulated by Deitz and Gleysteen[182] ; the cocoanut chars were found to give linear Langmuir plots whereas the bone chars yielded type II adsorption isotherms. Harkins and Jura[183] have also used the Langmuir equation to determine 'Vm' from an isotherm for nitrogen on charcoal. The use of the Langmuir method for evaluating surface areas has been discussed by Maggs[184]. The Langmuir method has also been applied to non-porous solid[185-187], but the results are generaly inadmissible on account of the poor fit of the equation.

The experimental methods used in gas adsorption have the disadvantage of being both complex and tedius in operation, and therefore the development of a simpler one is desirable. In this situation, the use of adsorption from solution in determining surface areas were undertaken. The experimental procedure is much simpler than in any method requiring vacuum apparatus, and, if routine measurements on a large number of samples are involved, it is usually much quicker than the gas adsorption method.

For a method based on adsorption from solution to be sound, two fundamental requirements have to be fulfilled. It be possible to (i) determine the conditions under which a complete monolayer of a given component is formed on the solid (ii) assign an accurate value to the area occupied by the adsorbed molecular species i.e. ' σm ' ; this normally means that the orientation of the adsorbed molecules must be known.

Measurements of surface area have usually been considered in terms of physical adsorption, but chemisorption does not have to be excluded from consideration. In determining the monolayer capacity when chemisorption occurs it is important to ensure that interaction with the solid does not go beyond the surface to a continuous reaction with the bulk of the solid. Further, if chemisorption is followed by physical adsorption, it must be possible to establish what proportion of the adsorbate is held in each layer.

The effective molecular area of the adsorbate normally remains constant if the molecules are physically adsorbed in a close packed layer. A major change in molecular area may occur if the orientation changes between one group of solids and another. If adsorption occurs at specific sites on the surface, eg through hydrogen-bonding or in chemisorption, the effective molecular area is a function primarily of the spacing of the sites, and so can vary from one solid to another. If only a proportion of the sites can be occupied even at the maximum degree of adsorption, the effective molecular area of the adsorbed molecules may vary even more from one solid to another as the proportion changes.

The adsorption of iodine from solution has frequently been used in measurements of the surface areas of charcoals and other carbons. It has been assumed that the adsorption of iodine is independent of the presence of oxide complexes on the surface, and therefore gives the true surface area of carbons. For this reason it has been used to follow the changes in surface area brought about when carbons are exposed to oxidising or reducing gases at various temperatures. This is important in studies of the effects of surface complexes on the adsorption of strong acids and strong bases from aqueous solution.

The adsorption of I_2 from solution has found favour in industry as a rapid method of determining the surface areas of powders[188]. A linear relation between the iodine and nitrogen surface areas has been reported by Smith et al.[189] for carbon blacks and by Zettlemoyer and Walker[190] for magnesia (although very slow adsorption from iodine solution has been reported for this material[191]), but there is considerable uncertainty as to the proper value of 'σ m', the molecular area of the adsorbed molecule. The values which have been used by many workers cover a wide range from $15A^{\cdot 2}$ to $49A^{\cdot 2}$ as shown in Table - 1.2.

TABLE - 1.2

Effective area of iodine Molecule(sq Å).	Basis of calculation	Reference.
15.6	Effective radius of molecule in vapour phase as given by viscosity measurements.	192,193
21.2	Gram molecular volume.	190
21.7	Limiting adsorption from aqueous solution on carbon blacks of known specific surface area.	194
22.1	Not explained.	195
23.5	Crystal structure.	196,197
23.7	Limiting adsorption of vapour and from some organic solutions on Graphon.	99
27.1	Limiting adsorption of vapour on Graphon.	198
27.4	Molecular dimensions.	198
30.0	Limiting adsorption from aqueous solution on Graphon.	198
33.0	Limiting adsorption from aqueous solution on carbon blacks of known specific surface area.	199
35.3	Adsorption from solution in CCl_4 on preferred position of the magnesium oxide surface.	200
42.0	Limiting adsorption from aqueous solution on carbon black of known specific surface area.	201
49.2	Atomic domain radius for iodine molecule.	202

1.10 OBJECTIVE OF THE PRESENT WORK:

It is clear from the above review that despite a great deal of work on adsorption equilibria, few kinetic studies was undertaken to the elucidation of the mechanism of adsorption from solution . Orders and activation energies of adsorption are important parameters which testify to the validity of a proposed mechanism. These parameters, specially for adsorption from solutions are hardly available in the literature.

This investigation was, therefore, undertaken with the objective of further studying adsorption kinetics and gaining an insight into the mechanisms of adsorption on activated carbon by determining experimentally the orders of adsorption with respect to adsorbates and activation energies of their adsorption. For the purpose, the present investigation is devoted to

(i) study the rates of adsorption of iodine and acetic acid at various concentrations and at different temperatures,

(ii) find out the correct orders of adsorption with respect to the adsorbate concentrations employing the differential method,

(iii) propose mechanisms of adsorption of iodine and acetic acid on the basis of the data thus obtained.

A further aim of this investigation is to find out the cause for specificity of adsorption on different carbons. It is well known that carbon has a memory. Activated carbon prepared from the same raw materials by using different methods show different adsorption characteristics. An attempt is made to understand such behaviour by using zinc chloride in the preparation of activated carbon from cocoanut shell.

Surface area of adsorbents is one of the most important parameters which determine the quality of an adsorbent. This investigation proposes a simple method that gives surface areas comparable with those determined by the BET (Brunauer, Emmett, Teller) method.

CHAPTER 2. EXPERIMENTAL

2.1 MATERIALS AND APPARATUS:

2.1.1 ADSORBENTS: Activated carbon - Three different samples of activated carbon were used in this investigation.

(a) A powdered carbon adsorbent (E. Merck. reagent No.2186, manufactured in W. Germany).

(b) Steam activated carbon - This sample of activated carbon was prepared in this laboratory by passing superheated steam over cocoanut charcoal (section 2.2.1)

(c) Zinc chloride ($ZnCl_2$) treated activated carbon - This sample of activated carbon was prepared from cocoanut charcoal by digesting it with zinc chloride (section 2.2.2).

2.1.2 ADSORBATES:

(a) Iodine, I_2 (E. Merck). Iodine solutions of different concentrations (0.26N, 0.36N, 0.49N, 0.54N) were prepared.

(b) Acetic acid, CH_3COOH (E. Merck). Acetic acid solutions of (0.24N, 0.35N, 0.44N, 0.57N) concentrations were prepared by mixing acetic acid with requisite amount of distilled water.

(c) Phenol, C_6H_5OH (E. Merck). Three solutions of phenol were prepared by dissolving 400 mg, 200 mg, and 100 mg of phenol per 1000 ml. respectively in distilled water. The pH of the solutions were adjusted to 6.5 with anhydrous trisodium phosphate - phosphoric acid.

(d) Potasium per manganate, $KMnO_4$ (E. Merck). Three solutions of (.17N, 0.31N, 0.60N) strength were prepared by disolving potassium permanganate in distilled water.

(e) Potassium perchlorate, $KClO_4$ (E. Merk). A 0.30N potassium perchlorate solution was prepared by dissolving 20.78 mg. of $KClO_4$ in conc. sulphuric acid and then diluting the solution to the desired volume (500 ml).

2.1.3 APPARATUS:

(a) pH meter - A Pye Unicam, Model 292 pH meter was used to measure the pH of the adsorbate solutions at a given temperature.

(b) Shaker - A mechanical shaker was used to shake the adsorbate and adsorbent mixture.

(c) Thermostat - A Jumo D.B.P. Type GOI, made in West Germany (a constant temperature bath) was used to study the kinetics of adsorption at different temperature ranging from 30°C - 90°C. The temperature could be kept constant within ± 2°C.

2.2 EXPERIMENTAL PROCEDURE:

2.2.1 Preparation of steam activated carbon from cocoanut shell - Cocoanut shell was first crushed to pass through 8 mesh sieve and then heated to a temperature of 600°C out of contact with air whereby charcoal was obtained. The charcoal was then activated by passing superheated steam at 750° - 800°C for one hour in a tube furnace. The product was dried at 150°C, ground to pass through a 900 mesh per cm^2 sieve and kept in a desiccator.

2.2.2 Preparation of zinc chloride treated activated carbon - Cocoanut shell was crushed to pass through 8 mesh sieve. 10 g. portions passing through 8-mesh sive and remaining on a 16-mesh sieve was soaked in zinc chloride solution containing HCl. (It has been found that maximum activity of carbon is obtained at $ZnCl_2$/shell ratio of 2.6 and HCl/shell ratio of 0.35 for iodine adsorption. The carbonisation at $800^{\circ}C$ for one hour produced carbon of the highest activity$^{211)}$. The soaked sample was digested for 2-3 hours at $100^{\circ}C$ so that a dark pasty mass was formed. The sticky mass was then dried and finally carbonized in a tube furnace at temperature range 600 - $800^{\circ}C$, the duration of carbonization being one hour. The carbonized product was cooled, plunged into 10% HCl solution washed with hot water till the washings were free from chloride ion, dried at 150° - $200^{\circ}C$ for 1½ hours, ground to pass through a 900 mesh per cm^2 sieve and stored in a desiccator.

2.2.3 Measurement of adsorption from different adsorbate solutions: The adsorptions of iodine, acetic, phenol, potassium permanganate and potassium perchlorate were determined by the volumetric method at temperatures $30^{\circ}C$, $40^{\circ}C$, $50^{\circ}C$, $60^{\circ}C$, $70^{\circ}C$, $80^{\circ}C$, $90^{\circ}C$ and at the atmospheric pressure. A microburette was used for the titration.

For each run, exactly 50 ml of the adsorbate solution was taken in a stoppered conical flask and kept in the thermostat at a given temperature. An accurately weighed quantity (1 g) of activated carbon was taken in a separate stoppered conical flask and thermostated. When both the adsorbent and adsorbate reached thermal equilibrium, the adsorbate solution was introduced into the adsorbent flask and stirred rapidly. At selected time intervals recorded by the stop watch, the stirring was stopped and about 5 ml were withdrawn from the conical flask by means of a syringe pipette and analysed by standard volumetric methods. A filter paper was tied around the tip of the syringe in such a way that no carbon particle was withdrawn along with the adsorbate solution. From the difference of initial and final concentrations of the adsorbate solution (before and after adsorption), amount adsorbed by the adsorbent was found out.

Phenol was determined by a modified Baylis - Colebough[3,205,206] method, potassium perchlorate by a modified method developed here (section 2.2.4). Iodine and potassium permanganate by iodometric method, and acetic acid by the acid-base titration method (NaOH and phenolphthalein).

2.2.4 Volumetric determination of perchlorates:

Several methods were available for the volumetric determination of perchlorates, the most common one involved the reduction of perchlorates by zinc amalgam to chloride ion in the presence of molybdenum catalyst.

When this Zn-amalgam method was applied to activated carbon, irreproducible results, varying from 0.2 to 20%, were obtained. Preliminary experiments carried out in this laboratory showed that the order of addition of reagents had an effect on the accuracy and reproducibility of the results. An investigation was therefore undertaken to improve upon the method. For the purpose the following reagents were prepared: (i) A 0.3oN sodium molybdate (BDH.Analytical Grade). (ii) A 4M sulphuric acid (E.Merck) solution. (iii) A 0.3oN potassium chlorate (E. Merck) (Prepared by dissolving solid potassium perchlorate first in conc. H_2SO_4 and then adding distilled water.)

(iv) Zn-amalgams (Prepared by washing 30 gm pure granulated zinc with dil H_2SO_4, heating it with 300 gram of mercury and 10 ml (1:4) of H_2SO_4 acid for one hour on a waterbath, cooling it to room temperature washing it several times with dil H_2SO_4 and finally separated by a funnel.

Procedure - In analysing the perchlorate, 10 ml 0.30N $KClO_4$, 30 ml 0.30N Na_2MoO_4 and 50 ml 4MH_2SO_4 were added to an Erlenmeyer flask containing zinc amalgam (just enough to cover the bottom of the flask) followed by boiling until the molybdenum was in the green trivalent state, transferred to a flask for titration. To it just enough potassium permanganate was added to oxidize the trivalent molybdenum to colourless molybdate, then an excess of standard silver nitrate solution was added, and the solution was titrated with standard potassium thiocynate solution to the red ferric thiocyanate end point.

The results obtained by varying the order of the addition of the reagents were recorded in Table 2.1.

TABLE - 2.1

Sl.No.	Order of addition of the reagent.	Amount of (ClO_4^-) perchlorate taken (in g.)	Amount of perchlorate obtained (in g.)	% Error
1	Zn-Hg $KClO_4$ Na_2MoO_4 H_2SO_4	0.0620	0.0619	-0.225
2	$KClO_4$ H_2SO_4 Na_2MoO_4 Zn-Hg	0.0620	0.0563	-9.25
3	Zn-Hg H_2SO_4 $KClO_4$ Na_2MoO_4	0.0620	0.0611	-1.39
4	Na_2MoO_4 H_2SO_4 $KClO_4$ Zn-Hg	0.0620	0.0592	-4.50
5	Zn-Hg Na_2MoO_4 H_2SO_4 $KClO_4$	0.0620	0.0582	-6.09

Table 2.1 shows that the order of addition of reagents affect the accuracy of the method appreciably. Addition of perchlorate solution to Zn-Hg followed by sodium molybdate and

sulphuric acid gave results which were only 0.22% too low whereas the determined value obtained by the addition of sulphuric acid to perchlorate followed by sodium molybdate and zinc amalgam was 9.25% lower.

Results obtained in other experiments by adding reagents in the order Zn-Hg-H_2SO_4-$KClO_4$-Na_2MoO_4, Na_2MoO_4 -H_2SO_4 -$KClO_4$- Zn-Hg, Zn-Hg - Na_2MoO_4- H_2SO_4-$KClO_4$ were too low by 1.39%, 4.5%, 6.09% respectively. Among the above five permutations, the first one namely the addition of $KClO_4$ to Zn-Hg followed by Na_2MoO_4 and H_2SO_4 gave the highest accuracy (-0.22%).

The time of reduction of perchlorate have also a significant effect on the accuracy of the method. Reduction periods of more than 150 minutes are needed to get maximum accuracy. The reduction of perchlorate to the chloride is indicated by the persistent green colour. Studies have shown that molybdenum(vi) is not reduced completely even to the pentavalent state as long as perchlorate is present. So, the colour change serves as a good indicator for completion of the reduction of perchlorate to chloride.

The low value obtained for chloride might be that some chloride is oxidized by the permanganate to elementary chlorine. According to Height and Sager[207] the results they obtained were 1-5% too low. They detected the order of elementary chlorine in the evolved gases.

2.2.5 Experiment to prove reversibility of adsorption process:

Equal amounts of carbon were weighed into two conical flasks (F1 and F2), fitted with ground stoppers. 100 ml of

N/10 solution were introduced into the flask F1, and simultaneously 50 ml of $\frac{N}{5}$ iodine solution were added to flask F2. After certain period of time (30 minute), 50 ml of solvent (distilled water) were added to the flask F2. The two flasks were kept in dark for 24 hours, both were then opened and a portion of the contents titrated for unchanged iodine by the iodometric method.

2.2.6 Experiment to show the effect of time on adsorption:

A number of experiments were carried out at room temperature (28°C ± 2°C). A portion (1g) of each carbon were mixed with 50 ml of the iodine solution. The suspensions were shaken mechanically in closed conical flasks for different intervals of time after which an aliquot of the clear supernatant liquid was estimated for unchanged iodine by iodometric method.

2.2.7 Determination of density of iodine solution:

The density of iodine solutions were determined by the pyknometer method[208] (Table - 3.1.1.11).

2.3 MEASUREMENT OF THE SURFACE AREA OF THE ADSORBENTS:

The surface areas of the carbon adsorbents were determined by nitrogen adsorption at liquid air temperature. If V_M was the volume of nitrogen at STP adsorbed on g grams of active carbon to form a monolayer, then the surface area S, of the sample was given by the relation

$$S = \frac{V_M \times N \times A \times 10^{-20}}{22400\ g} \ m^2 g^{-1} \quad \ldots\ldots\ldots \quad (2.1)$$

where, A was the area in square Augstrom occupied by a single molecule of nitrogen in the completed monolayer and N was the Avogadro number, m stands for meter. The volume V_M adsorbed to form a monolayer was determined by a modified BET[28] method suggested by Bugge and Kerlogue[178]. The BET isotherm[28] is

$$\frac{P}{V(P_o-P)} = \frac{1}{V_M C} + \frac{C-1}{V_M C} \cdot \frac{P}{P_o} \quad \ldots\ldots\ldots\ldots \quad (2.2)$$

where, V = volume adsorbed at pressure P.

P_o = saturation vapour pressure of the adsorbate.

C = a constant.

Emmett[28] pointed out that a line drawn through the origin and one adsorption point at a relative pressure of 0.35 usually differed in slope by less than 5% from that drawn using several points. Therefore it was quite reasonable to simplify the BET equation(2.2) into the following form

$$\frac{P}{V(P_o-P)} = \frac{C-1}{V_M C} \cdot \frac{P}{P_o} \quad \ldots\ldots\ldots\ldots \quad (2.3)$$

Thus, measurement of adsorption at one pressure was sufficient to obtain the value of V_M. However, it would be shown (sect. 2.3.3) that for the elimination of deadspace measurements, it was necessary to measure adsorption at three different pressures.

2.3.1 <u>Description of the apparatus</u>: A diagram of the apparatus used for measuring nitrogen adsorption was shown in Fig. 2.1. F was the adsorption flask of known volume and M was a mercury manometer. The volume, Vs , between stop cock S2, S3, S4 (ABCD) was obtained by expanding He gas from ABCD to ABCDF and applying Boyles' law. The measured volue was 167.5 ml. The system could be evacuated to a pressure of 10^{-2} torr.

2.3.2 Procedure : A known amount of activated carbon was taken in the adsorption flask F. The system was evacuated to a pressure of 10^{-2} torr. The outgassing of the sample was done for a long time by slight heating (80°C) and evacuated. The adsorption flask F and the volume V_s were then separated with the stopcocks S4 and S3. Nitrogen gas from the cylinder, purified by passing through silica gel and over heated copper, was then admitted to the volume V_s at a certain pressure (i.e. the mercury level was adjusted to B and the pressure was noted) through the stop cock S1. The adsorption flask F was then surrounded by a Dewar flask containing liquid air and the stop cock S4 was then opened. The pressure in the system was measured after equilibrium was obtained, taking care to adjust the mercury level in the manometer to the definite mark. Measurements were repeated with two other initial pressures of nitrogen, the adsorbent being degassed in between the runs.

2.3.3 Calculation:

Let P', P'', P''' be the initial and P_1, P_2, P_3 be the final pressures, G be the dead space at unit pressure (the dead space was the volume of the sample flask and the stem upto D minus the volume of the adsorbent powder), T be the room temperature, V_1, V_2, V_3 be the volume of nitrogen at pressures P_1, P_2, P_3 respectively, and Vc_1, Vc_2, Vc_3 be the volumes of nitrogen without adsorbent in the sample flask at pressures P_1, P_2, P_3 respectively.

Bugge and Kerlogue[178] found it possible, where the substance was known to give S-shaped isotherm, to avoid the determination of dead space. According to them, the dead space was given by the relation

$$P_1(1+\alpha)G \simeq P_1 G$$

where G was the dead space at unit pressure and α was a correction factor equal to 6.58×10^{-5} at unit pressure. Hence, the value of Vc_1, the volume of nitrogen in the sample flask, was given by

$$V_1 = Vc_1 - P_1 G$$

$$V_2 = Vc_2 - P_2 G$$

and $$V_3 = Vc_3 - P_3 G.$$

Hence,

$$V_1 = Vc_1 - P_1 \cdot \frac{Vc_3 - V_3}{P_3}$$

From equation (2.3) it follows that

$$V_1(P_o-P_1) = V_2(P_o-P_2) = V_3(P_o-P_3)$$

Therefore;

$$V_1 = Vc_1 - \frac{P_1}{P_3} \cdot \left[Vc_3 - \frac{V_1(P_o-P_1)}{(P_o-P_3)} \right]$$

Rearranging,

$$V_1 = \frac{Vc_1 - Vc_3 \cdot \frac{P_1}{P_3}}{1 - \frac{P_1}{P_3} \cdot \left(\frac{P_o-P_1}{P_o-P_3} \right)}$$

and similarly for

$$V_2 = \frac{Vc_2 - Vc_3 \cdot \frac{P_2}{P_3}}{1 - \frac{P_2}{P_3} \left(\frac{P_o - P_2}{P_o - P_3} \right)}$$

Thus the values of V_1 and V_2 could be determined from the adsorption data at three pressures.

In the plot of P/P_o against $\frac{P}{V(P_o-P)}$ according to equation (2.3), the monolayer volume V_M was the reciprocal of the slope, if C was assumed to be very large.

Therefore,

$$V_M = \frac{\dfrac{P_2-P_1}{P_o}}{\dfrac{P_2}{V_2(P_o-P_2)} - \dfrac{P_1}{V_1(P_o-P_1)}} .$$

This would involve determination of three adsorption points, but no dead space. Data are given in Table 3.4.3 (Appendix III), and the various steps for the calculation of the surface area of the activated carbon samples. The value of A and P_o were assumed to be 16.2 square Augstrom per molecule and 760 mm Hg respectively.

It has been shown by Bugge and Kerlogue[178] that the values of surface area obtained by the above simplified procedure employing evacuation to a pressure of 10^{-2} torr agree with the value obtained by evacuation to a pressure of 10^{-5} torr within 3%. Since Emmett[28] claims only an accuracy of 20% for his BET method, it was evident that the difference of this pressure was insignificant. The time saving was thus considerable as a vacuum of 10^{-2} mm Hg was rapidly attained, whereas one of 10^{-5} mm Hg needed several hours pumping.

2.4 DETERMINATION OF ZINC IN ZINC CHLORIDE TREATED ACTIVATED CARBON:

An electrographic method devised by Hermance and Wadlow[209,210] was used to detect the presence of zinc in zinc chloride-treated activated carbon. The specimen to be tested was made anodic and the electrolyte in its vicinity was tested for cations produced by anodic attack. The electrolyte (either hydrochloric acid, ammonium chloride solution or sodium nitrate solution) was poured on to a filter paper and the specimen was pressed on to this with a cathode (or counter-electrode) of aluminium on the other side. After the application of a potential difference of a few volts for about one minute, the paper was removed and tested by means of suitable reagents for the metal ions.

This method was applied for identification of zinc as shown in Fig. 2.2 . For the purpose, a 20 g portion of the activated carbon prepared by the zinc chloride treatment was taken in a porcelain crucible, heated to 650°C in a muffle furnace for about three hours when it turned into ash, cooled to room temperature and dissolved in aqua regia. A small piece of filter paper soaked in ammonium chloride solution (5 g in 100 ml) was placed on a glass sheet and a few drops of the aqua regia solution was sprinkled on it. An aluminium sheet (cathode) and an iron rod (anode) were placed on this filter paper for about one minute whereby zinc was liberated. This was identified by adding spot reagents, mercury thiocyanate (8 g mercuric chloride and 9 g. ammonium thiocyanate diluted to 10 ml with water) followed by cobaltous chloride (0.05 g.

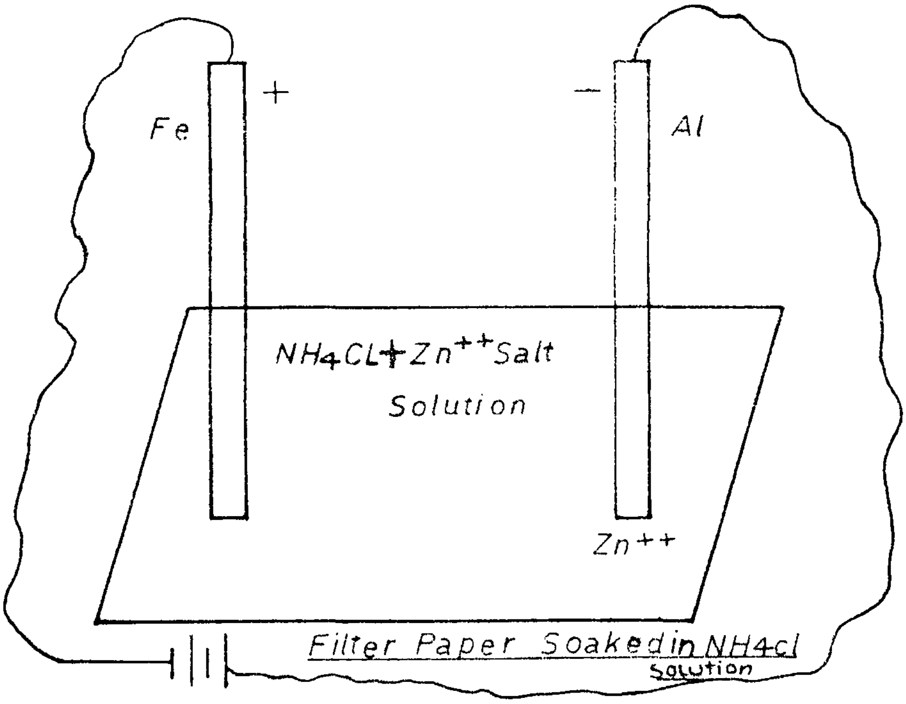


FIGURE: 2.2 A. SCHEMATIC DIAGRAM OF THE EXPERIMENTAL SET UPS.

in 100 ml 0.5 N Hydrochloric acid). The reactions are represented as follows:

$$HgCl_2 + 2NH_4CNS \longrightarrow Hg(CNS)_2 + 2NH_4Cl$$

$$Zn^{++} + \left[Hg\ (CNS)_4\right]^{-2} \longrightarrow Zn\left[Hg\ (CNS)_4\right]$$

$$Co^{++} + Zn\left[Hg\ (CNS)_4\right] \longrightarrow \underset{\text{blue ppt.}}{Co\left[Hg(CNS)_4\right]}$$

A similar run with activated carbon (not treated by $ZnCl_2$) gave no positive test for zinc.

CHAPTER 3. RESULTS & DISCUSSION.

3.1 THERMODYNAMICS.

3.1.1 ADSORPTION ISOTHERMS.

An isotherm is essentially the representation of the variation of volume with pressure at constant temperature. Adsorption equilibrium can be expressed as isotherms, isobars and isosteres. A set of curves of any one type may be converted to a set of either of the other two types, and therefore it is sufficient to consider simply one of the three types. Isotherms have been plotted using the necessary data obtained in the course of adsorption studies. In the present investigation, two different adsorbates i.e. acetic acid and iodine solutions have been used and steam activated carbon is employed as the adsorbent. The preparation of the adsorbent and the adsorbate solutions have been described in chapter 2 (section 2.1.2, 2.2.1, 2.2.2).

3.1.1.1 Acetic acid adsorption isotherms: The adsorption data i.e. the amount of acetic acid adsorbed on activated carbon at various equilibrium concentrations, represented in Table 3.1.1.1 (Appendix I) have been utilized to construct the isotherms at temperatures 303°K, 313°K, 323°K, 333°K, 343°K, 353°K and 363°K. The isotherms are shown in Fig. 3.1.1.1 (a-b).

All the isotherms obtained are similar in nature. Invoking Brunauers' five principal forms of adsorption isotherms as shown in Fig. 1.3 (section 1.4.1), it is apparent that the isotherms we obtained are similar or nearly similar to the type V. This type of isotherm is also exhibited by adsorption of water

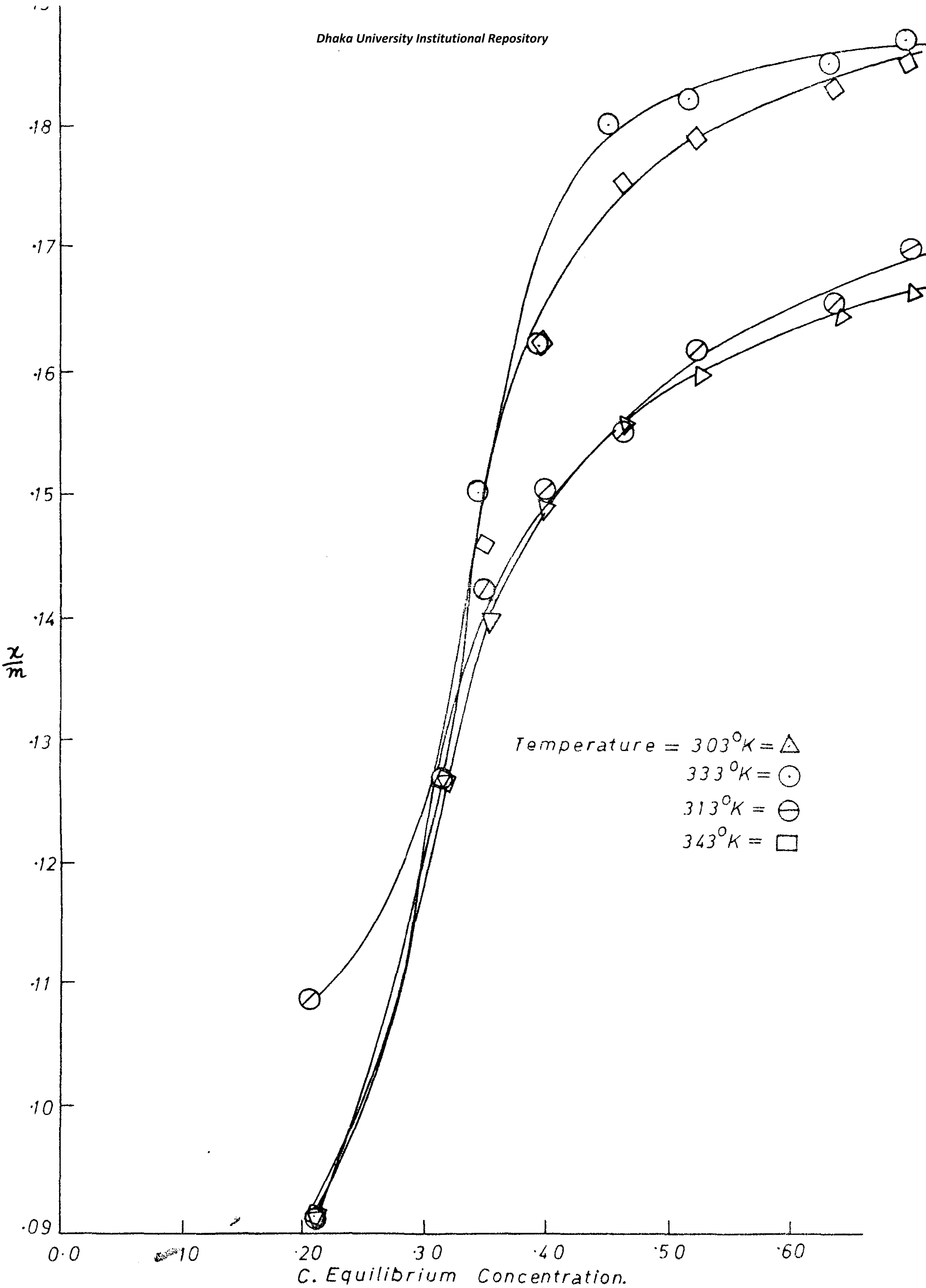


FIGURE :- 3.1.1.1 (a). CH_3COOH ADSOPTION ISOTHERM. x/m vs C.

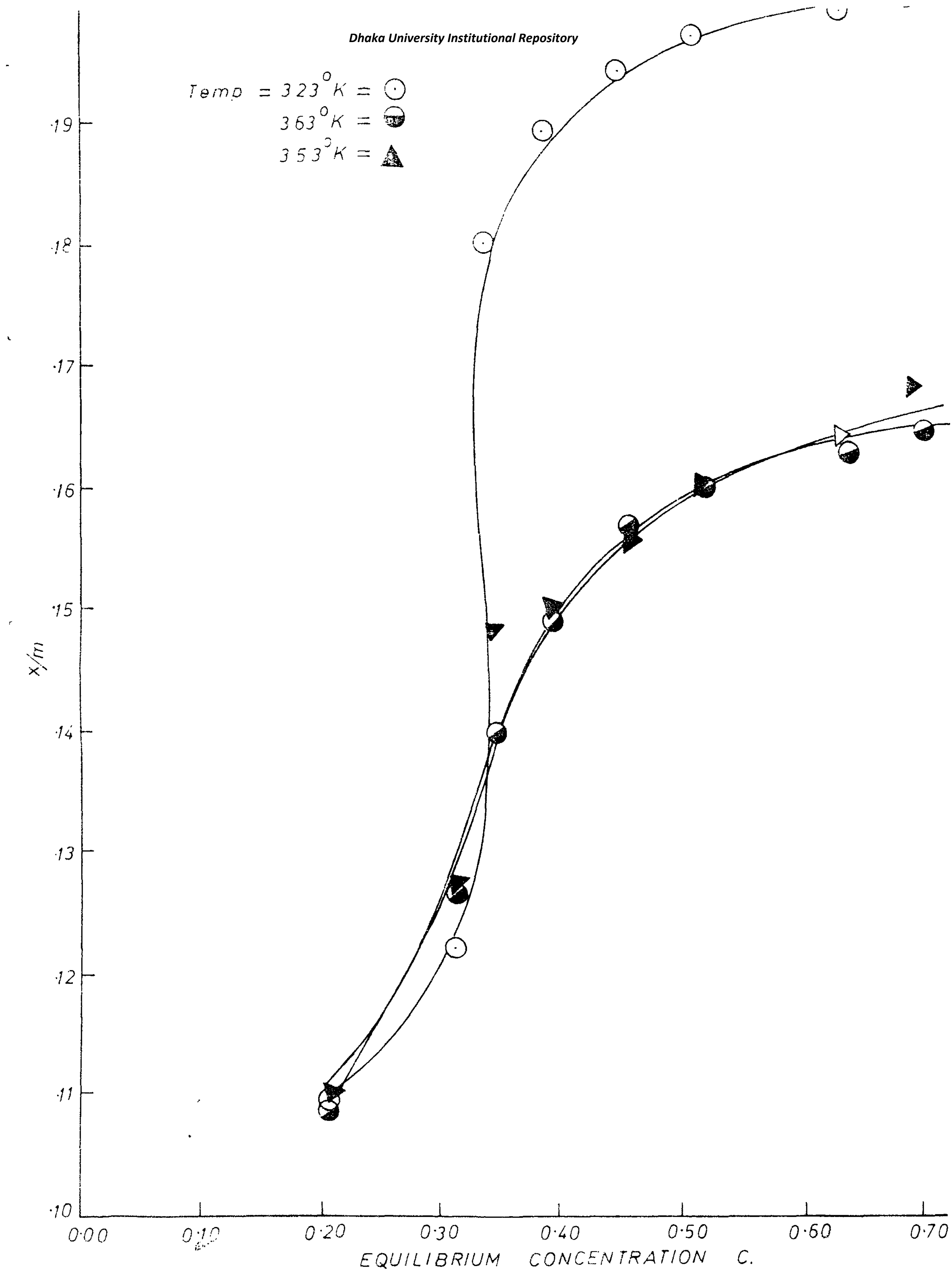


FIGURE:- 3.1.1.1 (b). CH_3COOH ADSORPTION.
Plot of (x/m vs C)(Isotherm).

vapour on charcoal[145] at 100°C. The general feature of these isotherms are that they indicate co-operative adsorption at the begining i.e. the amount adsorbed at a particular equilibrium concentration or pressure enhance the adsorption at higher equilibrium pressure or concentration. Though the pattern of higher the concentration higher the amount adsorbed is maintained, there is an abrupt increase in the adsorption above an equilibrium concentration of about 0.30N at temperature 323°K. The abrupt increase may be explained in the light of multimolecular theory and penetration in the pores and capillaries of the adsorbent above a certain value of the equilibrium concentration. Although it is not possible to ascertain whether the process of adsorption is physical or chemical and to tell exactly which part is due to multilayer type is to be expected specially as the concentration is increased, since the Vander Waals force of the adsorbate molecules in the first layer tends to hold a second layer and so on. At higher equilibrium concentration, the amount of acetic acid adsorbed on carbon tends to reach a saturation value. The overall pattern of the isotherms also indicate that the activated carbon used in the present investigation is highly porous since this type of behaviour is exhibited by porous solid.

Comparing with Giles[98] classification of the adsorption isotherms for solid-liquid system as shown in Fig. 1.5 (section 1.7) it appears that the isotherms obtained belong to the type "S". This type of isotherm is obtained if the major axis of the adsorbed molecules are perpendicular to the surface. The curves have long plateau at higher equilibrium concentration, which can be explained

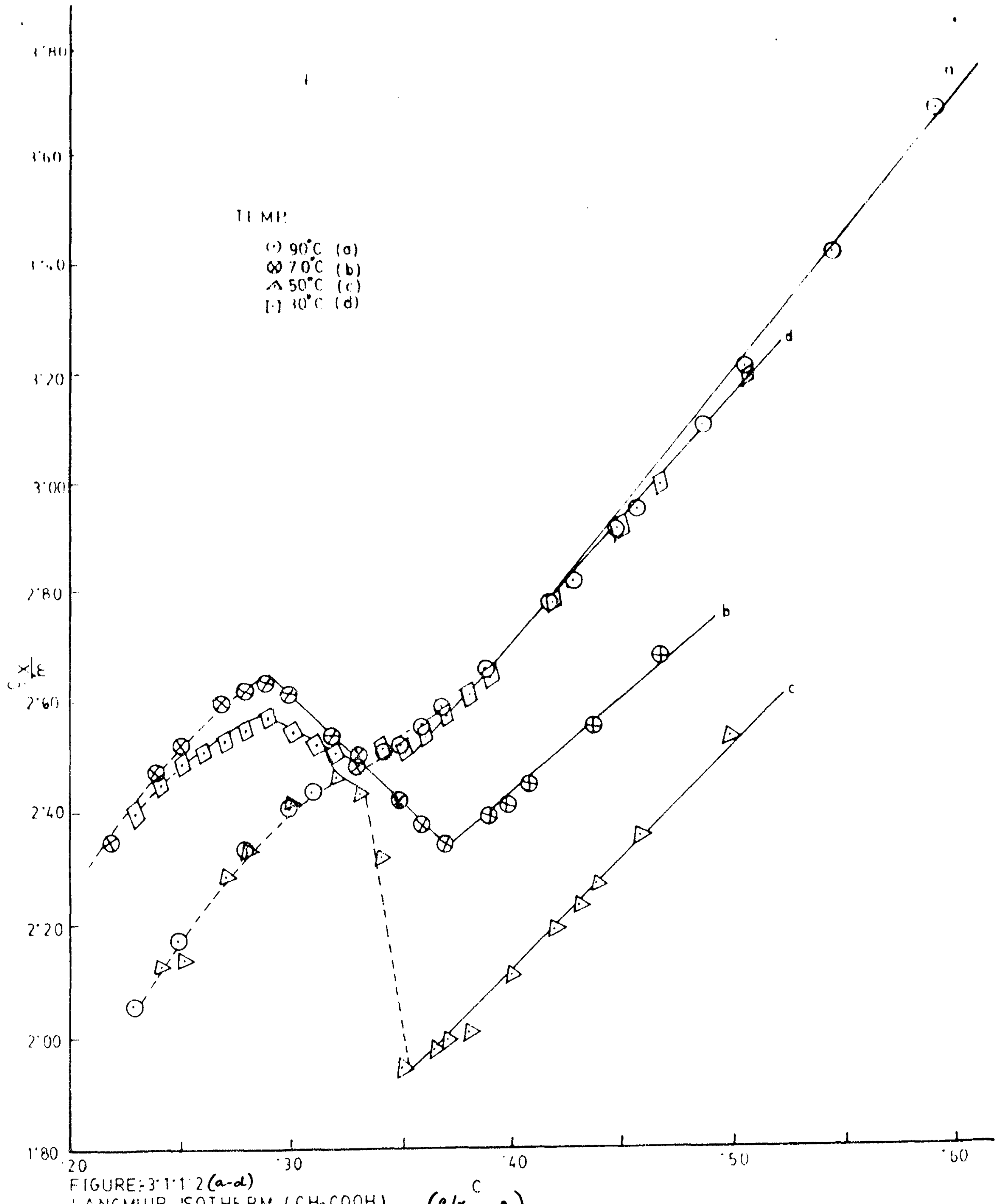


FIGURE:-3·1·1·2 (a-d)
LANGMUIR ISOTHERM (CH$_3$COOH) $\left(C/\frac{x}{m}\ \text{vs}\ C\right)$.

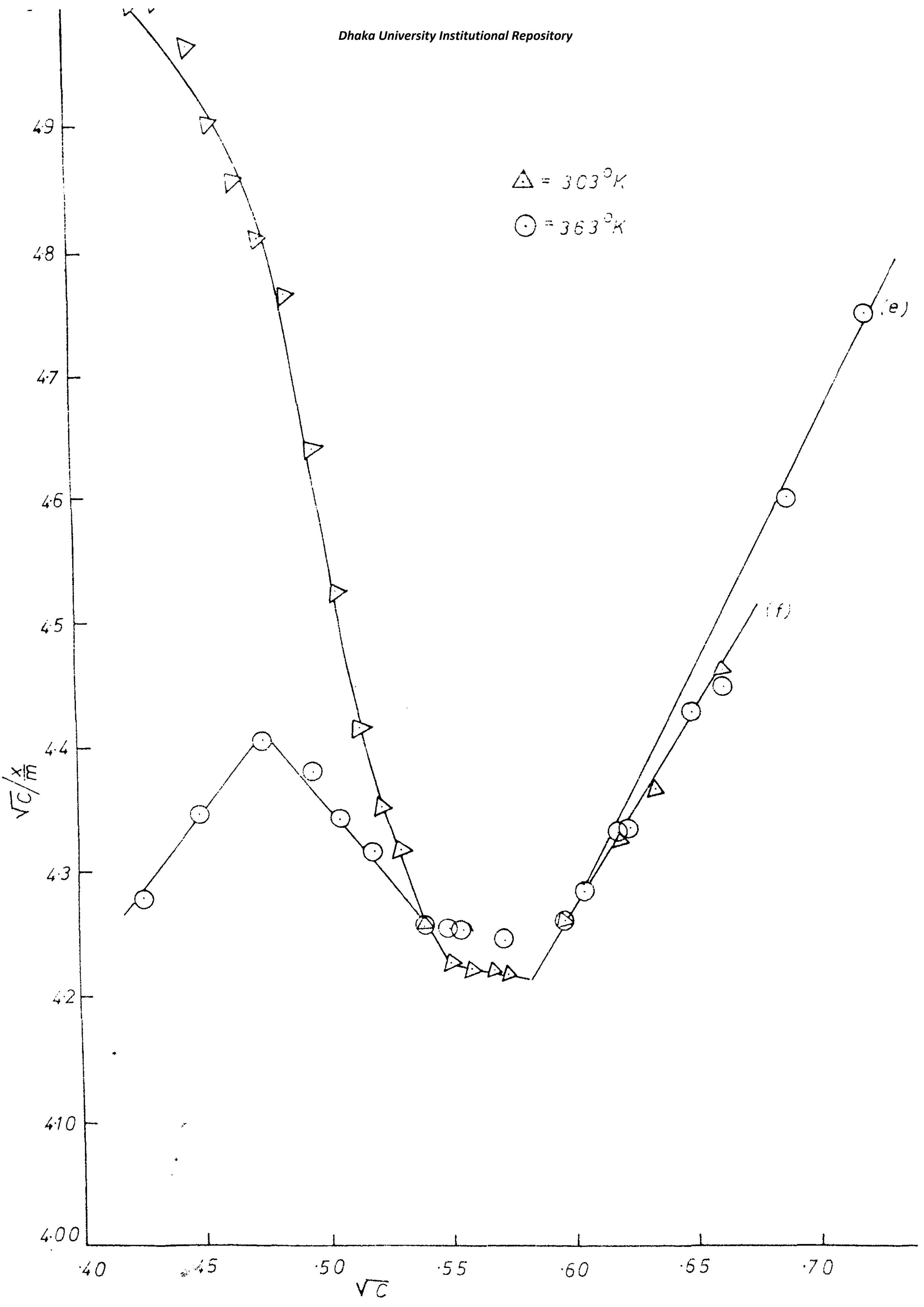


FIGURE:- 3.1.1.2.1 (e,f) LANGMUIR ISOTHERM FOR DISSOCIATIVE ADSORPTION (CH_3COOH).

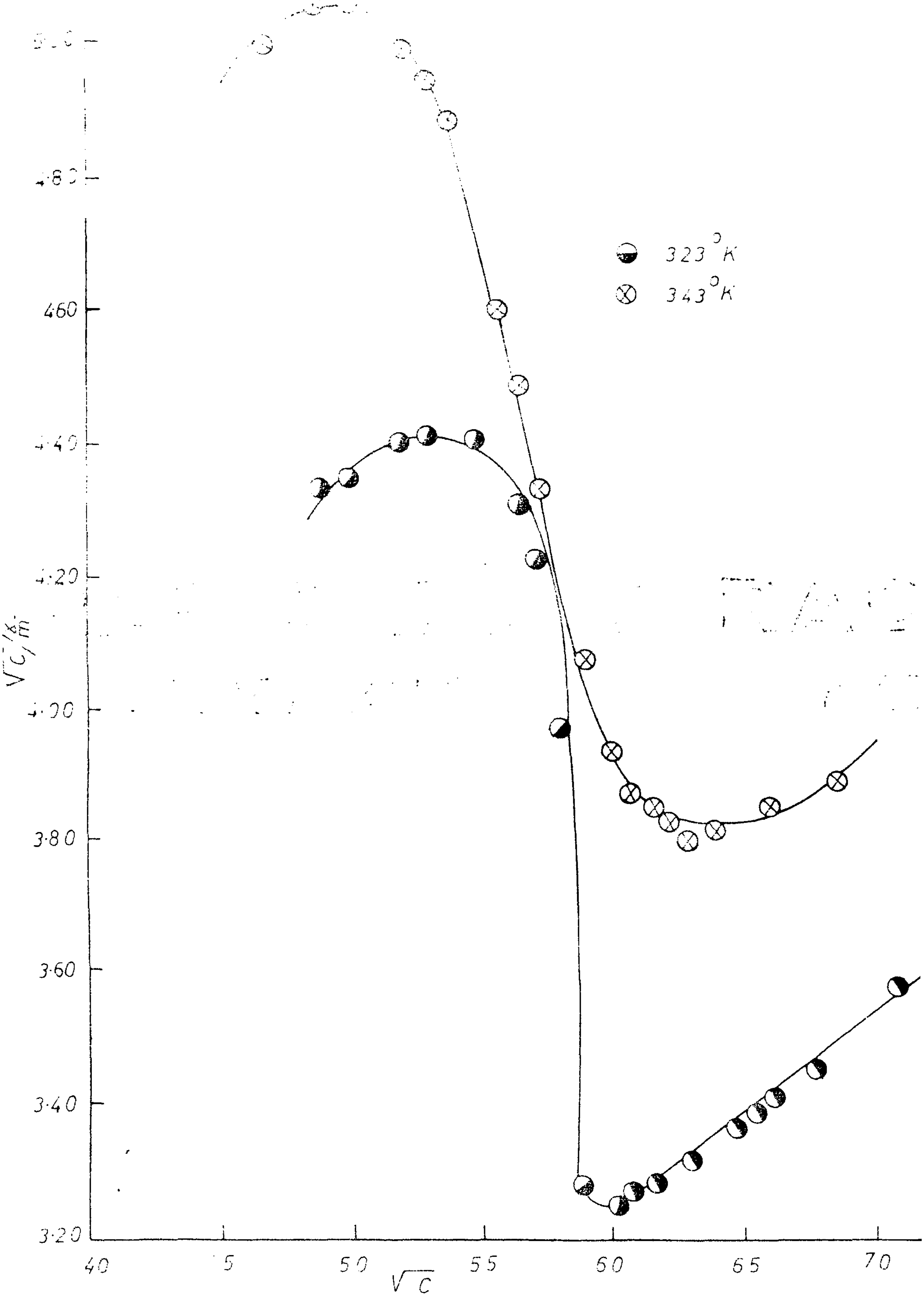


FIGURE:- 3.1.1.2.1(g,h). LANGMUIR ISOTHERM FOR DISSOCIATVE ADSORPTION (CH_3COOH).

that the adsorbed solute molecules in the monolayer are so oriented that the new surface they present to the solution has low attraction for more solute molecules.

3.1.1.2 Langmuir Isotherms: We tested our observed isotherms to find out whether they obey the Langmuir equation (1.1) (section 1.4.1). For this purpose, additional data have been derived from the experimental isotherms, and these are given in Table 3.1.1.2 (Appendix I). Fig. 3.1.1.2(a-d) show the plots of $c/\frac{x}{m}$ against C at temperatures $363^{\circ}K$, $343^{\circ}K$, $323^{\circ}K$ and $303^{\circ}K$. For Langmuir isotherms, such plots should give straight lines. The nature of the graphs clearly indicate that the isotherms do not obey Langmuir equation and there is clear deviations from the Langmuirs' isotherm. The isotherms seem to obey the Langmuirs' equation at higher equilibrium concentration following an initial deviation.

The isotherms have also been tested to see whether they fit the Langmuir isotherm for dissociative adsorption i.e.

$$\frac{\sqrt{P}}{q} = \frac{1}{\sqrt{a}\, q_m} + \frac{\sqrt{P}}{q_m} \qquad \text{(Section 1.4.1.1)}$$

Fig. 3.1.1.2.1 shows the plots of $\sqrt{c}/\frac{x}{m}$ vs $\sqrt{c}$ for these isotherms. Obviously linear variation of $\sqrt{c}/\frac{x}{m}$ with $\sqrt{c}$ is not found over the concentration range studied, indicating that the adsorption process is rather complicated.

3.1.1.3 Freundlich isotherms: Although the experimental isotherms do not apparently look like Freundlich isotherms, for a confirmatory test, log x/m has been plotted against log c (according to equation 1.4

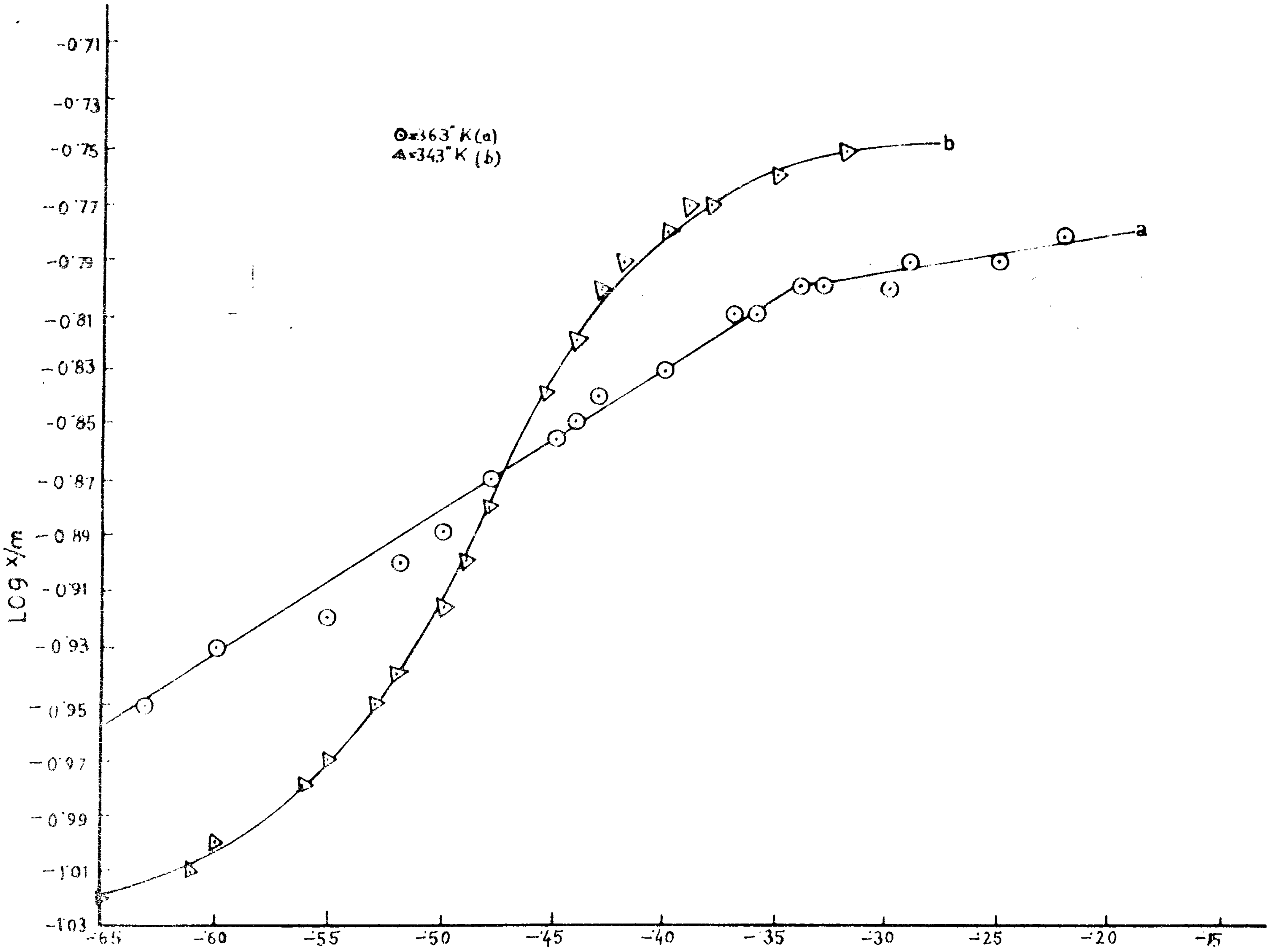


FIGURE:-3·1·1·3(a.b) FREUNDLICH ISOTHERM (CH_3COOH) (log x/m vs log C).

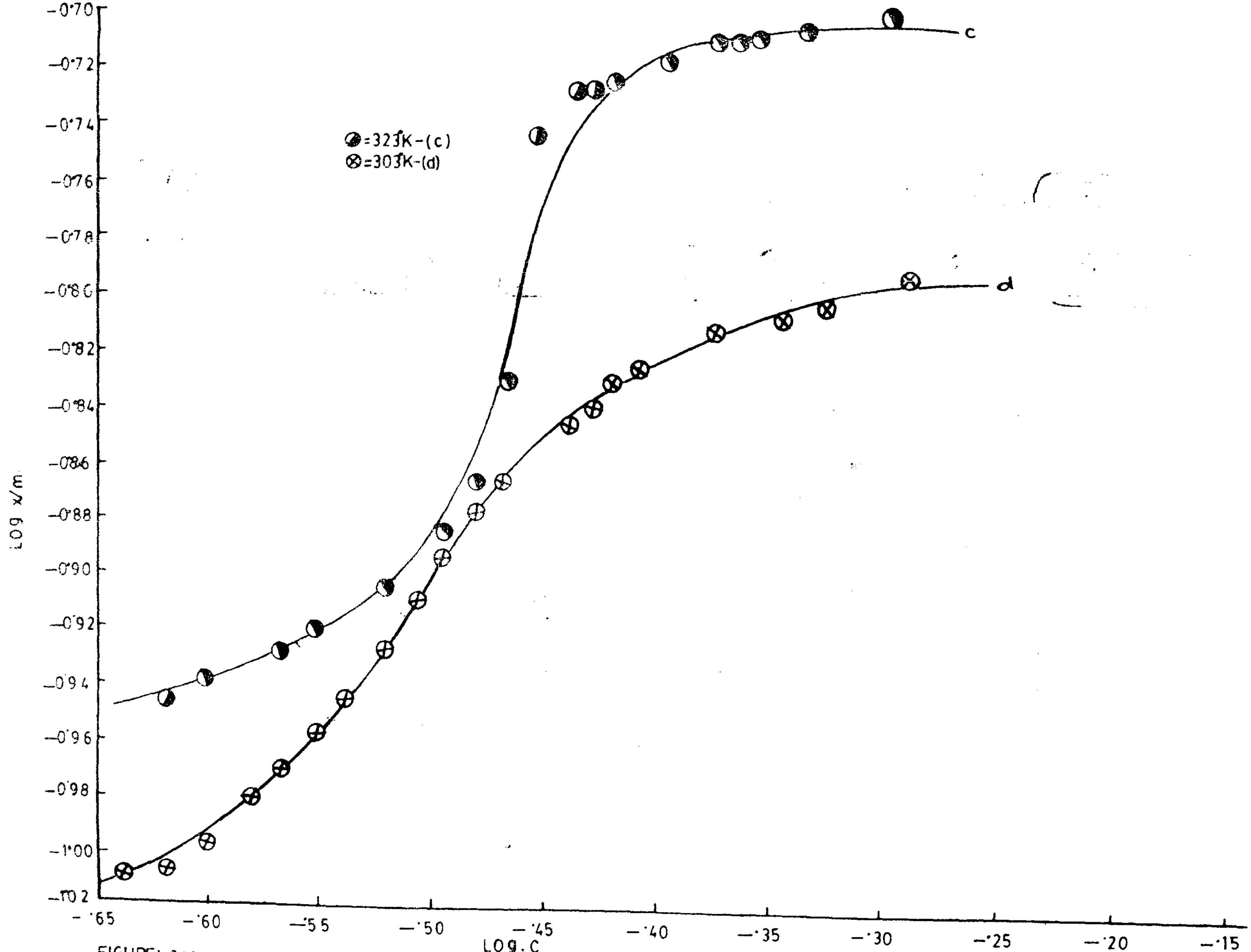


FIGURE:-3·1·1·3 (c,d) FREUNDLICH ISOTHERM (CH_3COOH)

section 1.4.1.1), using derived data from the experimental isotherms. The derived data are included in Table 3.1.1.3 (Appendix I). The plots are shown in Fig. 3.1.1.3 . The nature of the isotherms clearly indicate that they do not obey the Freundlich equation.

Since the isotherms obtained in the present study do not obey either the Langmuir or Freundlich relationship thus rendering the use of BET (Brunauer, Emmett and Teller) equation unnecessary.

3.1.1.4 Iodine adsorption isotherms: The isotherms for iodine adsorption at 303°K, 313°K, 323°K, 333°K, 343°K, 353°K and 363°K are presented in Fig. 3.1.1.4 . The data for adsorption isotherms are given in Table 3.1.1.4 (Appendix I). The isotherms obtained are nearly similar in nature. The isotherms at lower temperatures is slightly different from the higher temperature curves in that at higher equilibrium concentration the isotherms show a linear behaviour. It is interesting to note that the isotherms obtained fall within the five general type of isotherms classified by Brunauer namely type III. This type is relatively rare - an example is that of the adsorption of Br_2 on silica gel at 79°C. The shapes of the curves can be explained by postulating the formation of multilayers of the adsorbate molecules. This multilayer type adsorption is expected specially as the concentration of the adsorbate solution is increased, since the molecules in the first layer tends to hold a second layer and so on by Vander Waals' forces. At higher concentrations the isotherms have attained almost linearity showing that the amount adsorbed is proportional to concentration increase.

If the curves are compared with Giles' classification,

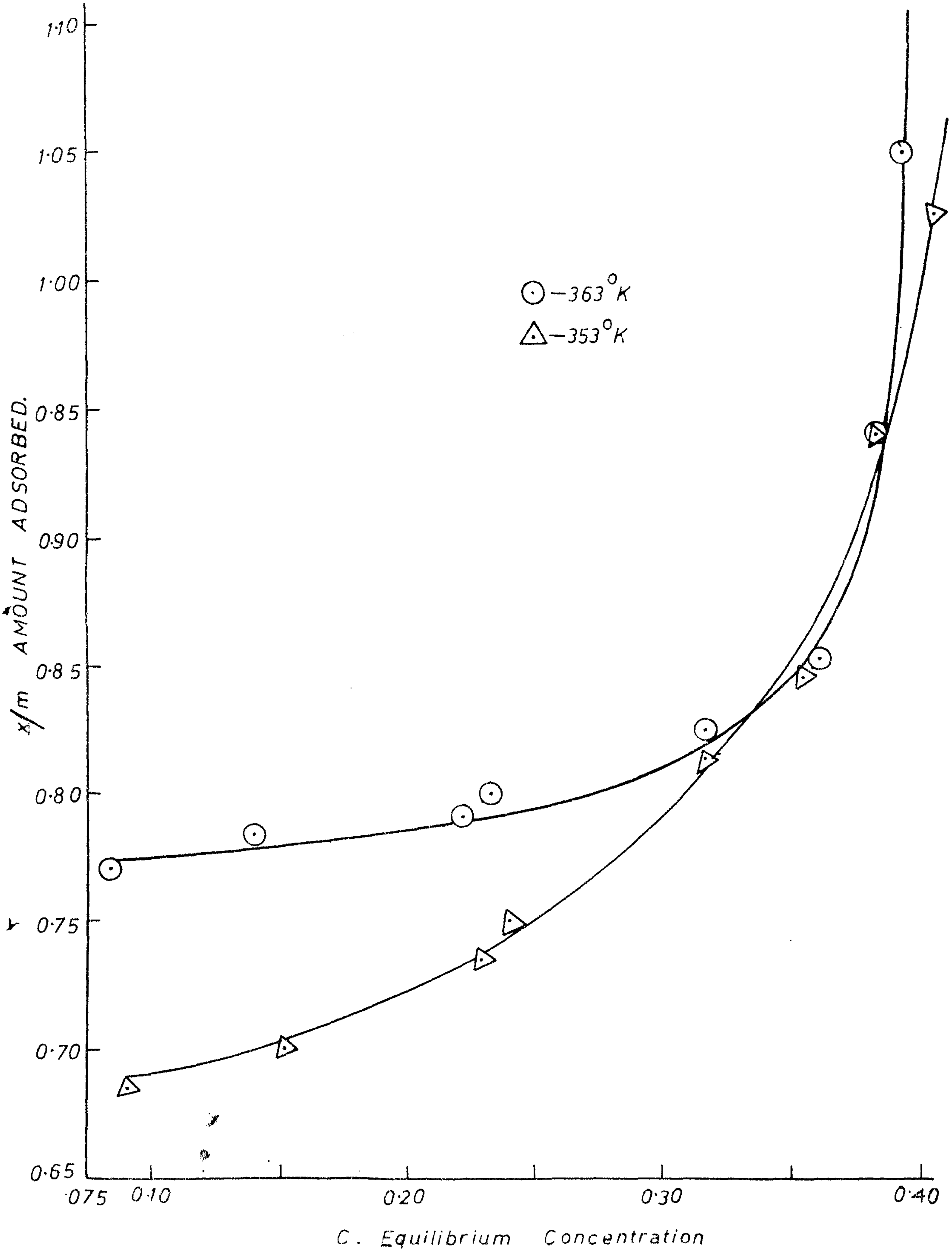


FIGURE: 3·1·1·4 (a) ADSORPTION ISOTHERM (I_2) x/m VS C.

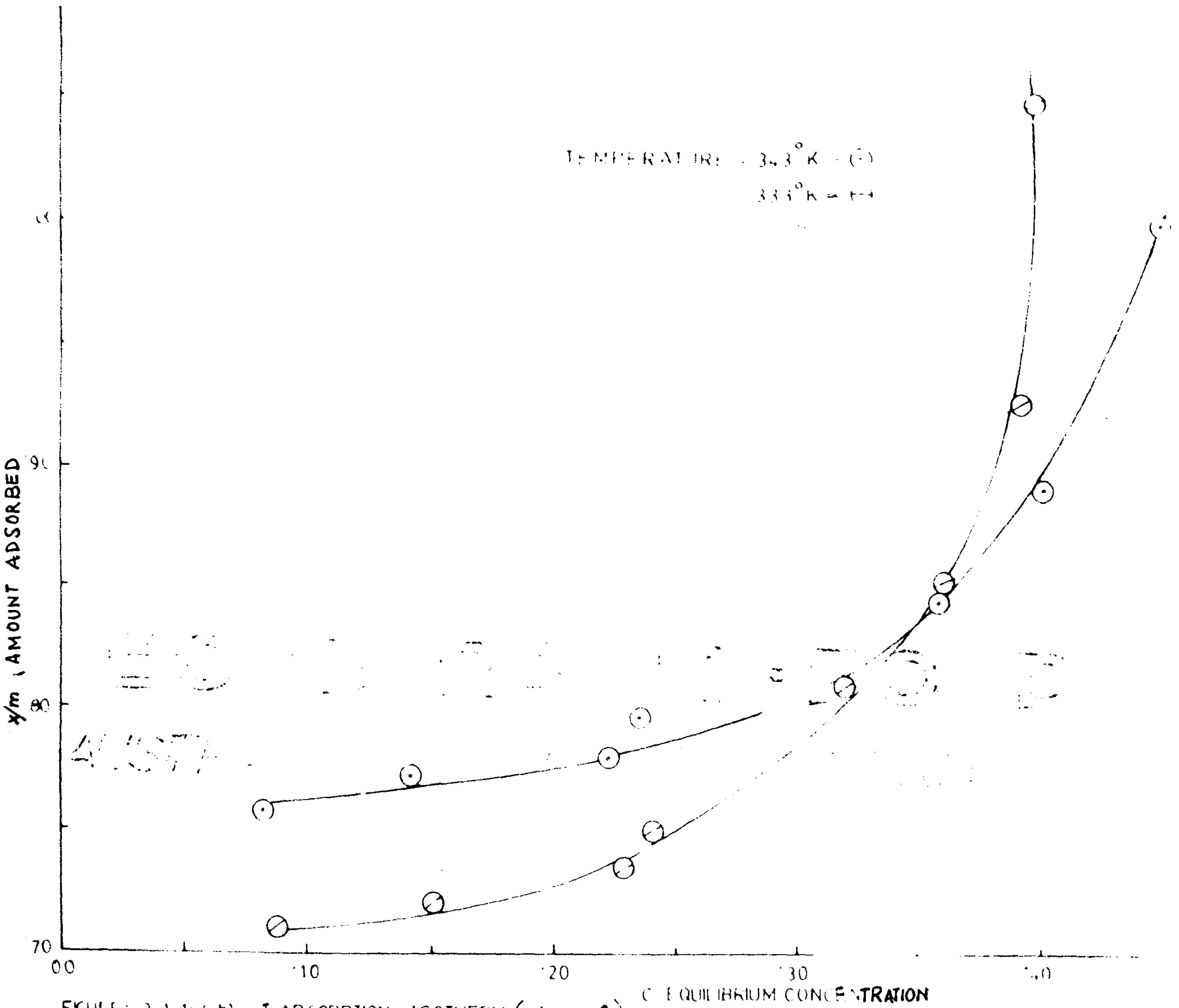


FIGURE :-3·1·1·4·b). I_2 ADSORPTION ISOTHERM (x/m vs. C)

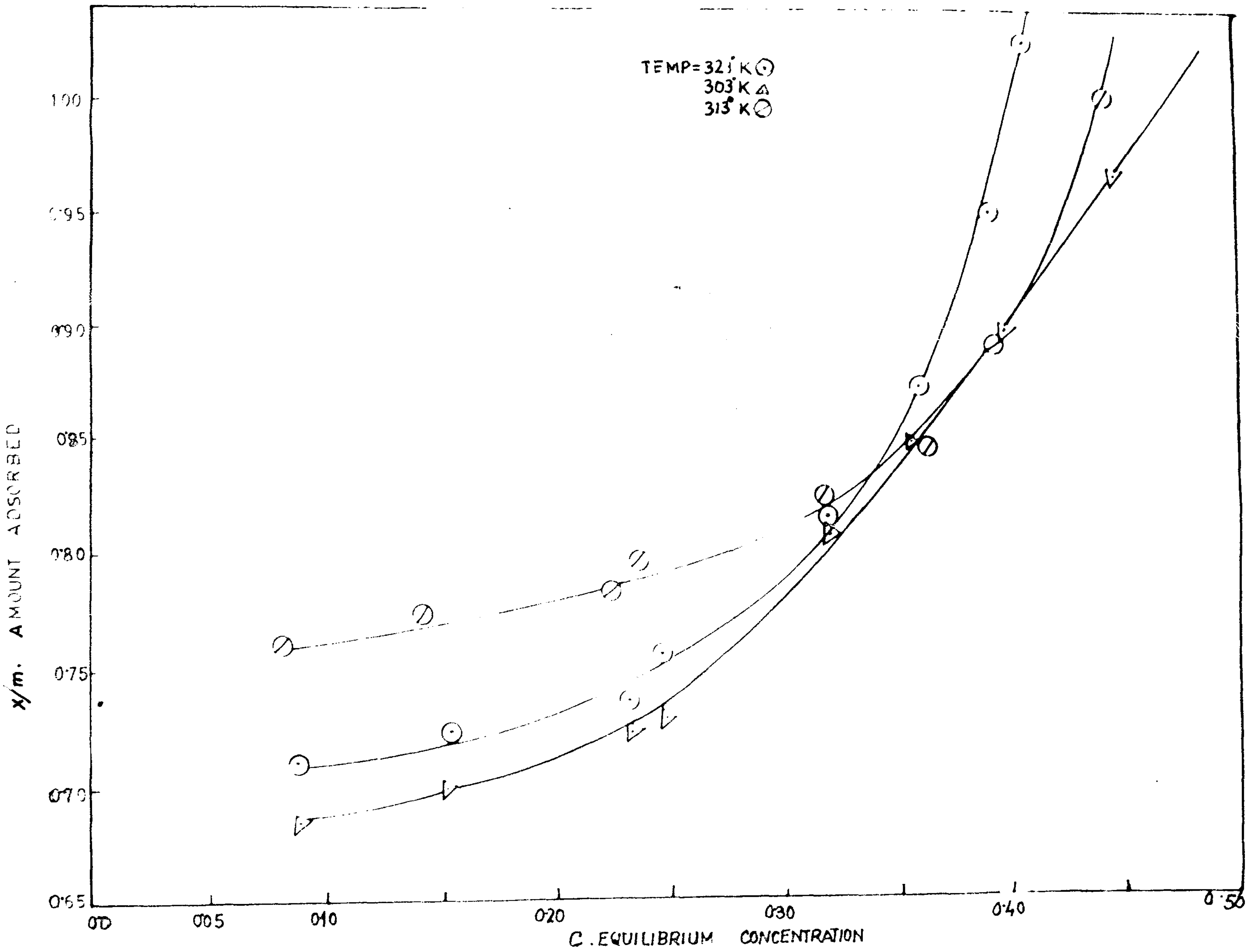


FIGURE . 3 1.1.4(C) I_2 ADSORPTION ISOTHERM. $(x/m \text{ vs } C)$.

it is apparent that they belong to "L" type and the general feature of this type is that there is no strong competition from the solvent for sites on the surface of the adsorbents. Another possibility is that, the adsorbate has linear or planer molecules, the major axis is parallel to the surface.

3.1.1.4.1 Langmuir isotherms for iodine adsorption: To find out whether the observed isotherms obey the Langmuir equation (1.1), additional data have been derived from the experimental isotherms, and presented in Table 3.1.1.4.1 (Appendix I). Fig. 3.1.1.[illegible]) show the plots of $c/\frac{x}{m}$ against c at temperatures $363^{0}K$, $353^{0}K$, $343^{0}K$, $333^{0}K$, $323^{0}K$, $313^{0}K$ and $303^{0}K$. It may be noted that all the isotherms have the same nature i.e. they obey the Langmuir equation upto an equilibrium concentration of about 0.27N. Above this concentration, there is a clear deviation from the Langmuir isotherms. The deviation might be due to the formation of multimolecular layer. Along ab(Fig. 3.1.1.5) Langmuirs' equation is obeyed, at b available surface is fully covered with a monolayer of iodine and between bc multilayer formation has occured. Thus the formation of multilayers are proved by the Langmuir and empirical isotherms and established that the process of adsorption of iodine is physical adsorption.

The isotherms at different temperatures ($363^{0}K$ - $303^{0}K$) have been tested to see whether these isotherms fit the one for dissociative adsorption. (Langmuir equation 1.2 section 1.4.1.1) Figs. 3.1.1.5.1 show the plots $\sqrt{c}/\frac{x}{m}$ vs $\sqrt{c}$ for these isotherms. Here linear variation of $\sqrt{c}/\frac{x}{m}$ vs $\sqrt{c}$ is not found over the concentration range studied, indicating that the adsorbate iodine

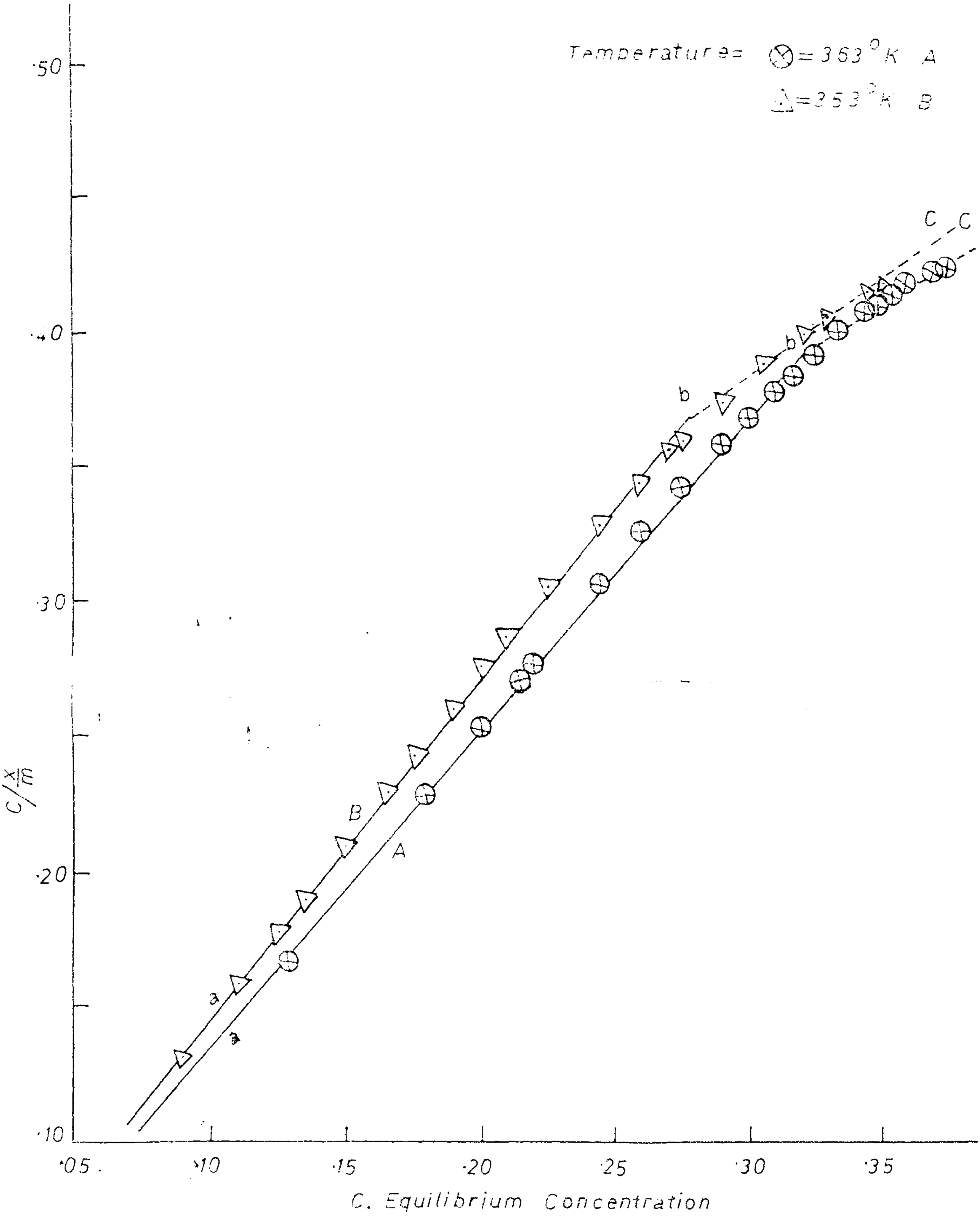


FIGURE 3·1·1·1(a). I_2 ADSORPTION. LANGMUIR ISOTHERM.

($C/\frac{x}{m}$ vs C).

(Stippled curve signify deviation)

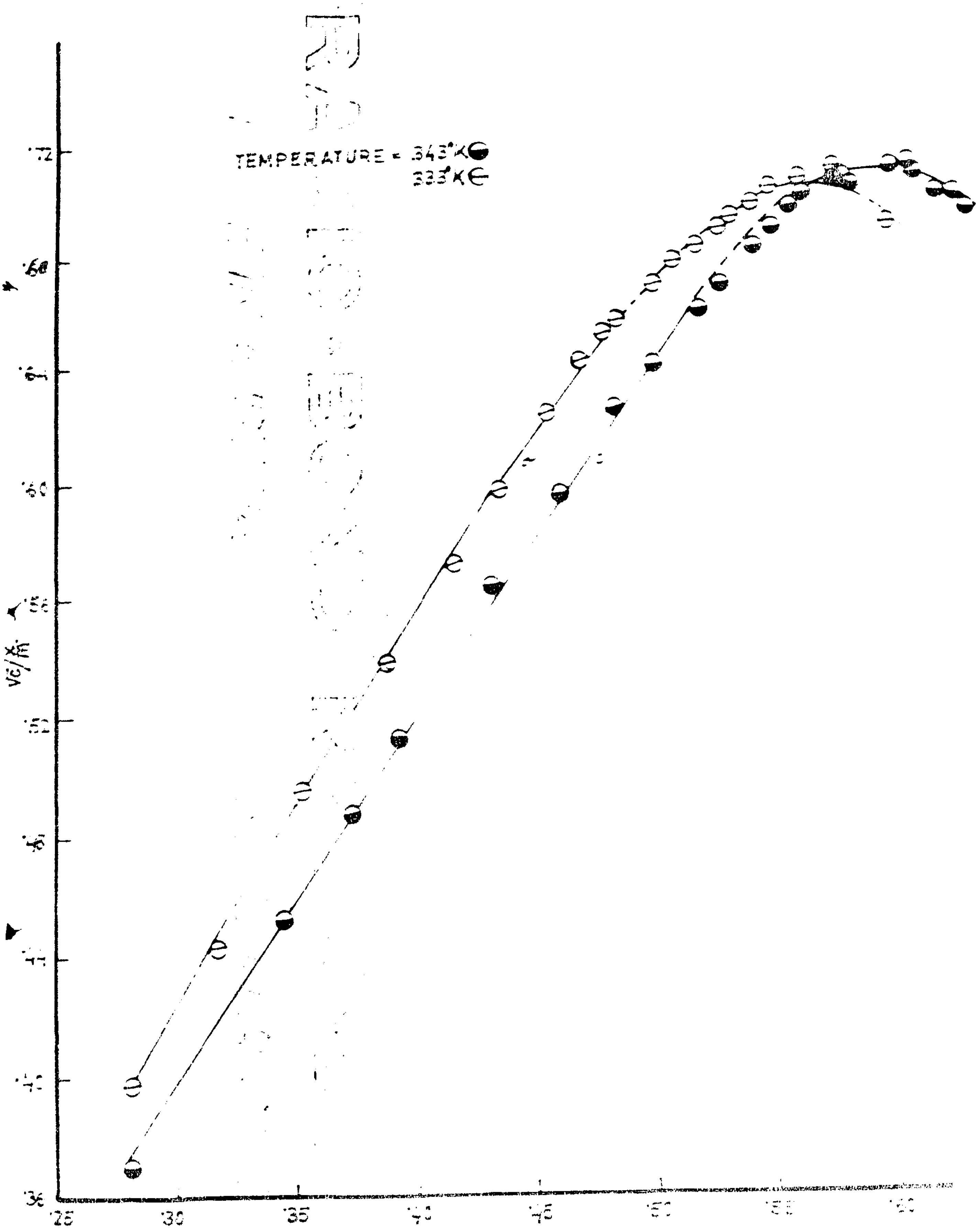


FIGURE-3·1·1·5·1(a) $\sqrt{C}$

LANGMUIR ISOTHERM FOR DISSOCIATIVE ADSORPTION (I_2) $\sqrt{C}/\frac{x}{m}$ vs $\sqrt{C}$ PLOT)

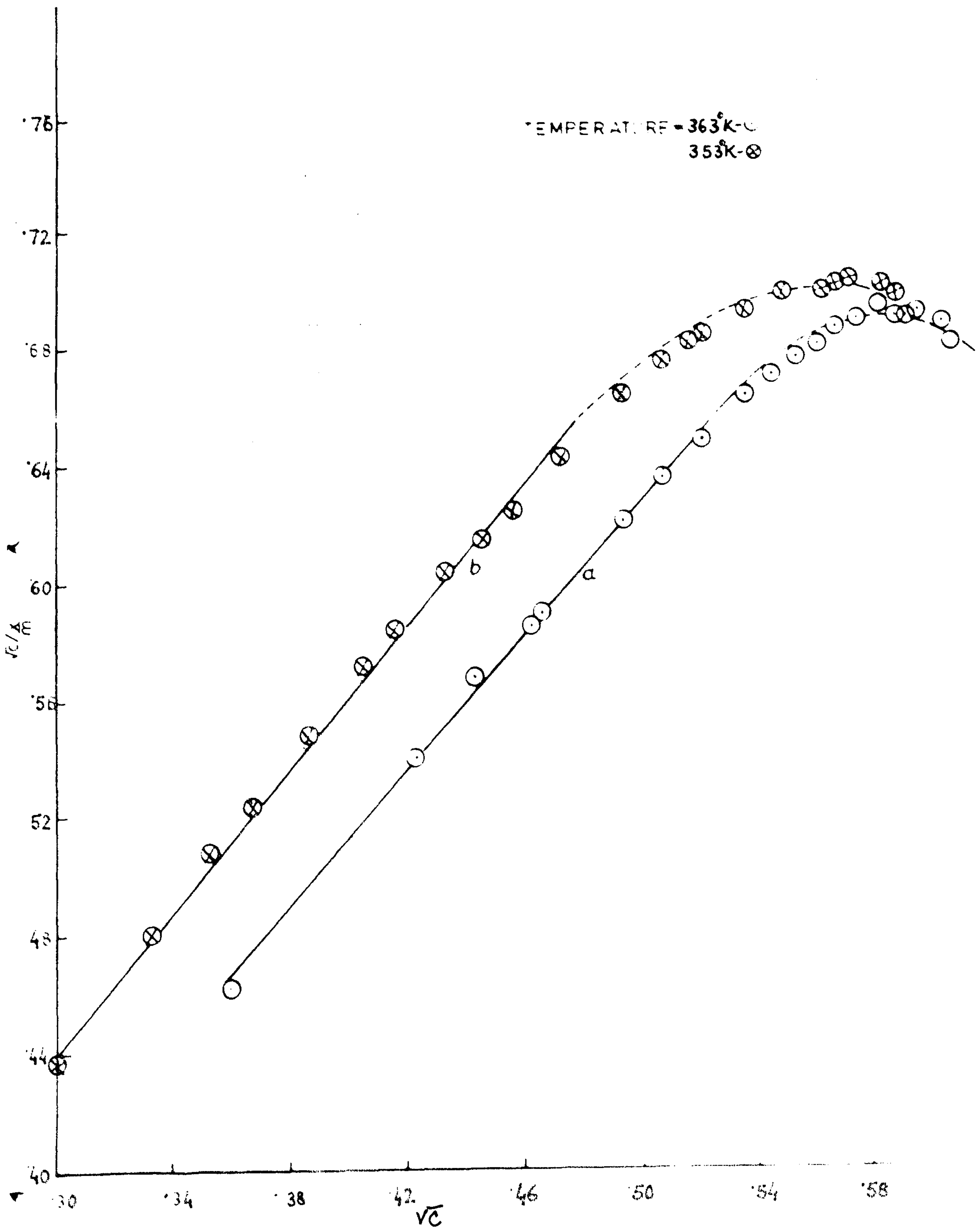


FIGURE 3.1.1.5.1(b)
LANGMUIR ISOTHERM FOR DISSOCIATIVE ADSORPTION (I_2) ($\sqrt{C}/\frac{x}{m}$ vs $\sqrt{C}$ PLOT).

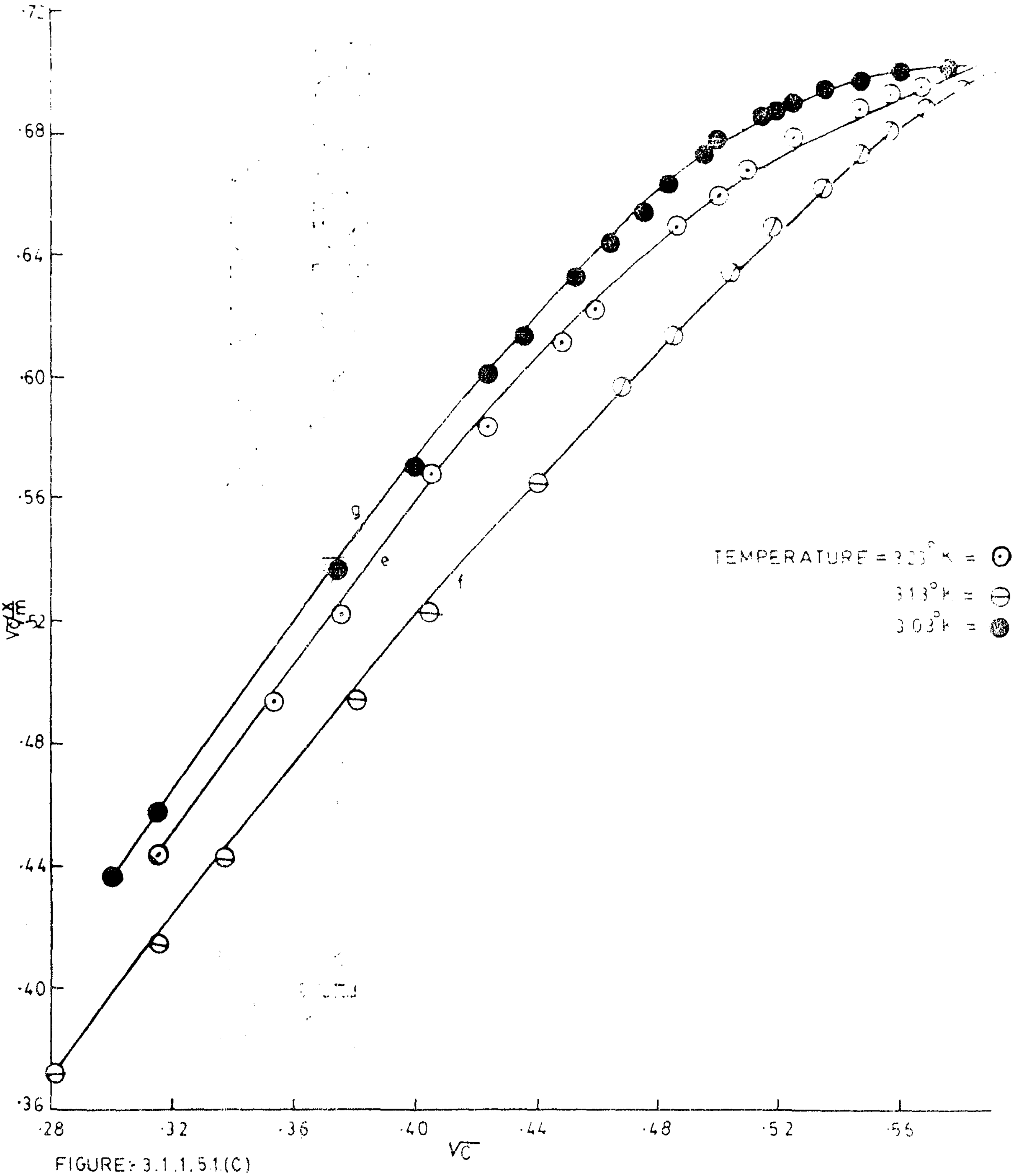


FIGURE:- 3.1.1.5.1.(C)

LANGMUIR ISOTHERM FOR DISSOCIATIVE ADSORPTION (I_2) $\sqrt{C}/\frac{x}{m}$ vs $\sqrt{C}$.

is not dissociated when adsorbed on the carbon surface.

3.1.1.4.2 Freundlich isotherm for iodine adsorption: The experimental isotherms have been used to derive data for Freundlich isotherms and are represented in Table 3.1.1.6 (Appendix I). To confirm whether they obey Freundlich equation, Figs. 3.1.1.6(a-d) have been drawn as log $\frac{x}{m}$ vs log c (according to equation 1.4 section 1.4.1.1). The isotherms at different temperatures show different nature and only the low temperature (303^{o}K) isotherm obey Freundlich equation at lower equilibrium concentration. The other three isotherms are completely different from the lower temperature isotherm and straight lines have not been obtained obeying Freundlich equation. The isotherms at 343^{o}K and 323^{o}K are similar in nature and the one at 363^{o}K show linear relationship at higher equilibrium concentration.

Although the adsorption of iodine from aqueous solution have been used for comparing carbon blacks for many years[199,212,213], no systematic work known to the author has been attempted until 1946 when Kendall[214] showed that the problem is more complex than the previous workers have assumed.

In a detailed investigation Benson and Sanlaville[215] concluded that the adsorption of iodine by carbon blacks is a very slow process and that multimolecular layer adsorption takes place. These claims contradicted those of all previous workers. However, they failed to recognize the dependence of adsorption on the free iodine concentration.

In adsorption from aqueous solution, potassium iodide

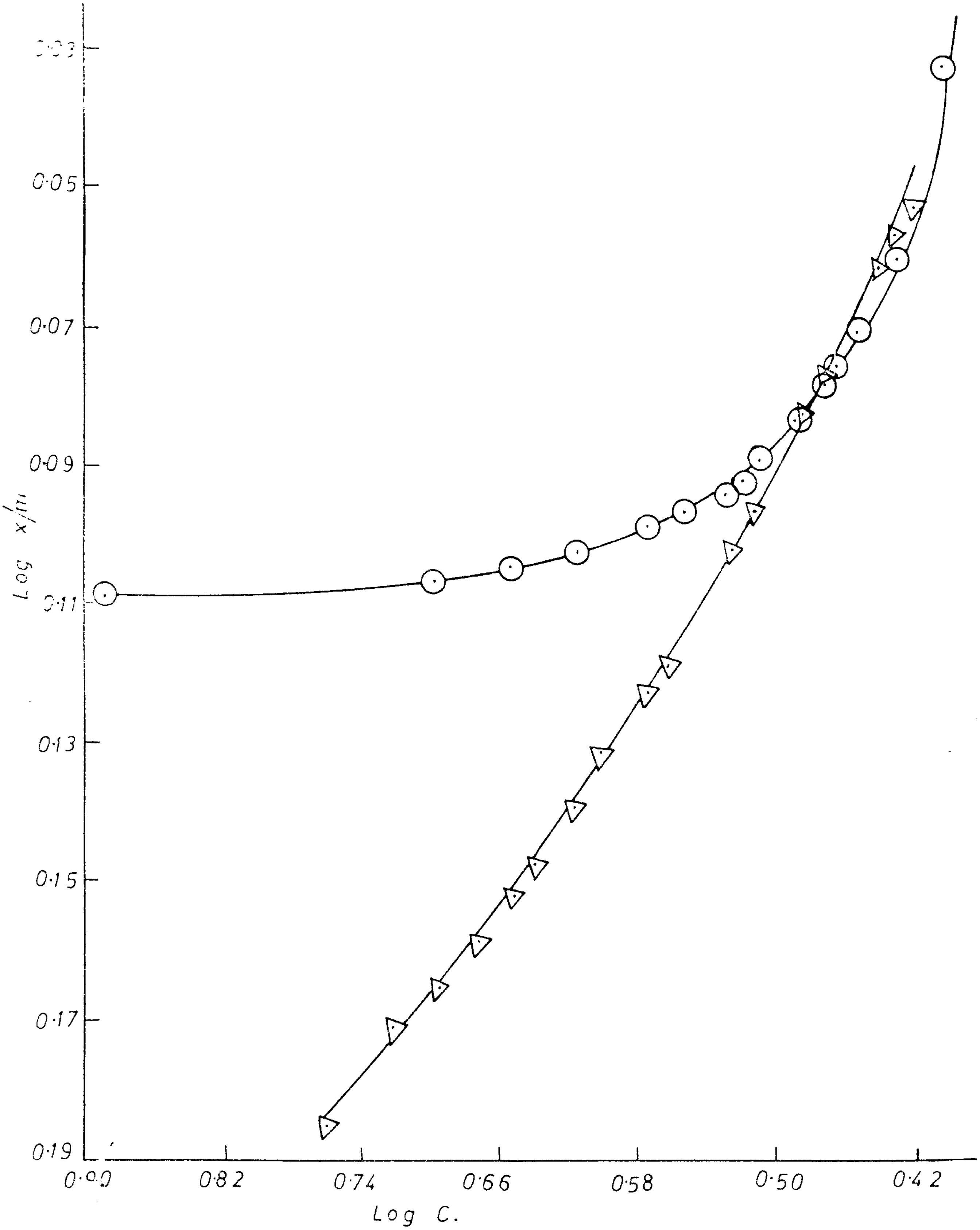


FIGURE :- 3.1.1.6. FREUNDLICH ISOTHERM (I_2).
(Log x/m vs Log C).

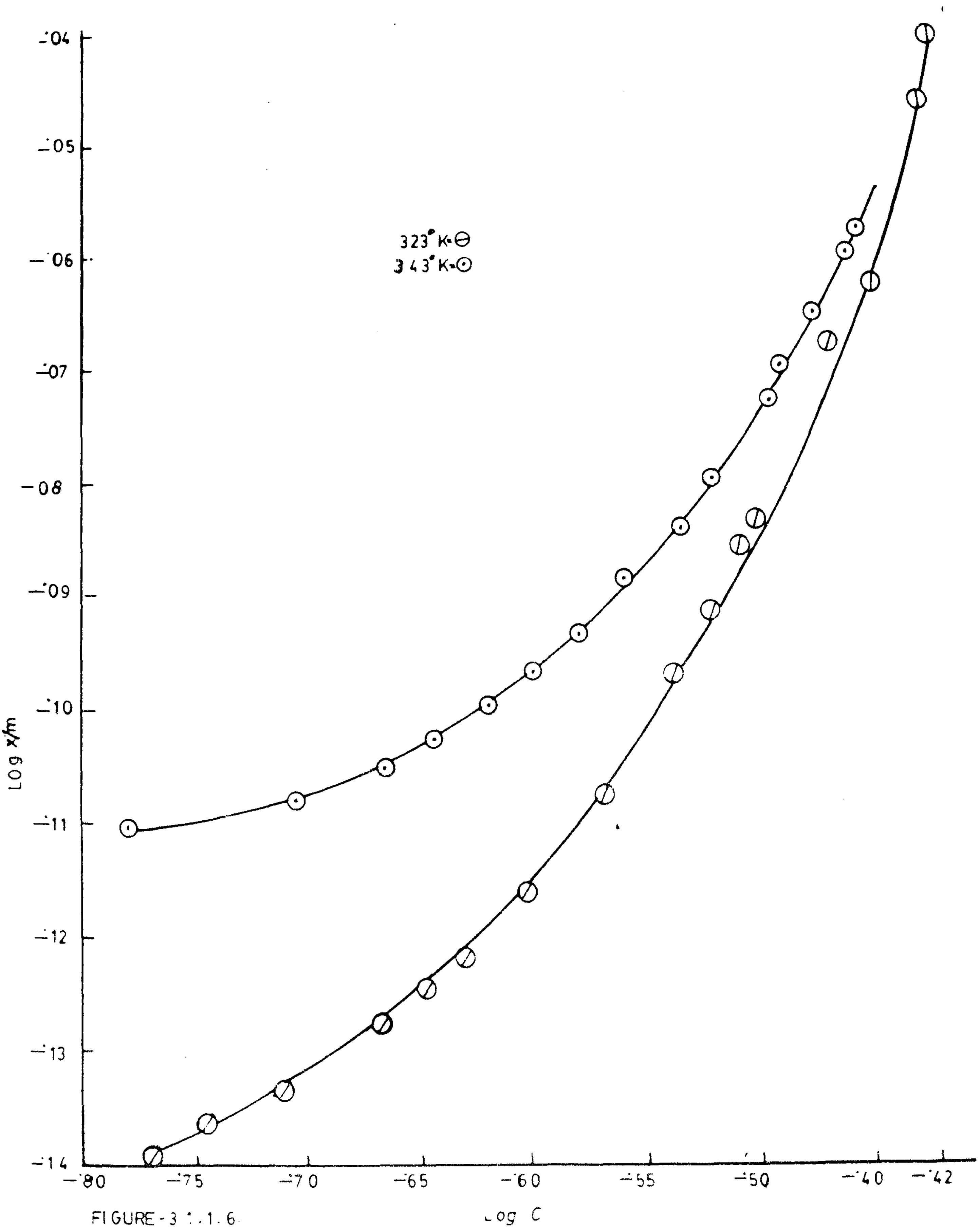


FIGURE-3.1.1.6
FREUNDLICH ISOTHERM (9_2)

is always present, hence some tri-iodide is formed and three species containing iodine can potentially be adsorbed. According to Kendall's[214] work an aqueous solution of iodine in potassium iodide is known to contain potassium iodide, potassium tri-iodide, and I_2 molecules because of the equilibrium,

$$KI + I_2 \rightleftharpoons KI_3 \ .$$

Hence, the identity of the adsorbed species need consideration. Watson and Parkinson[216] have shown that only free iodine is adsorbed by carbon black. It has similarly been shown that I_2 is adsorbed by platinum surface preferentially to I^- or I_3^- and can cover nearly a monolayer[217], molecular iodine is here the least soluble component of the solution.

Watson[216] also found that some of the iodine adsorbed by carbon blacks can not be recovered. The unrecoverable iodine is, in part, retained by the carbon black (presumably chemisorbed), and in part reduced to iodide which remained in the solution. This suggested the possible dehydrogenation of carbon by molecular iodine, and also the adsorption of products of hydrolysis.

$$I_2 + H_2O \longrightarrow HOI + HI$$

$$\text{Carbon} + HOI \longrightarrow \text{Carbon(OH).I}$$

$$\text{or} \quad \text{Carbon} + HOI \longrightarrow \text{Carbon(O)} + HI$$

The iodine chemisorbed by sugar charcoal is recovered by evacuation at 1200°C. A much greater amount of iodine, however, is converted to hydrogen iodide, and results in a corresponding increase in oxygen content of the charcoal[218], detectable as carbondioxide when the charcoal is evacuated at 1200°C.

Kendall[214] performed blank experiments which showed that potassium iodide is not adsorbed. Adsorption isotherms have been plotted for a number of carbon blacks, and the isotherms are independent of the amount of potassium iodide in solution when the adsorption is expressed as a function of the free iodine concentration. These facts proved that only neutral iodine molecules have been adsorbed.

In the present investigation, analysis of the iodine solution, before and after adsorption, showed only a small decrease in the total potassium iodide (KI) concentration (Table 3.1.1.7) Appendix I proving that the adsorbed species are nearly all free iodine molecules, consequently sorption is plotted as a function of the free iodine concentration.

Marsh and Hill[219] used iodine/iodide/water and HOAC/water systems to study adsorption by activated (Polyvinylidene chloride) carbons and by activated cocoanut charcoal. They showed that the adsorption of iodine from aq I_2/KI solution is very similar to adsorption of CO_2 at 195°K and N_2 at 77°C. Complete pore filling by iodine occurs in the activated carbons and it is suggested that multilayer formation can occur with carbon blacks. The isotherms representing iodine adsorption used the concentration of free I_2 in solution and not total iodine concentration. They showed differences in the processes of adsorption of I_2 from solution and I_2 from the vapour phase. Monolayer and multilayer adsorption is by I_2 only. No adsorption of I^- or I_3^- can be detected by them.

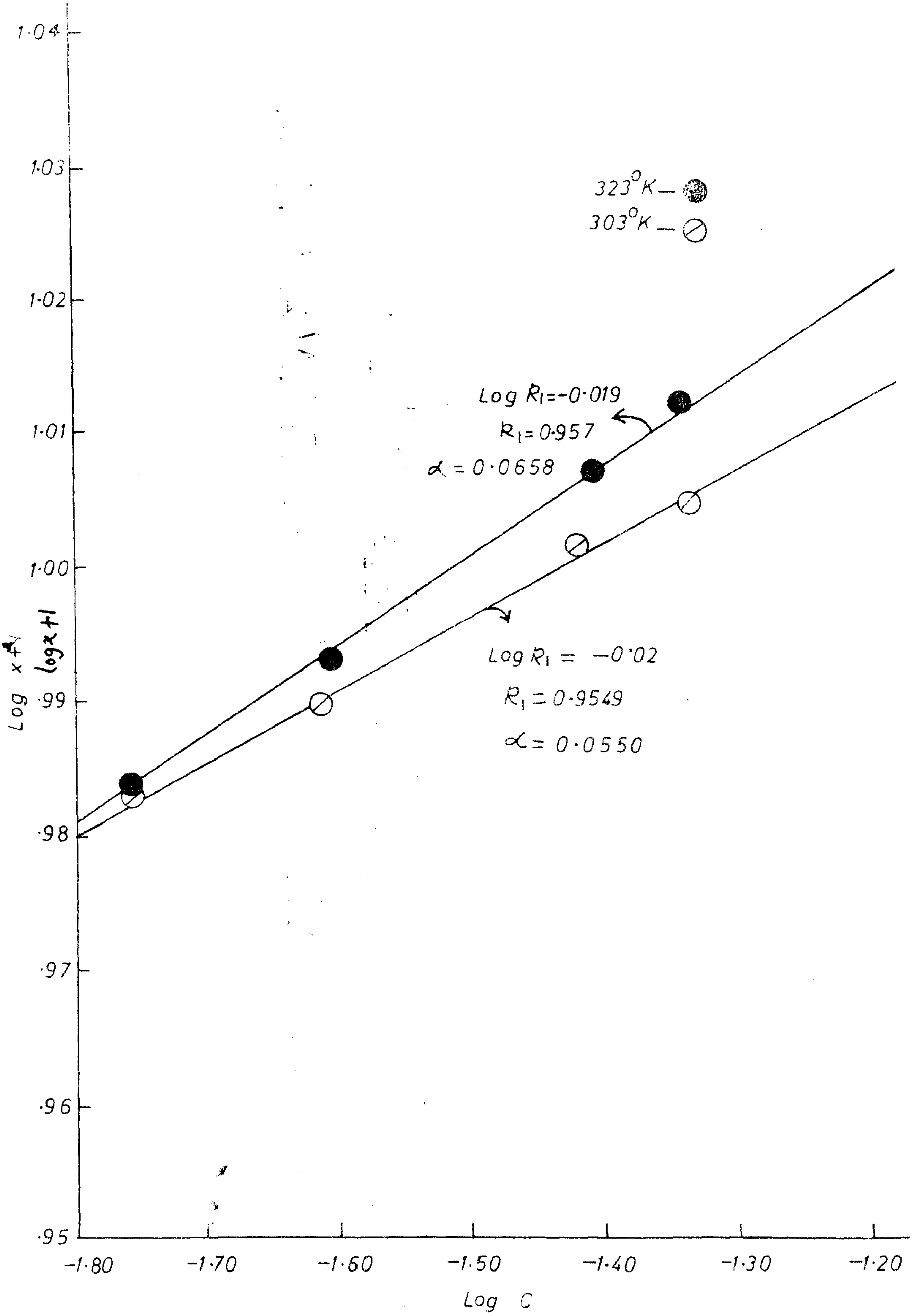
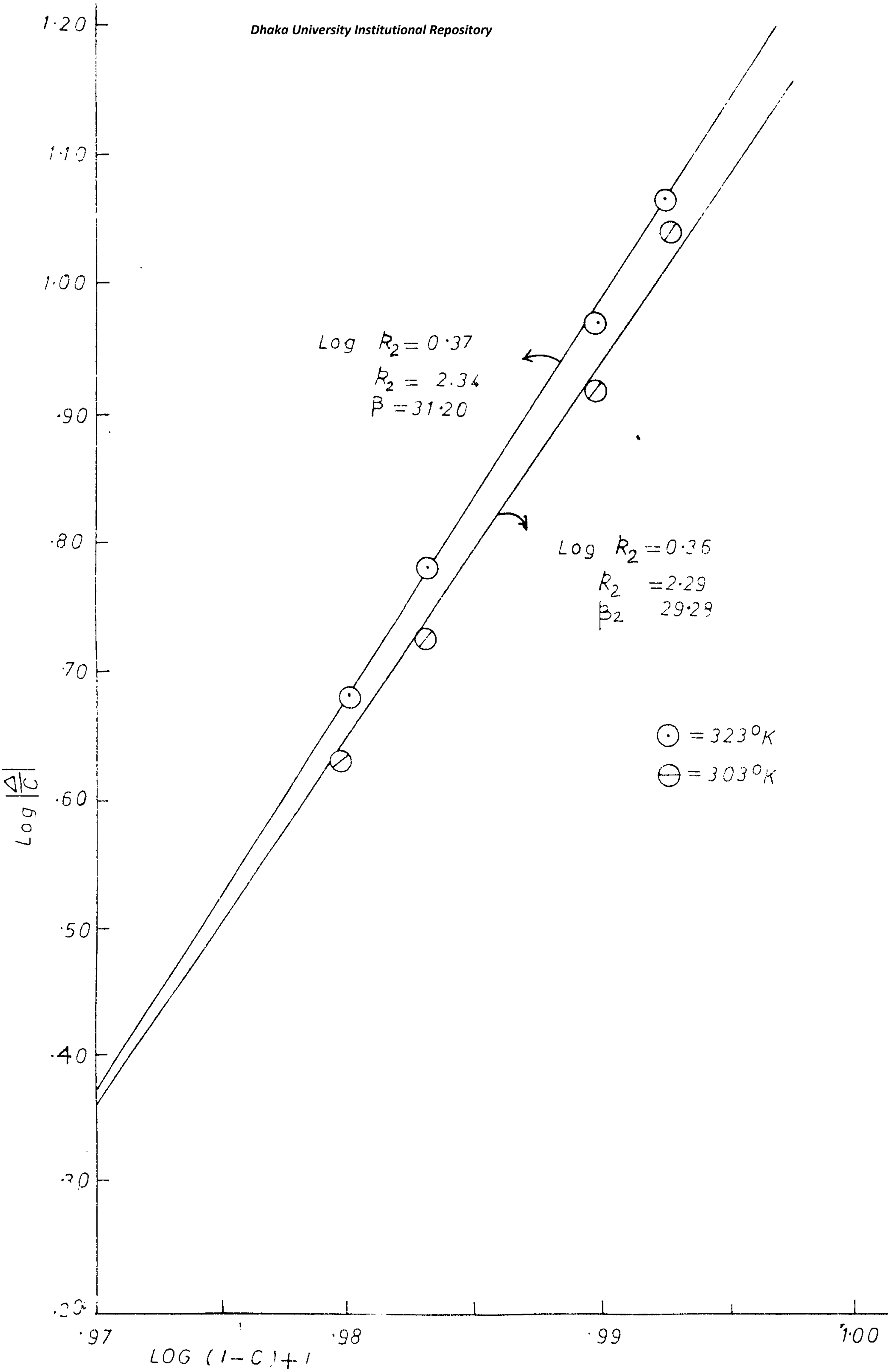


FIGURE:- 3·1·1·8 Log x VS Log C (I_2 ADSORPTION).


1·20
1·10
1·00
·90
·80
·70
·60
·50
·40
·30
·20
Log $\left|\frac{\Delta}{C}\right|$
·97
·98
·99
1·00
LOG (1−C)+1
Log R_2 = 0·37
R_2 = 2.34
β = 31·20
Log R_2 = 0·36
R_2 = 2·29
$β_2$ 29·28
⊙ = 323°K
⊖ = 303°K

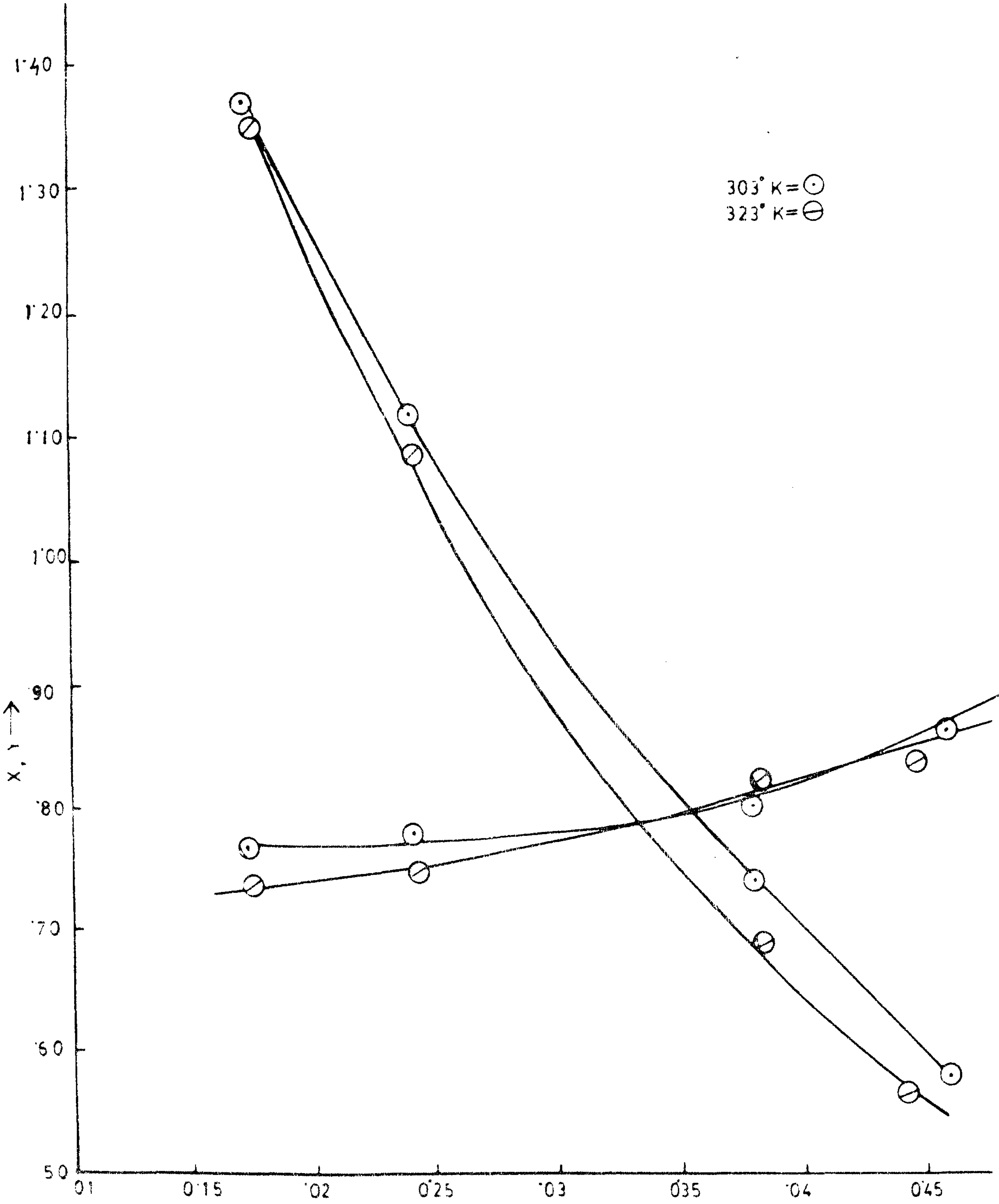


FIGURE:- 3·1·1·10
X, Y VS. C (I_2 ADSORPTION)

In the present investigation Langmuirs' modified formula (equation 1.21 and 1.23 section 1.7) is used in case of adsorption of iodine solution by activated carbon. The results and data are recorded in Table 3.1.1.8 , 3.1.1.9 and 3.1.1.10 (Figs. 3.1.1.8 , 3.1.1.9 and 3.1.1.9). From the graphs it is clear that the system obey this modified form of Langmuir's equation and so we can conclude by saying that both the solute and solvent are adsorbed by carbon surface. Amounts of solute and solvent adsorbed are shown in Fig. 3.1.1.10. The amount of solvent adsorbed falls rapidly with the increase of concentration of iodine (From 1.3694 g. to 0.5766 g. at 303°K and 1.3476 g. to 0.5608 g. at 323°K). In comparison with the solvent, the solute adsorption however rises rather slowly with concentration (From 0.7778 g. to 0.8602 at 303°K and 0.7333 g. to 0.7800 g. at 323°K).

Adsorption of HOAC (acetic acid) from aqueous solution involves competition with solvent molecules and the composite isotherm cannot be used to evaluate the surface sites. In the present investigation we have not tried to apply this modified Langmuirs equations (1.21) and (1.23) (section 1.7) in case of acetic acid carbon system as there are a number of previous studies on this system by many workers[104].

3.1.2 <u>ADSORPTION ISOBARS</u>: The fact that a number of mechanisms by which the same adsorbate may be taken up by the same adsorbent is usually manifested by the shape of the isobars, which represent the effect of temperature on the amount of uptake at a constant pressure.

If the adsorption proceeds by a simple mechanism with the evolution of heat then the principle of mobile equilibrium suggests decreasing adsorption with increasing temperature. This picture is attractively simple unless it is perturbed by some underlying complicacy that may have arisen out of a number of factors, such as the variation of the mechanism with temperature. This situation is frequently encountered under the circumstances at which chemisorption and activated adsorption phenomena play the dominant role. The presence of maxima and minima in the adsorption isobars reveal variations in the mechanism of adsorption which is operative at various temperature ranges. In nearly all adsorption (chemisorption) processes the isobars are seen to share this common feature. The actual state of affairs responsible for such adsorption maxima and minima are not always certain and according to a group of surface chemists[220,221], the low temperature adsorptions, which are limited to temperatures near the boiling point of the gas (adsorbate) concerned and are associated with low heat changes, are reversible physical adsorption, while the high temperature adsorptions with high heats are chemisorption. According to another group[222] the low temperature process is both physical and non-activated chemical adsorption, and the high temperature process is absorption.

The variation of the heat of adsorption with temperatures also establishes such a phenomenon and we shall have time to discuss on it while dealing with the heat of adsorption in the subsequent sections. The presence of high temperature adsorption proceeding with an activation energy, and with a heat too large for physical adsorption is a simple contemplation in so far as it is viewed through Taylor's[220] theory of activated adsorption. This can be exemplified by numerous instances, such as the adsorption of hydrogen on various manganous oxide[223], ZnO and certain iron catalyst[224,225]. The hydrogen isobars have shown two minima and two maxima ; thus suggesting two different kinds of activated adsorption.

3.1.2.1 Acetic acid adsorption isobars: In Fig. 3.1.2.1 , the amount of acetic acid adsorbed at different equilibrium concentration are shown as a function of temperature ranging from 303°K to 363°K. For the construction of isobars, data have been obtained from the experimental isotherms and they are represented in Table 3.1.2.1 (Appendix I).

It is apparent from the nature of the isobars shown in Figs 3.1.2.1 , that the mechanism of adsorption of acetic acid on activated carbon does not remain the same in the temperature range 303°K - 363°K. If it has been the case, the amount of acetic acid adsorbed at a certain equilibrium concentration may continuously decrease with increasing temperature. The temperature region in which the amount of acetic acid adsorbed increases with temperature may be regarded as a transition region, making the onset of a new process of adsorption. In this region, as the temperature increases, the rate of the new process increases because the new process is obviously an activated one. We notice an apparent increase in the amount of acetic acid adsorbed.

(i) Isobars at 0.50N and 0.40N - If we consider the isobars shown in Fig. 3.1.2.1 at the equilibrium concentration of 0.50N and 0.40N,

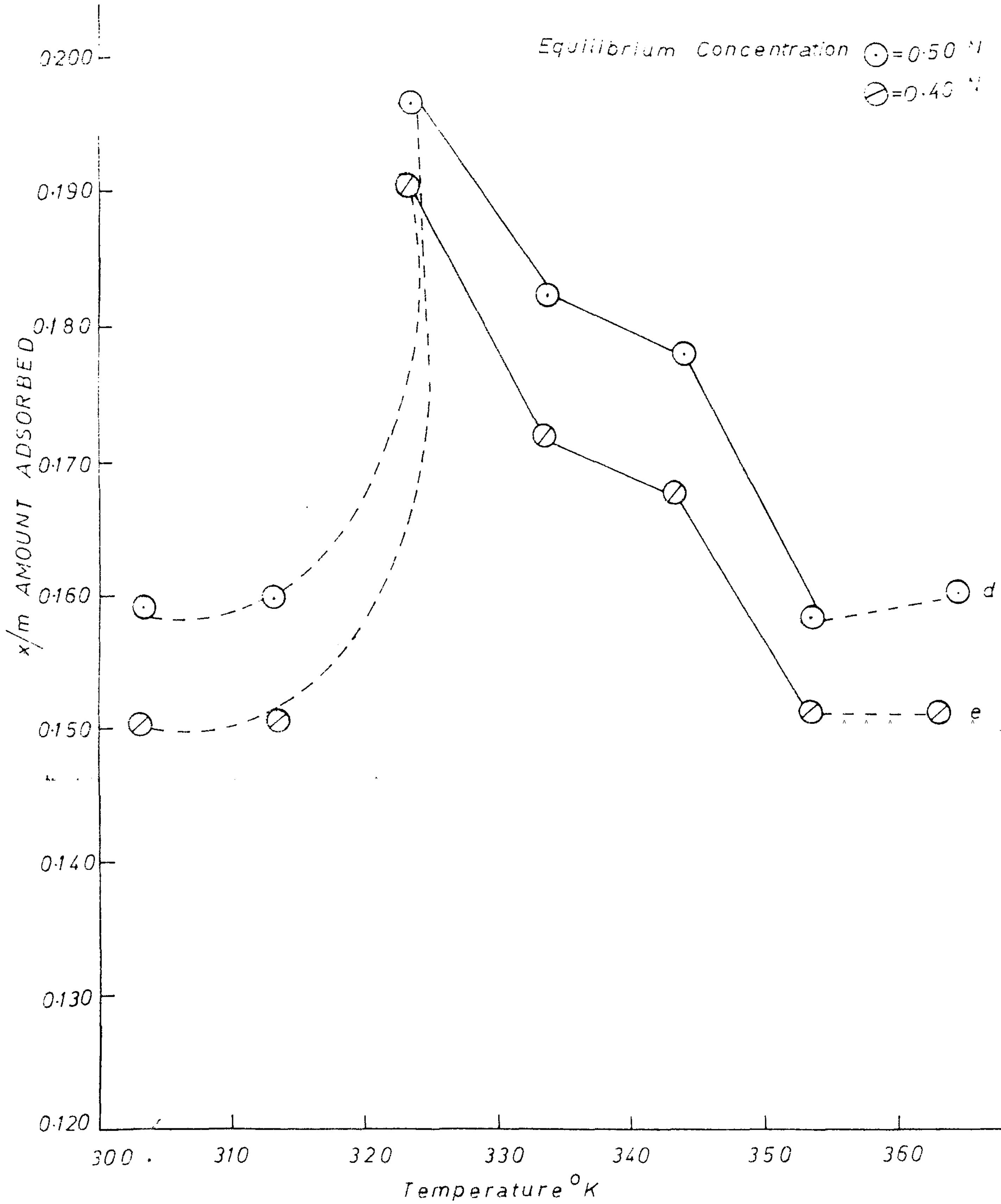


FIGURE:- 3.1.2.1 (d e). (x/m vs T)(ISOBAR).
CH_3COOH ADSORPTION

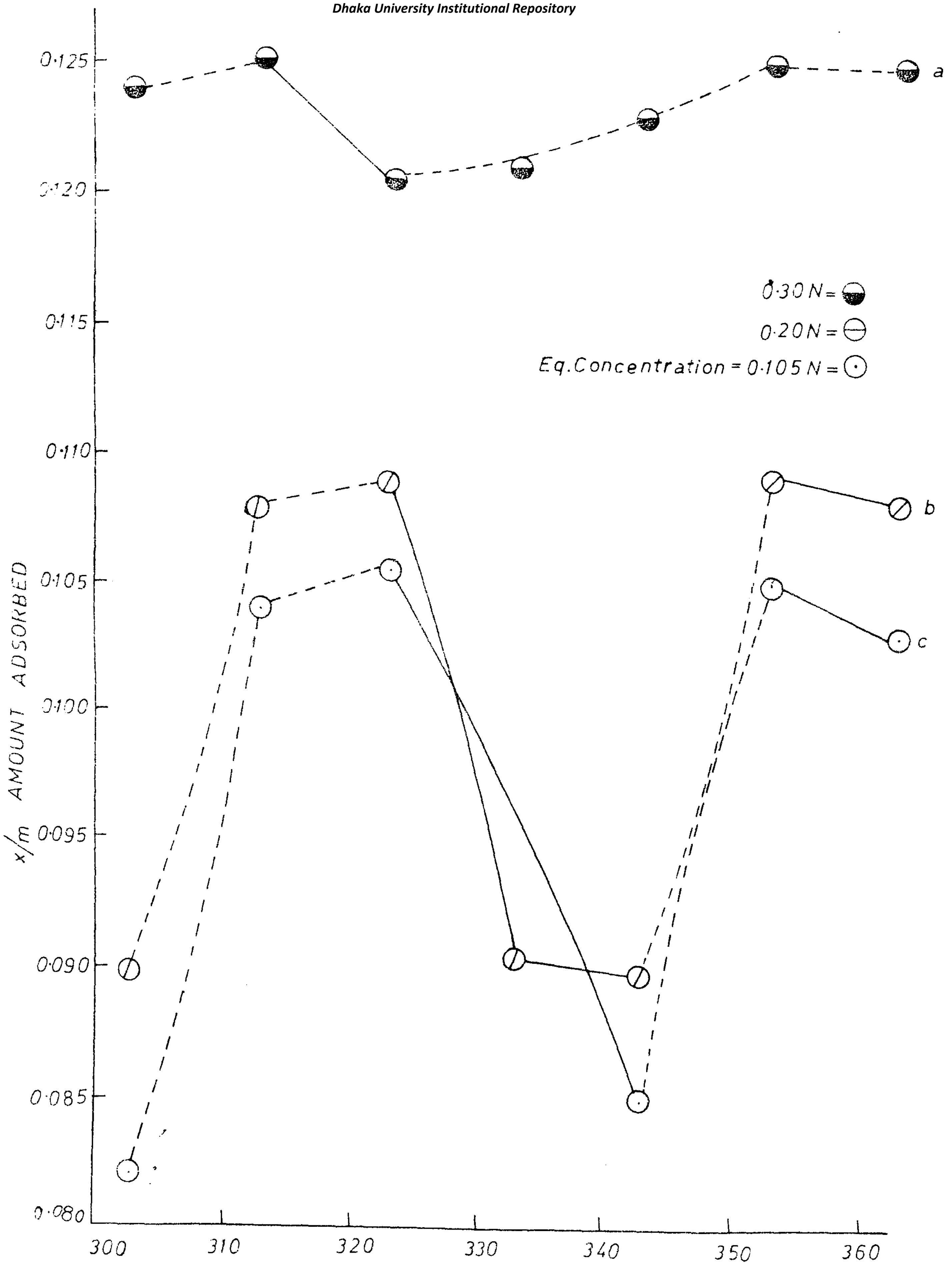


FIGURE 3·1·2·1 (a,b,c) CH_3COOH ADSORPTION x/m vs Temp (ISOBAR) we notice that the amount of acetic acid adsorbed on carbon first increases (shown by dotted lines) in the temperature ranges 303°K - 323°K and with increase of temperature (323°K to 363°K) the amount of adsorption of acetic acid decreases (full line in the figures). The curves showed two maxima and two minima. One of the maxima is very sharp at 323°K and another at 343°K with low adsorption than the lower temperature maxima. The two minima are at 313°K and 353°K. The isobars reveal two types of mechanism.

(ii) Isobars at 0.30N - The isobar at 0.30N equilibrium concentration is different from isobars at 0.50N and 0.40N. This isobar having two maxima and one sharp minima at 323°K and the shift of the lower and higher temperature maxima (by 10°) to 313°K and 353°K with much lower adsorption are the features that distinguishes this from the 0.50N and 0.40N isobars.

(iii) Isobars at 0.20N and 0.105N - The isobars at lower equilibrium concentration (0.20N and 0.105N) show a different shape. Here the adsorption increases from 303°K to 323°K (similar to 0.50N and 0.40N equilibrium concentration isobars) then in the temperature range 323°K to 343°K, the amount of adsorption decreases and again in the range 343°K - 363°K it increases i.e. at lower equilibrium concentration the mechanism of adsorption is different from the higher concentration. These isobars have two maxima and one minima. The double-hump maxima at 323°K and 353°K are separated by the minima at 343°K. Thus, the overall consideration of the isobars lead us to the conclusion that two types of adsorption mechanism are

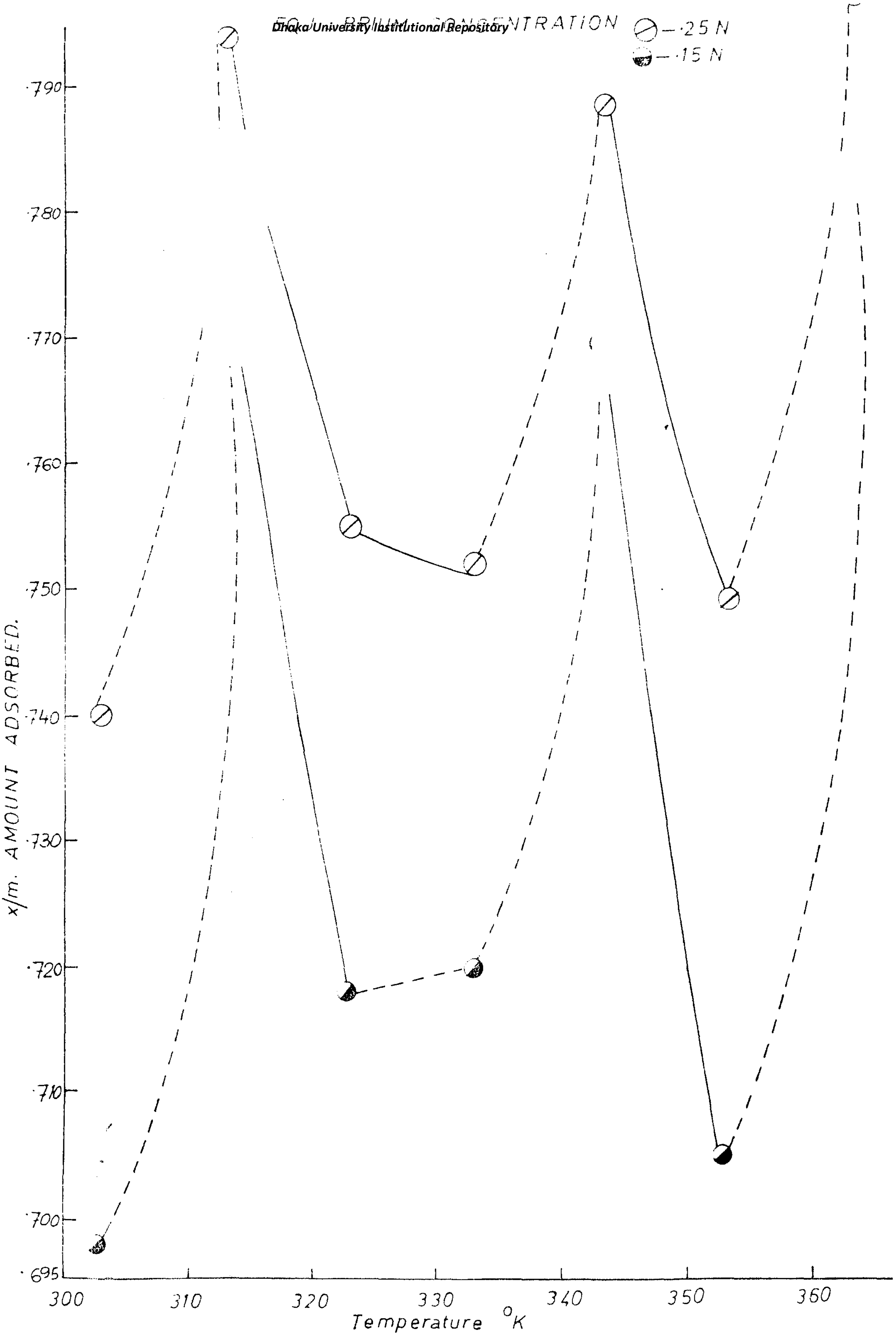


FIGURE: 3.1.2.2(a,b) I_2 ADSORPTION ISOBARS x/m VS T

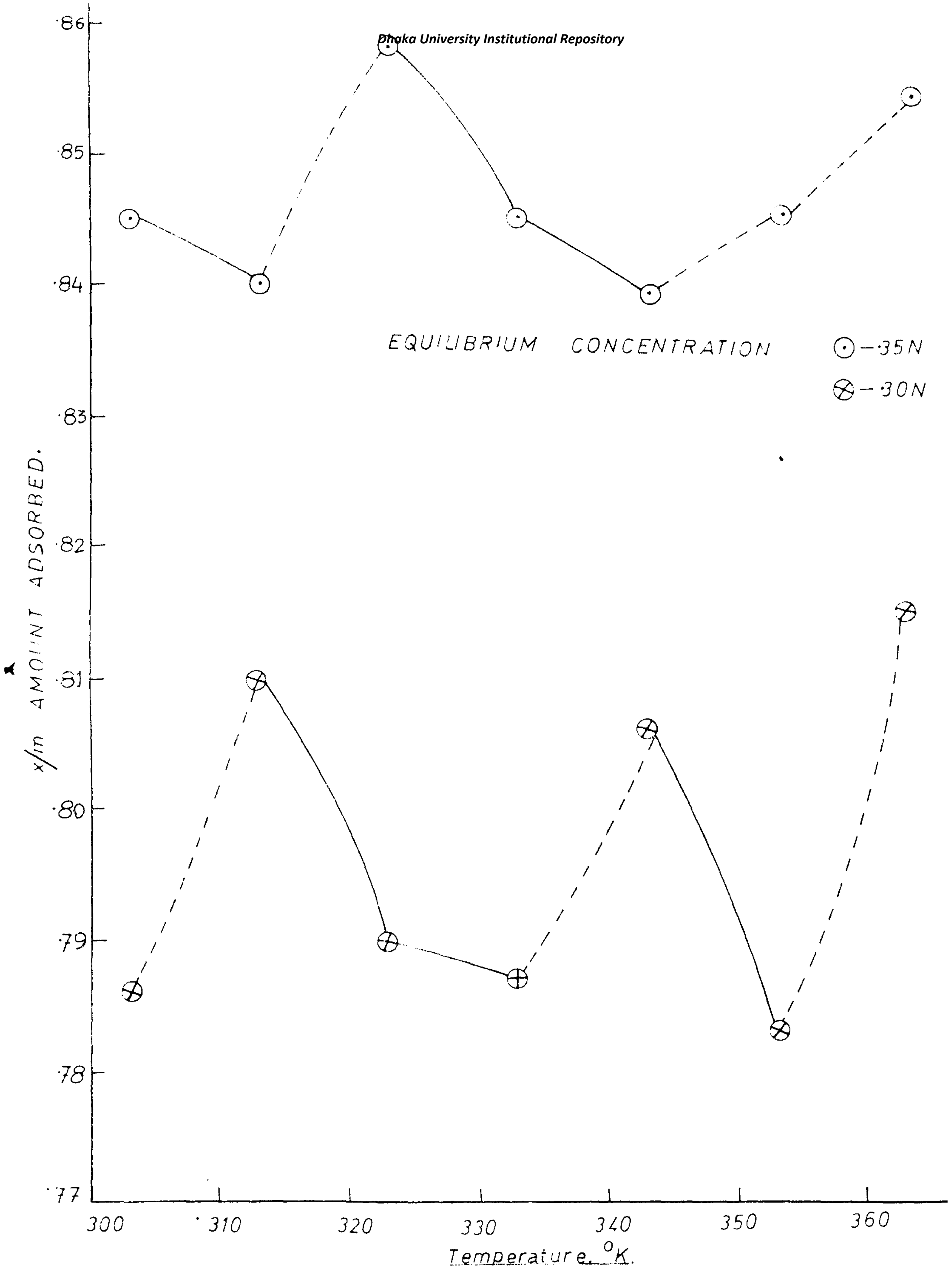


FIGURE: 3.1.2.2 (c,d). I_2 ADSORPTION ISOBARS. x/m vs T.

operative in the temperature ranges 303°K - 323°K and 323°K - 353°K Depending on the equilibrium concentration. The variation in magnitude of heat of adsorption with temperature is consistent with the occurence of maxima and minima in the isobars i.e. the existence of different adsorption mechanism.

3.1.2.2 Adsorption isobars for iodine: For the construction of the isobars, data have been obtained from the experimental isotherms and these are presented in Table 3.1.2.2 (Appendix I), In Figs. 3.1.2.2, the amount of iodine adsorbed at different specific equilibrium concentration (0.15N, 0.25N, 0.30N, 0.35N and 0.375N) are shown as a function of temperature ranging from 303°K to 363°K.

From the nature of the isobars as shown in Figs. 3.1.2.2, it is apparent that the mechanism of adsorption of iodine on carbon does not remain the same in the temperature range 303°K - 363°K.

(i) Isobars at 0.15N, 0.25N and 0.30N : The three isobars at 0.15N, 0.25N and 0.30N equilibrium concentrations have similar shape i.e. the amount of iodine adsorption increases and then decreases at regular intervals. The adsorption increases at temperature regions 303°k - 313°K, 333°K - 343°K and 353°K - 363°K and decreases at temperature regions 313°K - 333°K and 343°K - 353°K i.e. for a 10° rise or fall of temperature the adsorption of iodine varies appreciably. The common feature of these isobars are that they show two sharp maxima and two minima. The maxima occuring at 313°K and 343°K and the minima at 323°K and 353°K. The amount of iodine adsorbed corresponding to maximum at higher temperature is smaller than the amount that adsorbed corresponding to maximum at the lower

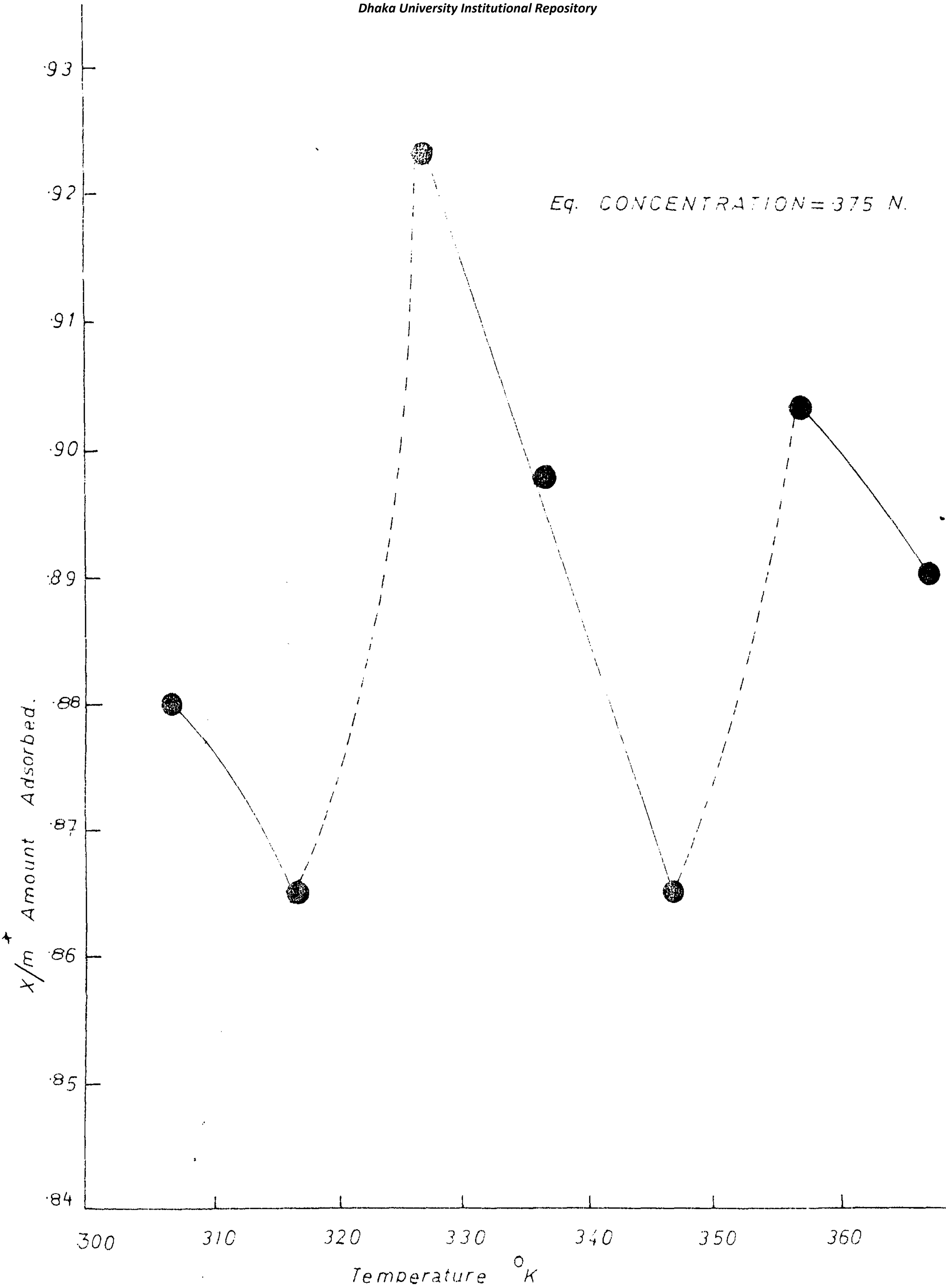


FIGURE: 3.1.2.2 (e). I_2 ADSORPTION ISOBAR. X/m. vs T.

temperature. The decrease in adsorption of iodine at temperature region 343°K- 353°K is more steeper than the fall in the temperature ranges 313°K - 333°K i.e. the minima at 353°K is very sharp.

(ii) Isobars at 0.375N and 0.35N : The two isobars at 0.375N and 0.35N equilibrium concentration are different from the lower equilibrium concentration (i.e. at 0.15N, 0.25N, 0.30N) isobars in that here the adsorption first decreases then increases. The isobars also show maxima and minima. The isobar at 0.375N equilibrium concentration have two sharp maxima and two sharp minima. The maxima are at 323°K and 353°K and the minima at 313°K and 343°K. The two maxima is separated by the minima at 343°K. The isobar at 0.35N equilibrium concentration isobar in that it has one maxima and two minima. The lone maxima is at 323°K similar to one of the maxima at 0.375N. One of the minima is sharp at 313°K and a broad minimum is observed in the temperature range 323°K - 343°K.

The temperature at which the amount of iodine adsorbed starts decreasing with rise of temperature may be regarded as the beginning of a new process of adsorption different from that in the temperature region where the adsorption increases with increase of temperature. The occurence of maxima and minima in the isobars (at 0.15N, 0.25N, 0.30N) at regular intervals reveal that different types of mechanism are operative in the temperature ranges 303°K - 363°K. The different values of the heat of adsorption at different temperatures also indicate the existence of different mechanism in the adsorption of iodine on activated carbon. The results are explicable if two different processes predominate in different

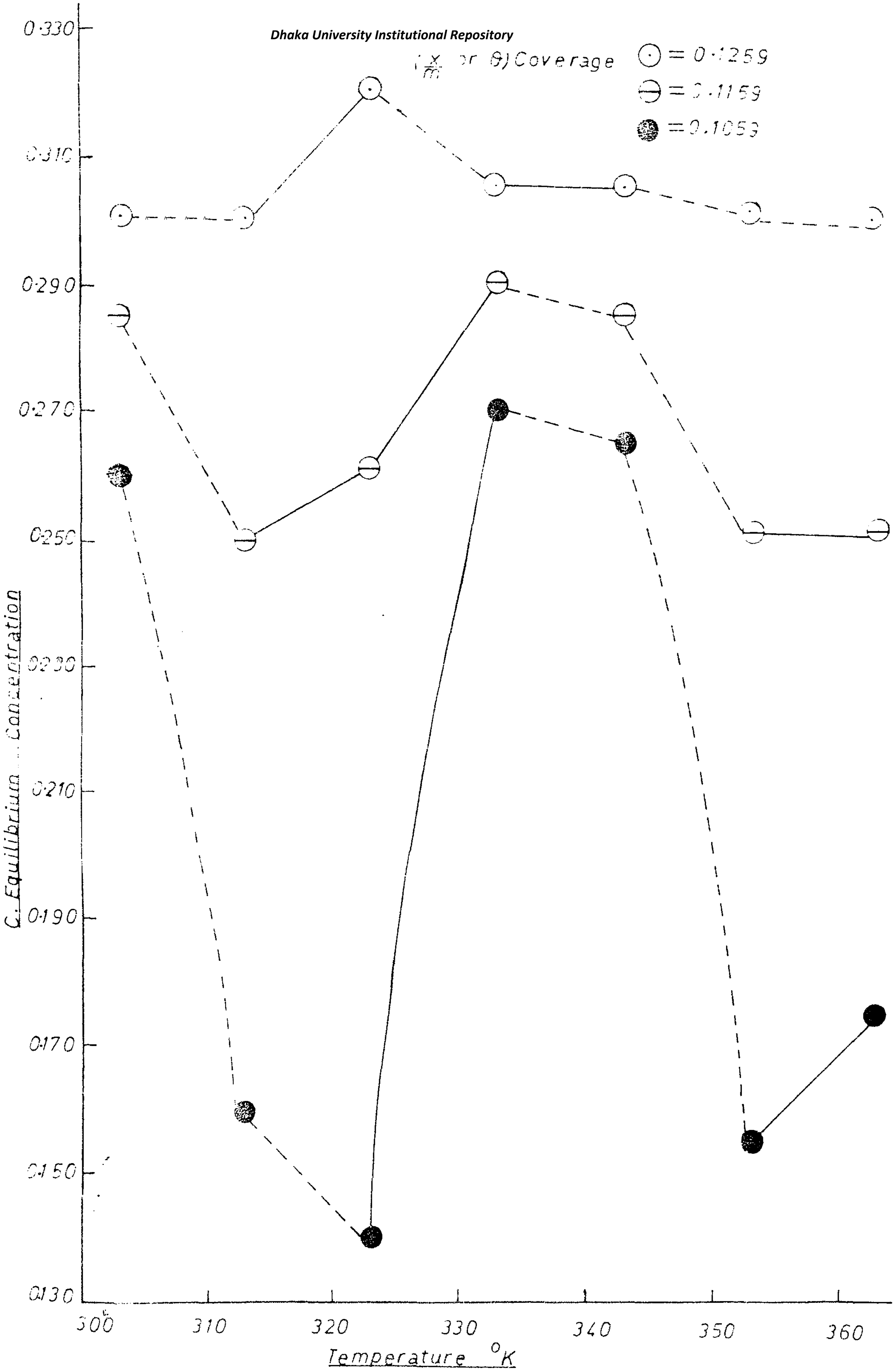


FIGURE:- 3.1.3.1(a) CH_3COOH ADSORPTION (ISOSTERE).

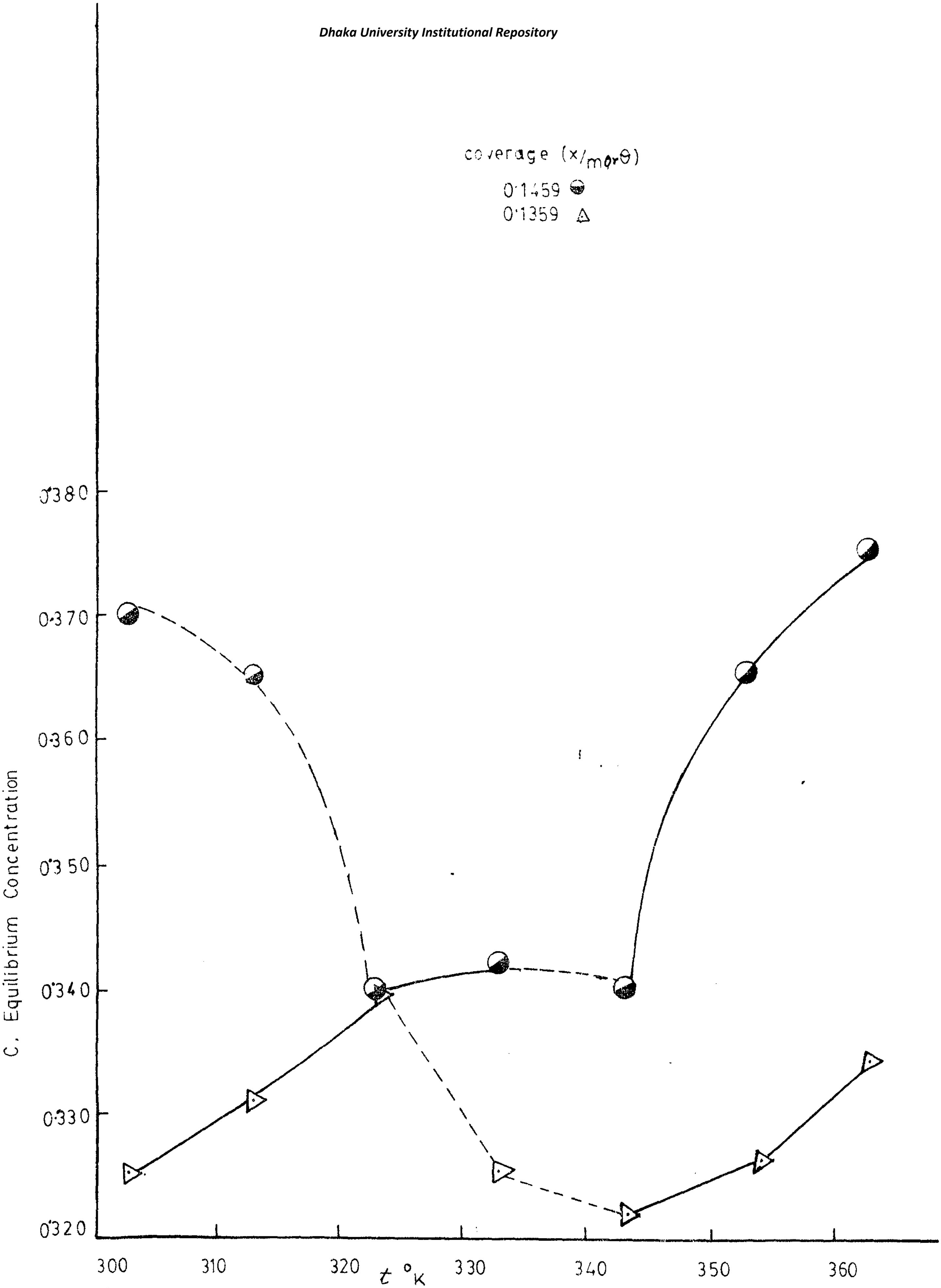


FIGURE 3·1·3·1(b) CH_3COOH ADSORPTION (ISOSTERE)

Eq. concentration vs. T

temperature ranges, but the nature of the two processes is still uncertain.

3.1.3 ADSORPTION ISOSTERES:

3.1.3.1 Adsorption isostere for acetic acid:

The adsorption isosteres representing the variation of equilibrium concentration with temperature, when the same amount of acetic acid is adsorbed by the activated carbon are shown in Fig. 3.1.3.1 . Five different values (namely 0.145 g. , 0.135 g. , 0.125 g. , 0.115 g. and 0.105 g.) for the amount of acetic acid adsorbed have been chosen. The required data obtained from the adsorption isotherm (from Figs. 3.1.1.1) are shown in Table 3.1.3.1 (Appendix I). The isosteres obtained are similar in nature showing the maxima and minima as have been normally expected and is another manifestation of the minima and maxima of the isobars. The isostere at coverage 0.135 g. is different from the other isosteres showing a broad minimum in the temperature region $333^{\circ}K$ - $353^{\circ}K$ and maxima at $323^{\circ}K$. The other isosteres have broad maxima and the maxima is situated around $333^{\circ}K$.

The use of all the isosteres are made in the estimation of the isosteric heat of adsorption and the cause of its variation with coverage is described in the subsequent section 3.1.4.2 .

3.1.3.2 Iodine adsorption isosteres:

The adsorption isosteres for iodine are shown in Figs. 3.1.3.2 . The required data obtained from the adsorption isotherms are shown in Table 3.1.3.2 (Appendix I). Five different values (0.875 g., 0.850 g., 0.825 g., 0.800 g., and 0.790 g.) for the amount of iodine adsorbed have been chosen.

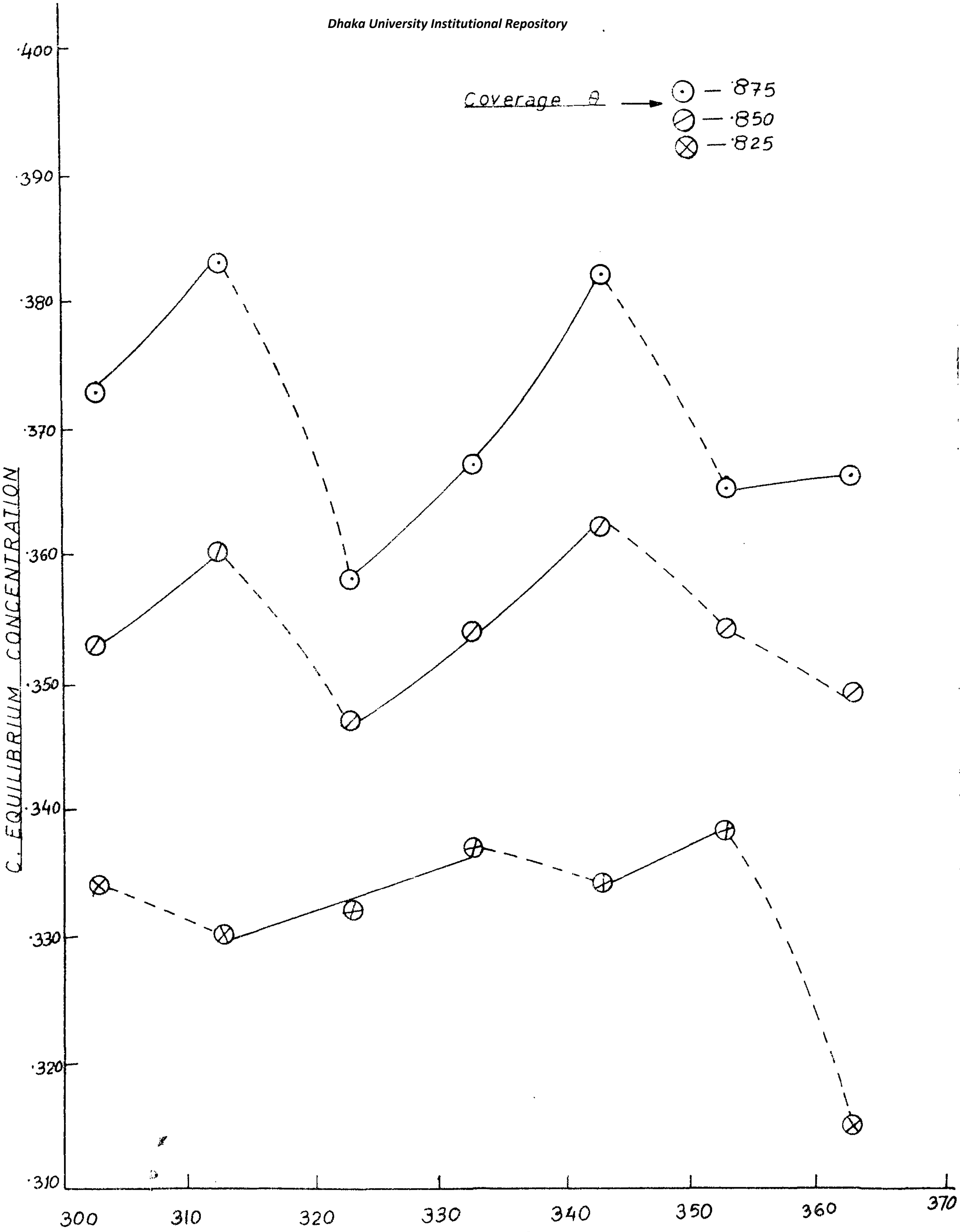


FIGURE 8·1.3.2 (a) I_2 ADSORPTION EQUILIBRIUM CONCENTRATION VS TEMPERATURE (C vs T).

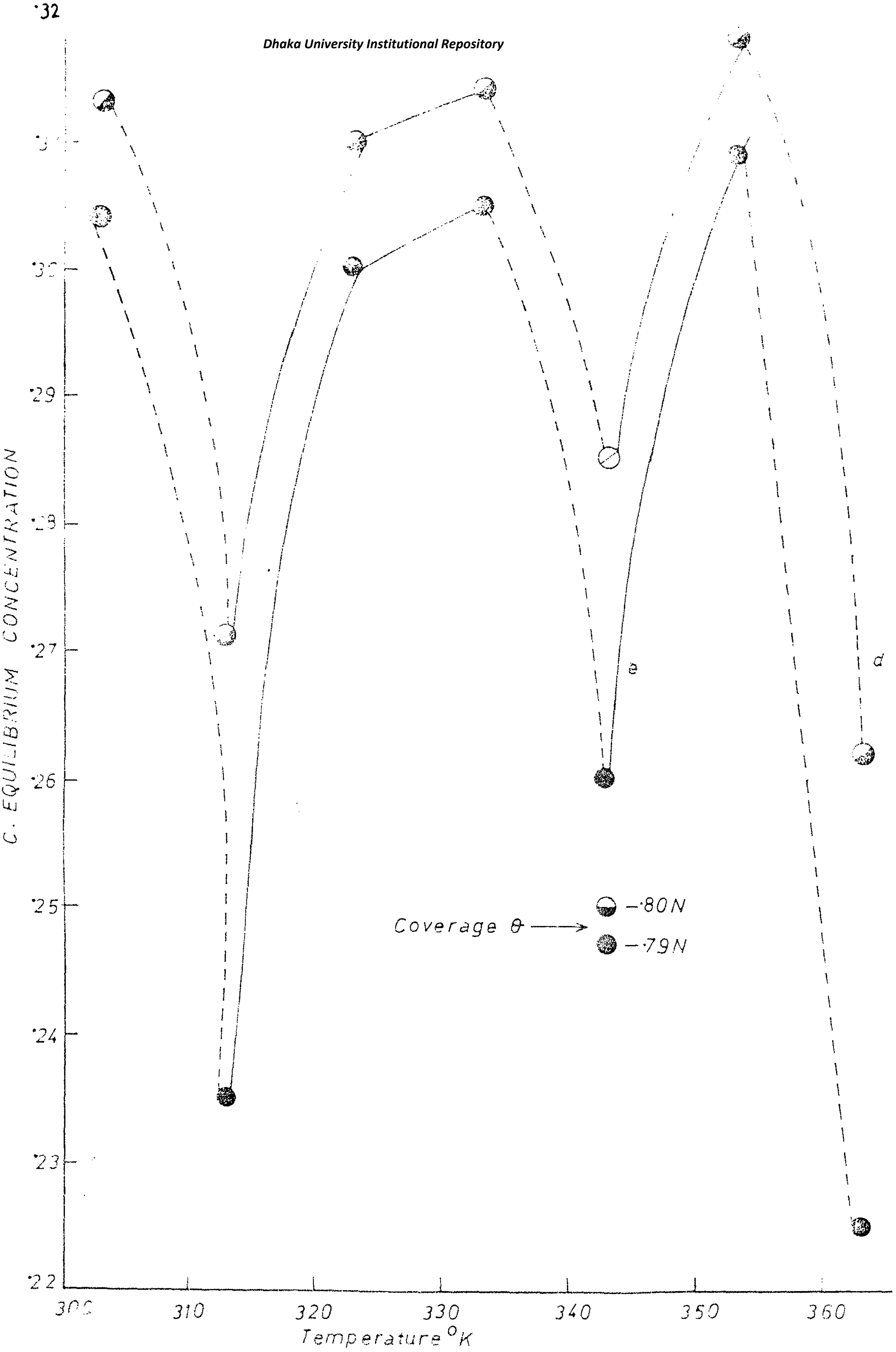


FIGURE :- 3·1·3·2 (b). I_2 ADSORPTION ISOSTERES.

(EQUILIBRIUM C vs T)

The three isosteres at 0.825 g., 0.800 g. and 0.790 g. are similar in nature showing two sharp minima at the temperature 313°K and 343°K and the sharp maxima at 353°K and a broad maxima at 333°K. This is expected because the isosteres are mirror images of the isobars. If we look at the isobars at 0.15N, 0.25N and 0.30N equilibrium concentration the same is reflected. The isosteres at 0.875 g. and 0.850 g. are similar in nature and as expected they are the mirror images of the isobars at 0.375N and 0.35N equilibrium concentration. Here we observed two maxima at 313°K and 343°K and two minima at 323°K and 353°K. The isosteres are used to get the value of isosteric heat of adsorption.

3.1.4 HEAT OF ADSORPTION: The differential heat of adsorption can be determined from the adsorption data using the thermodynamic relation between the equilibrium constant and temperature. By the application of Clausius-Clapeyron equation,

$$\left(\frac{\partial \ln P}{\partial T}\right)_\theta = \frac{q_{st}}{RT^2} \qquad \ldots\ldots\ldots \qquad (1.9)$$

to the adsorption data at different temperatures, the isosteric heat of adsorption q_{st} can be calculated. Equation (1.9) can be put in the definite integral form

$$q_{st} = 2.303\ R\ \frac{T_2 T_1}{T_2 - T_1} \log \frac{P_2}{P_1}$$

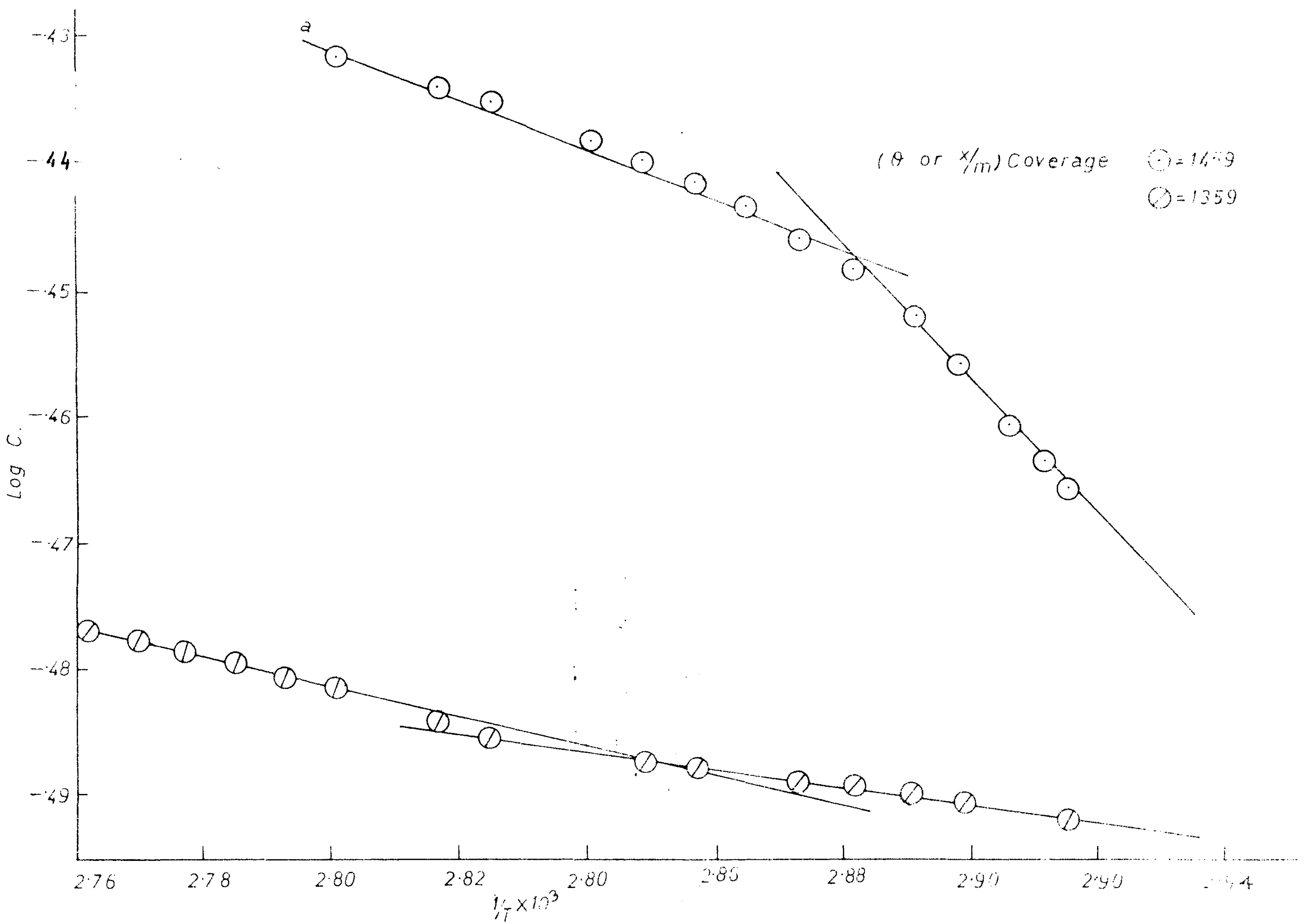


FIGURE 3·1·4·1 (a). Plot of (Log C vs $1/T$). CH_3-COOH ADSORPTION.

Or, in the indefinite form

$$\log P = \frac{-q_{st}}{2.303\ RT} + \text{Const.} \qquad \ldots\ldots.. \qquad (1.12)$$

$$\text{or} \quad \log C = \frac{-q_{st}}{2.303\ RT} + \text{Const.}$$

From the nature of the adsorption isobars and isosteres obtained for acetic acid and iodine (Figs. 3.1.2.1 , 3.1.2.2 , 3.1.3.1 , 3.1.3.2), it follows that the amount of the adsorbate adsorbed decreases as the temperature is increased and reaches a minimum. It may therefore be assumed that true thermodynamic equilibrium is attained during adsorption measurements in the temperature region $303^{o}K$ - $363^{o}K$, and so an attempt is made to calculate the heat of adsorption in this temperature region ($303^{o}K$ - $363^{o}K$).

3.1.4.1 Heat of adsorption for acetic acid: In order to determine the heats of adsorption, requisite data have been derived from the adsorption isosteres as represented in Figs. 3.1.3.1 , and recorded in Table 3.1.4.1 (Appendix I). Plots of log c against 1/T, where c is the equilibrium concentration to bring about the adsorption of a definite amount of adsorbate (i.e. to reach a certain coverage) at a definite temperature T, are shown in Figs. 3.1.4.1 . If there have been a single adsorption process operative in the whole temperature region under study, a single straight line can be drawn passing through all the points and the slope of the straight line gives the heat of adsorption. The isobars have indicated different adsorption process at various temperature regions. In the plots of log c vs 1/T (Figs. 3.1.4.1), the same is also reflected and we

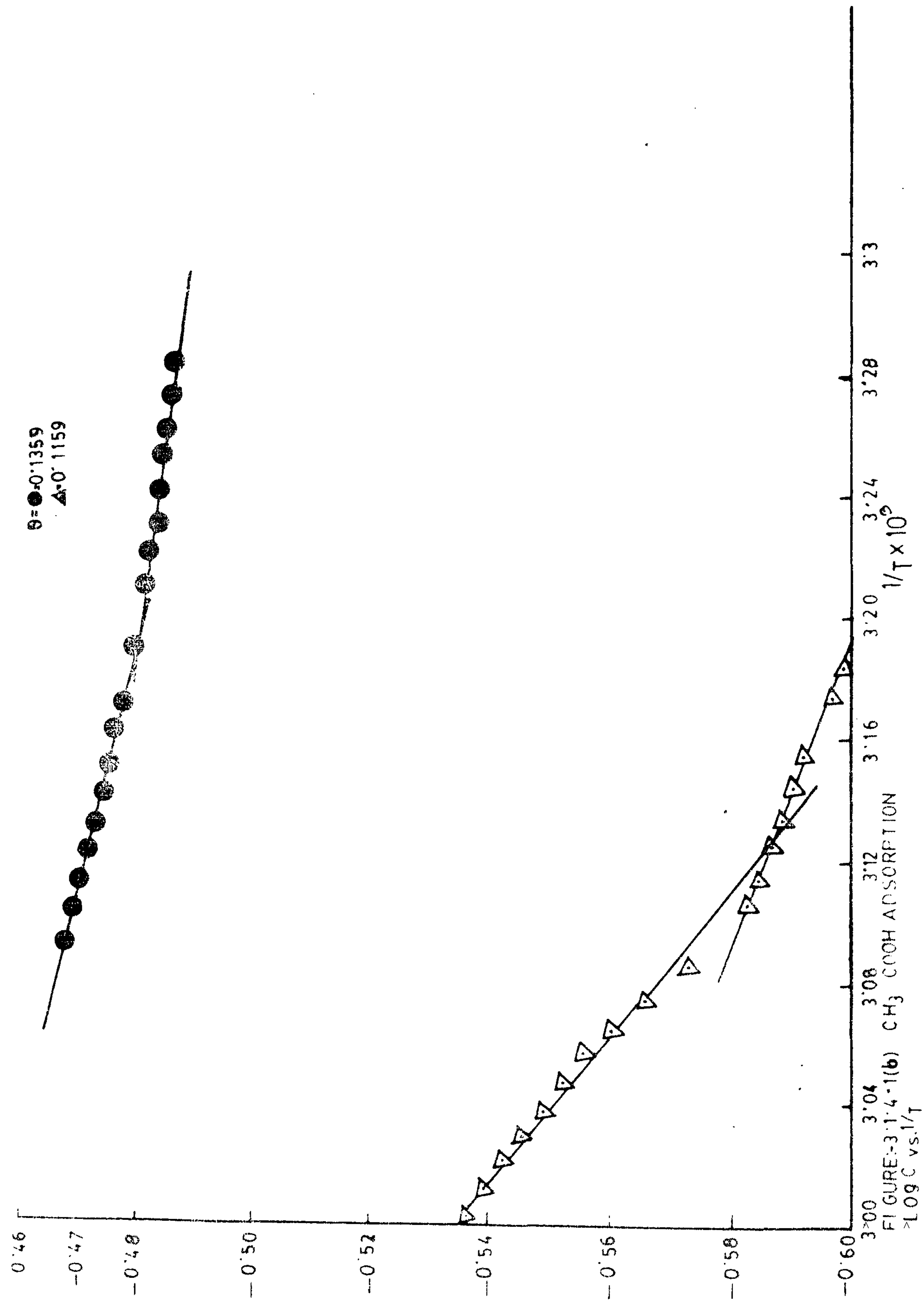


FIGURE-3.1.4.1(b) CH_3 COOH ADSORPTION >Log C vs. 1/T

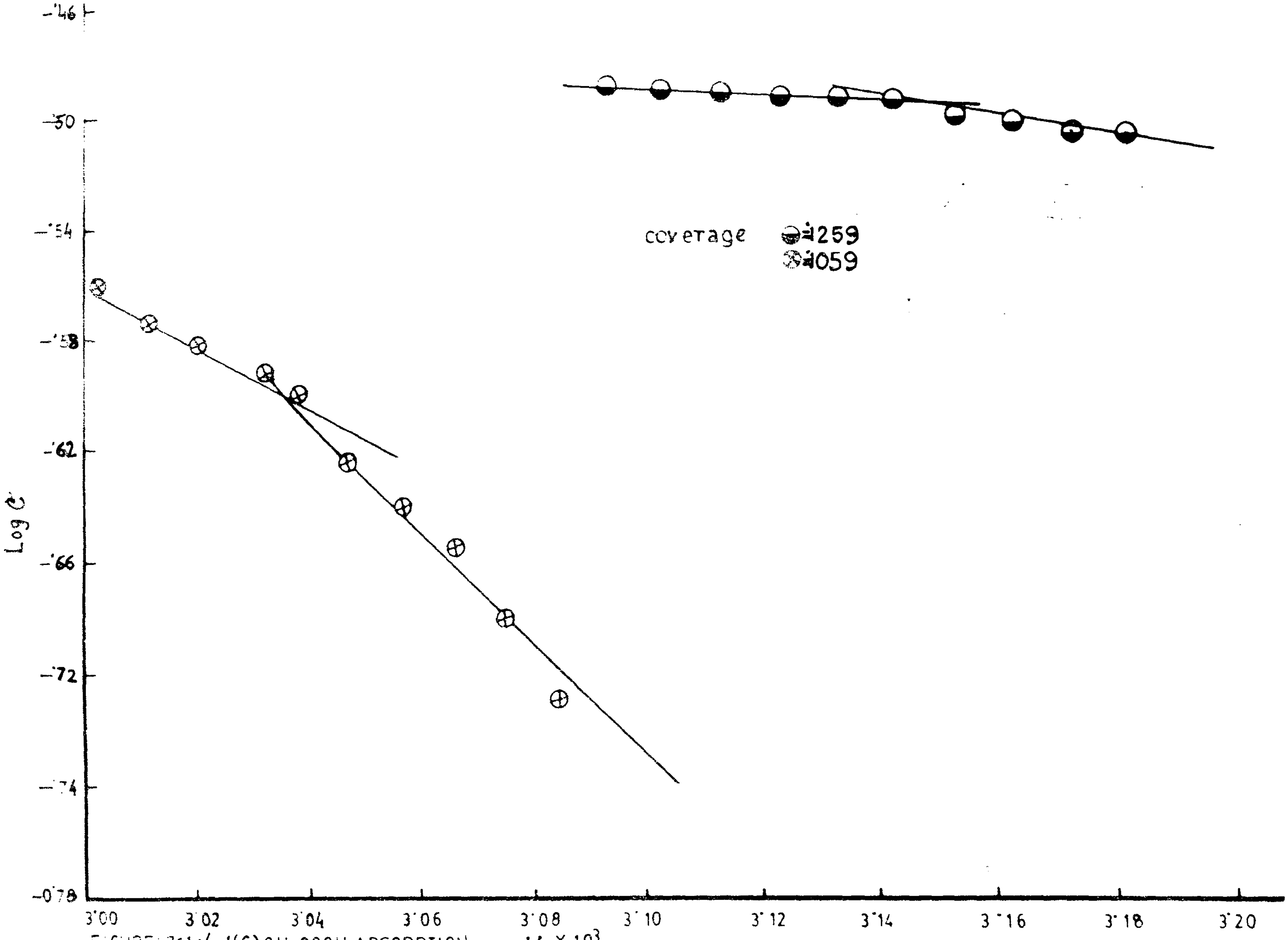


FIGURE-3·1·4·1(G) CH_3COOH ADSORPTION.
(Log C vs 1/T)

obtained two major groups of points at low and higher temperature regions through which we can probably draw straight lines. This has been done and values for heats of adsorption have been obtained for various coverages. These are recorded in Table 3.1.4.1 . It may however be noted that the points in each group, particularly those in the intermediate temperature range do not strictly fall on a straight line ; the deviation is not random, it is rather systematic. This is understandable because in each temperature region a unique adsorption process may not be operative and there may be gradual change from one type of adsorption to the other. The predominance of one type of adsorption over the other seem to be dependent on the temperature. Therefore, the heat of adsorption obtained from the plots of log c vs 1/T at different temperature regions is an average of the various processes occuring simultaneously, and so its value cannot indicate the type of adsorption in the respective temperature regions.

It is observed that the heat of adsorption of acetic acid on active carbon decreases with coverages (i.e. amount adsorbed) which also proves the heterogeneous character of the carbon surface because the more active sites are occupied earlier. In the present case of adsorption of acetic acid on carbon, we have found that the heat of adsorption decreases with coverages (0.105 g. - 0.135 g.) from 7.45 KCals per mole to 0.44 KCals/mole but at the higher coverage (0.145 g.) there is an increase in the value of heat of adsorption (1.68 KCals/mole. Fig. 3.1.5.1). This may be due to the fact that the adsorbed species have practically no mobility at higher coverages,

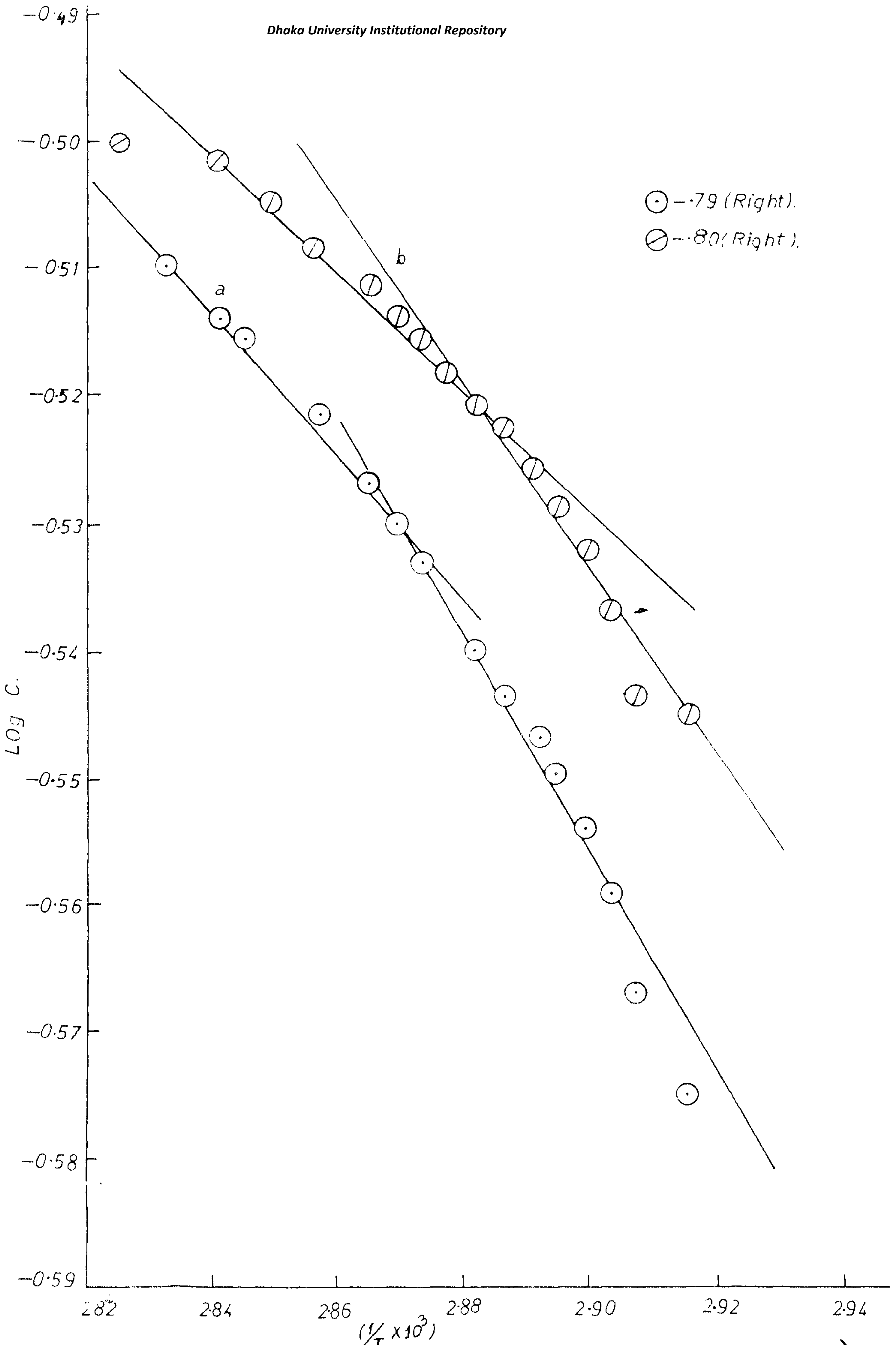


FIGURE: 3.1.4.2 (a) PLOT OF (LOg C VS $^1/_T$) (I_2 ADSORPTION).

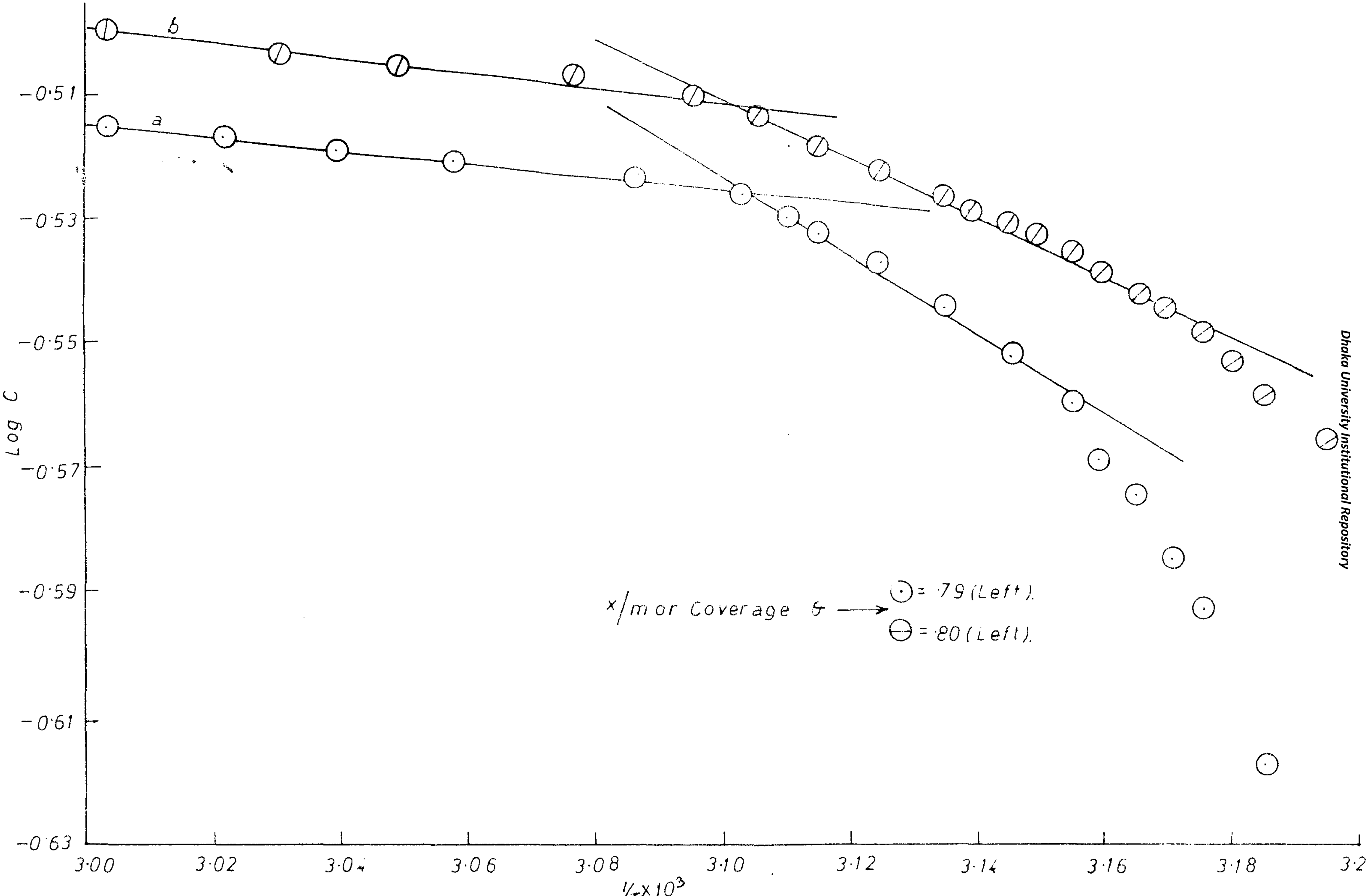


FIGURE:- 3.1.4.2 (b). I_2 ADSORPTION. (Log C vs $1/T$).

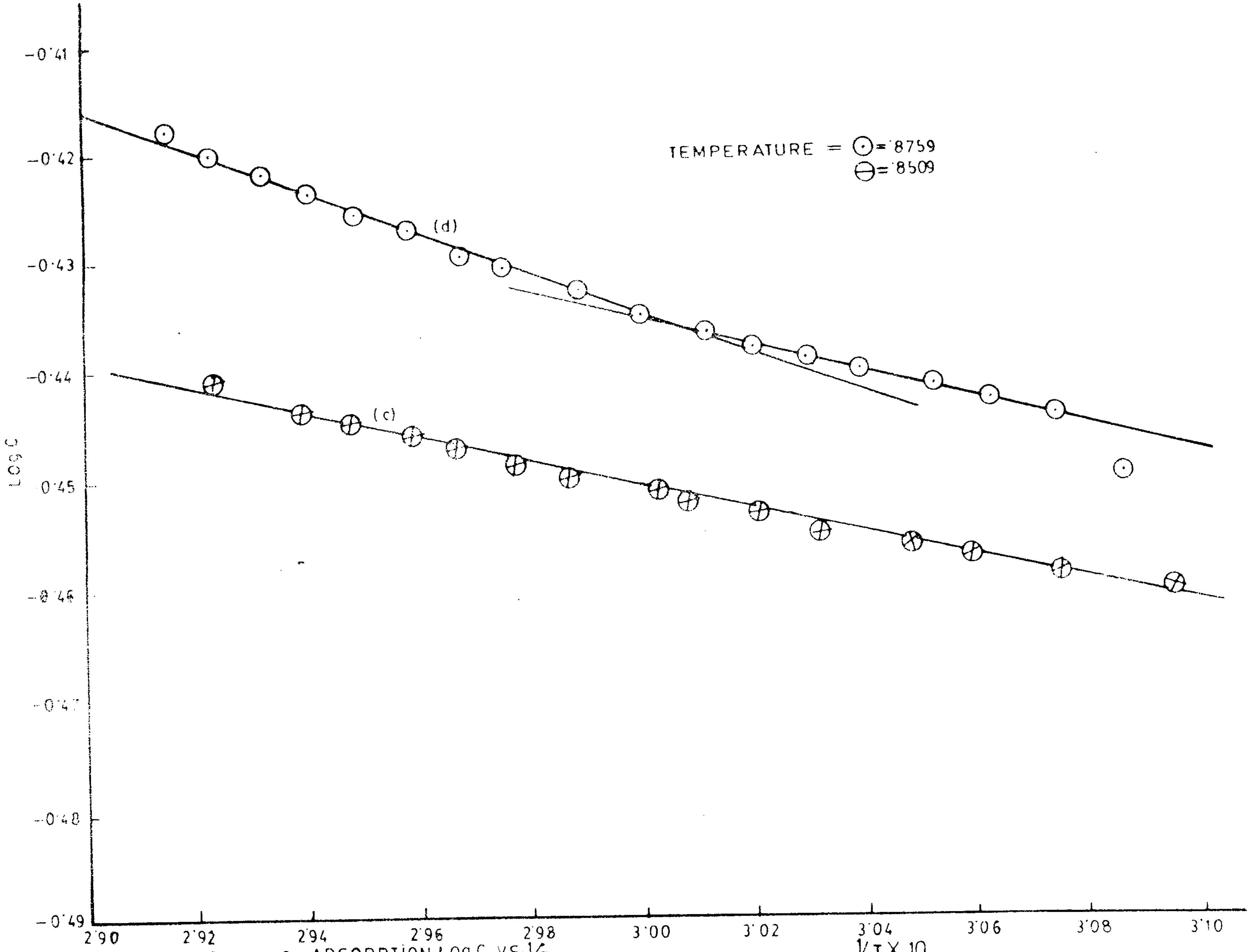


FIGURE-3·1·4·2(c) I_2 ADSORPTION·LOG C VS·1/T so that the number and type of sites covered are purely dependent on the probability of being hit by an adsorbate molecule and not on the activity of the sites. Literature survey indicates that such effect is more pronounced on a porous adsorbent, where some active sites in the pores are not easily available to the adsorbate at higher coverages. The porous character of the carbon surface is also manifested by the shape of the adsorption isotherms. An alternative explanation for the increase of heat of adsorption with with coverage may be that at high equilibrium concentration of acetic acid, the surface of active carbon becomes partially reduced.

3.1.4.2 Heat of adsorption for iodine: The linear graphs (Figs. 3.1.4.2) have been obtained by plotting log c vs 1/T, complying with the requirements of the equation (1.12) and from the slope the isosteric heat of adsorption is calculated. The data are recorded in Table 3.1.4.2 (AppendixI). The different values of heat of adsorption at different coverages can be regarded as an indication of the different mechanisms that are operative in the adsorption of iodine on activated carbon. In the plots of log c vs 1/T, we have obtained two major groups of points, at low and higher temperature regions through which two straight lines have been drawn and the values for heats of adsorption have been calculated for various coverages.

The value of the heat of adsorption obtained is too low. The minimum value 0.4919 KCals/mole has been obtained for coverage 0.85 g. and the maximum 3.0926 KCals/mole is found to be for coverage 0.79 g. The values are presented in Table 3.1.4.2 (Appendix I), and the variation of heat of adsorption with coverages are shown in Fig. 3.1.5.1. In the temperature ranges 313°K - 353°K the heat of adsorption falls with coverages (0.790 g. - 0.850 g.) as expected. But in the temperature range 323°K - 343°K, the heat of adsorption does not decrease with coverages as expected. There is rather an increase. This is rather unexpected and indicates that besides adsorptio-n some sort of surface reactions which may lead to the incorporation of the adsorbed species into the adsorbent lattice are perhaps taking place. Taylor and his co-workers[226,227] suggested that a change in mechanism of adsorption can account for this irregular change in the heat of adsorption. With a number of systems a rise in temperature while adsorption is proceeding causes a fairly rapid desorption followed by slow readsorption. Certainly two types of adsorption are taking place, so that when the temperature is raised, desorption takes place from places where the activation energy and heat of adsorption are relatively low, and readsorbed on areas where they are high. Occurence of different mechanisms, a rather particular type of heterogeneity, may best explain the phenomenon. It has also been observed for a number of adsorption on oxide and metal powders, as well as in hydrogen chemisorption on tungsten films[228]. It is worth mentioning that if an adsorption obeys the Freundlich isotherm, the differential heat falls logarithmically with increasing coverage. In the adsorption of iodine on carbon we have found that the adsorption has not obeyed Freundlich equation over the whole of the temperature region 303°K - 363°K. It obeys only at 303°K (low temp.) and partially at 363°K. Halsey and Taylor[229] have shown this to be explicable only interms of an exponential distribution of energy among sites on a heterogeneous surface. Rapid heat falls at low (coverage) θ values are in general regarded as indicative of heterogeneity, as interactions are not large under these conditions.

In addition to the above explanations for the unusual value we have obtained for the heat adsorption of iodine and acetic acid on activated carbon (the heat of adsorption initially falls with increasing coverage as expected but rises with coverage at the latter stage), the following conception of bottle-shaped macro and micropore structure of activated carbon can best explain the phenomenon. According to Kadlec et al.[230] active carbon prepared from cocoanut shell by steam activation contains macropores with narrowed entrances, the size of which corresponds to the dimensions of transitional pores. The origin of the bottle shaped macro and micropores in activated carbon, is probably due to the mechanism of the method of activation[231]. In the course of activation at 550°C - 650°C , the carbonized carbonaceous raw material is in a plastic state. By thermal decomposition, released gases may form hollows in the plastic matter , from which they escape through small passages. This may be the cause of the creation of the bottle shaped pores. In course of adsorption, the adsorbate when enters through the narrow entrance into the centres(the hollows of which have larger dimensions than the dimensions of the bottlenecks) of the pores, it finds new sites for adsorption and as a result the adsorption is accompanied by the largest evolution of heat and so we have observed an increase in the enthalpy change with increasing coverage.

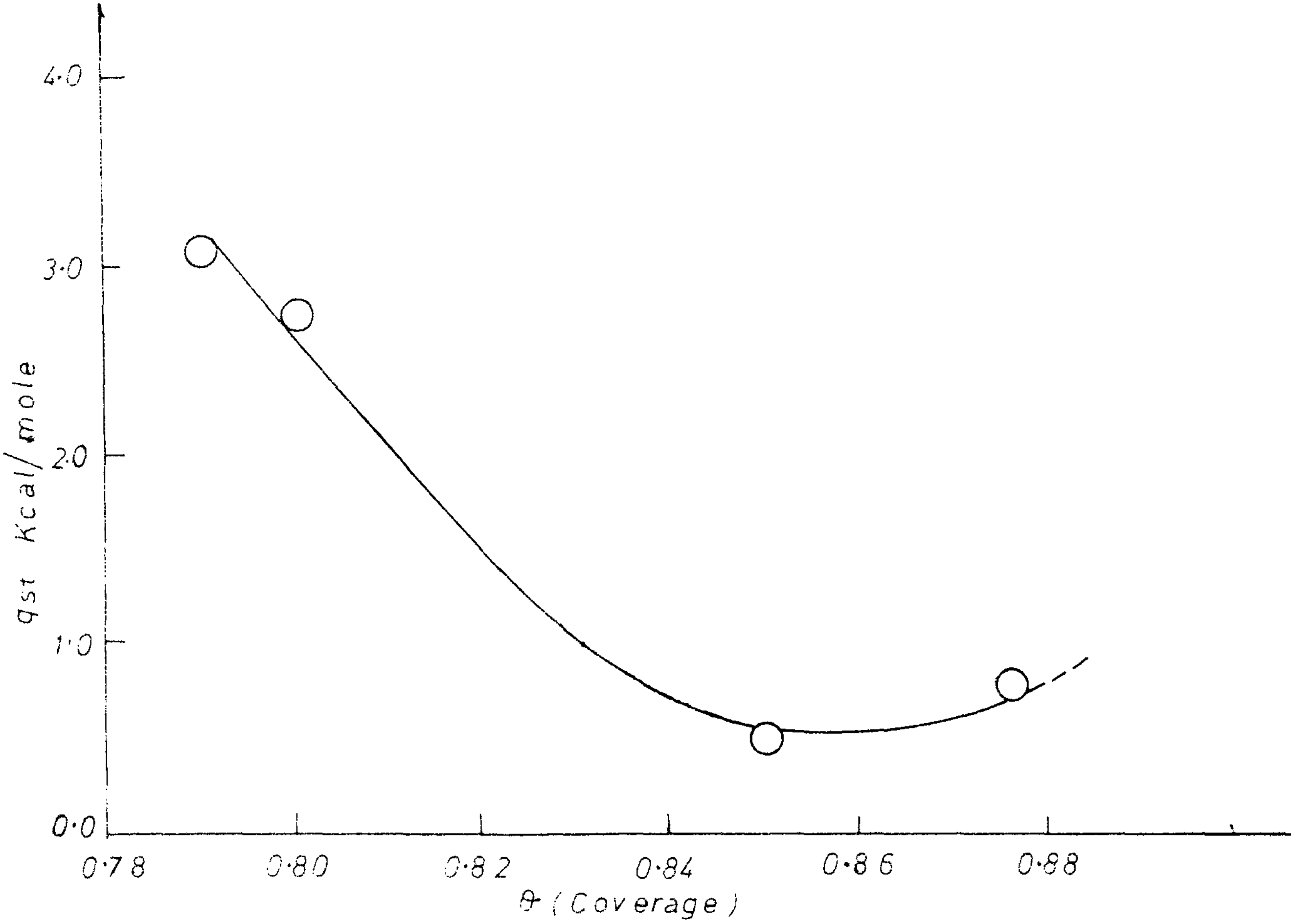


FIGURE:- 3.1.5.2. (qst vs θ) I_2 ADSORPTION

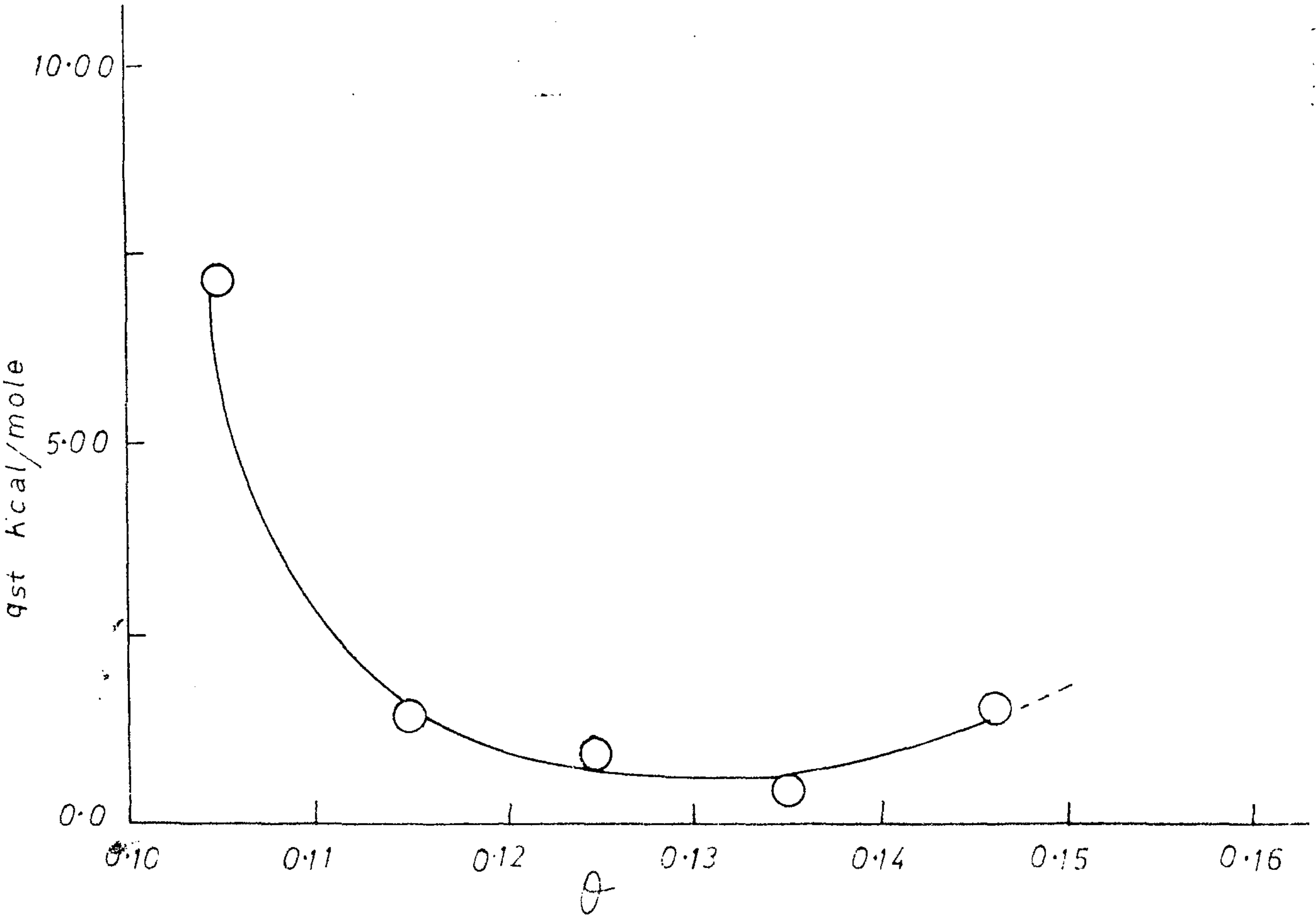


FIGURE:- 3.1.5.1. CH_3COOH ADSORPTION (qst vs θ).

3.1.5 STUDY OF THE SURFACE MOBILITY: When a substance is adsorbed on a surface, the particles adsorbed may be localized or move from site to site. Two factors control whether or not a layer is mobile under defined conditions. The first is the magnitude of the activation energy of migration. The more strongly adsorbed layers have a greater tendency to immobility, so that there may be an increase of activation energy of migration as well as heat of adsorption. Since differential heats of adsorption decrease with increasing surface coverage, mobility also proceeds more easily at high coverages that at low coverages. The second factor deciding mobility is temperature.

Two indirect methods of investigating mobility are available. Potentially the more important method is the calculation of the entropy of adsorption. From this quantity it is in theory possible to decide how many degrees of freedom have been lost on adsorption. The second indirect method is to observe the form of the curve relating the experimental heat of adsorption and the amount of adsorbate adsorbed. There is evidence that this may vary according to as the layer is mobile or immobile, provided the adsorbent is porous and possesses a considerable internal surface.

To get an idea about the heterogeneous nature of the adsorbate surface (activated c) and to make predictions about whether the adsorbed acetic acid or iodine is mobile or immobile, the heats of adsorption value as presented in Table 3.1.4.1 and 3.1.4.2 have been plotted against surface coverage (θ) for the temperature region $313^{\circ}K - 353^{\circ}K$. Figs. 3.1.5.1 and 3.1.5.2 show the $q_{st} - \theta$ relationship respectively for the temperature region.

The interpretation of the surface mobility in terms of the variation of the differential heat of adsorption with the extent of surface coverage is attempted by Beeck[232]. The earlier explanation is due to Constable and Taylor[229]. They have postulated a distinction between mobile and immobile adsorbed layers according to whether the heat of adsorption fall or remain unchanged with the increase in the surface coverage. The surface heterogeneity is presumed to be two fold, firstly due to the presence of internal surfaces with varying accessibility towards the adsorbate and secondly due to the variation of the site activity following the same distribution pattern over all types of surfaces. Under such a situation, the adsorption at initial stage takes place over the most accessible sites giving off essentially an integral heat of adsorption corresponding to the distribution of the site activities provided that the surface mobility is sufficiently low. The subsequent entry of the adsorbate leads adsorption on more and more inaccessible surfaces having the same distribution of surface activity with a result that the constancy of the heat of adsorption is maintained. On the otherhand, if the surface mobility is considerable, the adsorption of the very first quantum is followed by the migration of the adsorbate to the most active sites, regardless of the accessibility of the surfaces to which they belong ; as a result, the initial adsorption is accompanied by the largest evolution of integral heat. The subsequent adsorption, under such circumstances are marked by the progressive diminuation of the enthalpy change owing to the adsorption on the sites of decreasing activity.

The second explanation is due to Roberts[233]. There are many instances of chemisorption[61,234] where the large fall of heat cannot be explained by Taylor's[229] theory. Robert[233] suggested this fall as due primarily to forces of repulsion between molecules in the adsorbed layer. That is to say that the heat of adsorption per molecule, q_a , at a coverage θ is the decrease in energy of the system when one molecule is adsorbed. Increasing surface repulsions cause a progressive fall in q_a values. Since repulsion forces depend on the distance between the particles concerned, this implies that the distance between neighbouring particles is fixed. In practice, this is unlikely to be the case. At high θ values, a particle tends to be symmetrically surrounded by other particles, and as a result it remains at the lowest point of the potential well in which it is situated. At low θ values, however, it tends to be unsymmetrically surrounded, and hence tend to climb out of the well in order to increase its distance from repelling particles. Thus, the distance separating two neighbouring particles are lower at higher θ values, and heat of adsorption falls. An approximate method for dealing with the effect has been developed by Miller and Roberts[235].

The third explanation, due to Eley[158] and Schwab[241], considers the electron transfer which constituted formation of the surface bond. If either an electron is donated by the adsorbate or a covalency is formed, electrons from the adsorbate enter the solid. Since in crystals there are bands of permitted electron energies, the first electron enters the lowest unoccupied level of the band system and then higher and higher levels are used as adsorption proceeds. Thus the heat falls. If on the otherhand electrons are donated by the solid to the adsorbate, the first electron comes from the highest occupied state, and then deeper and deeper levels are used and again, the heat falls.

From a judicious inspection of the q - θ relationship (i.e. heat of adsorption as a function of surface coverage) as studied in the present investigation and presented in Figs. 3.1.5.1 and 3.1.5.2 (for acetic acid and iodine) it indicates that the heat of adsorption of acetic acid after an initial fall remains more or less independent of coverage. The initial fall of heat of adsorption with the increasing adsorption can be explained by the Taylor-Constable[229] interpretation of the surface mobility as described earlier. It also shows that upto a certain degree of adsorption (i.e. surface coverage 0.115 g. to 0.135 g.), where the heat of adsorption change is very negligible and have remained virtually constant, the surface layer can be treated as immobile. The shape of the curve is convex to the abscissa and this sort of behaviour is encountered for adsorption of caesium on tungsten[236] and hydrogen on tantalum[232]. The q - θ relationship (Fig. 3.1.5.2) for iodine shows a relatively slow heat fall at low θ values, when spreading can take place efficiently and minimize interactions.

3.2 KINETICS:

3.2.1 KINETICS OF ADSORPTION:

The study of adsorption kinetics gives very interesting information about the type and the mechanism of the adsorption process concerned. The preliminary work on adsorption kinetics have been confined to study the adsorption characteristics of five different adsorbates viz iodine (I_2), acetic acid (CH_3COOH), potassium permanganate($KMnO_4$), phenol (C_6H_5OH) and potassium perchlorate ($KClO_4$), on activated carbon (E.Merck) at room temperature ($28^{o}C + 2^{o}C$) and at the atmospheric pressure. The experimental procedures are described in chapter 2 (Section 2.2.3).

The basic kinetic data, the variation of concentration of the adsorbate with time are recorded in Tables 3.2.1.1, 3.2.1.2, 3.2.1.3, 3.2.1.4, 3.2.1.5 and plotted in figures 3.2.1.1, 3.2.1.2, 3.2.1.3, 3.2.1.4, 3.2.1.5 for iodine, acetic acid, potassium permanganate, phenol and potassium perchlorate respectively applying the Liszi equation (1.17)

$$v = \frac{t}{\gamma + \delta t} \quad \ldots\ldots \quad (1.17).$$

From the nature of the curves thus obtained it is apparent that the data agree with the Liszi equation. This equation (1.17) has been used to find out the initial rate of adsorption, and other parameters such as order of adsorption, limiting rates, rate constants and activation energies. The rearrangement of the Liszi equation (1.17) leads to

$$\frac{1}{v} = \frac{\gamma}{t} + \delta \quad \ldots\ldots\ldots \quad (1.17a)$$

and $$\frac{t}{v} = \gamma + \delta t \quad \ldots\ldots\ldots \quad (1.17b)$$

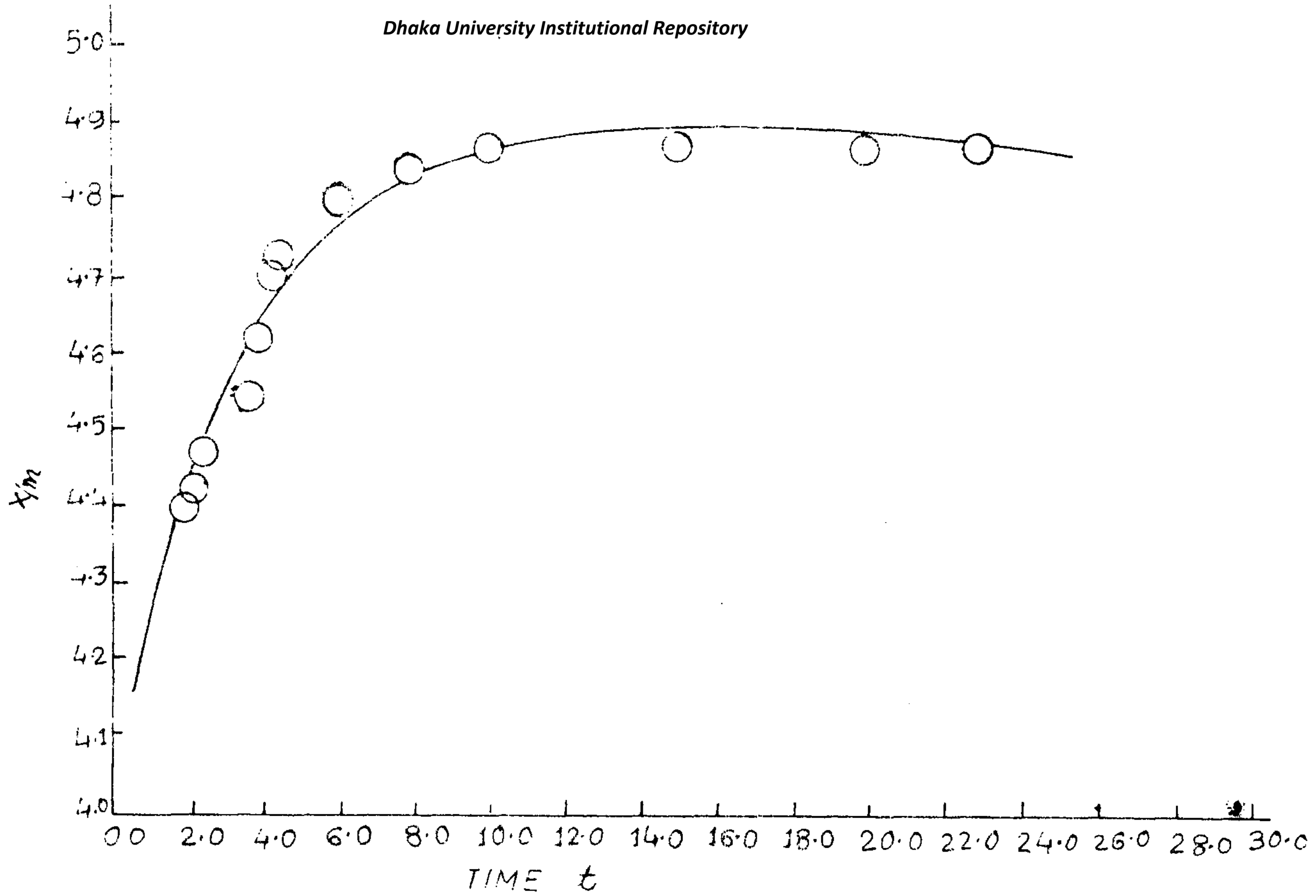


FIGURE:- 3.2.1.1. LISZI (X/m vs t) PLOT FOR 0·519 N ACETIC ACID ADSORPTION AT (28°C ± 2°C).

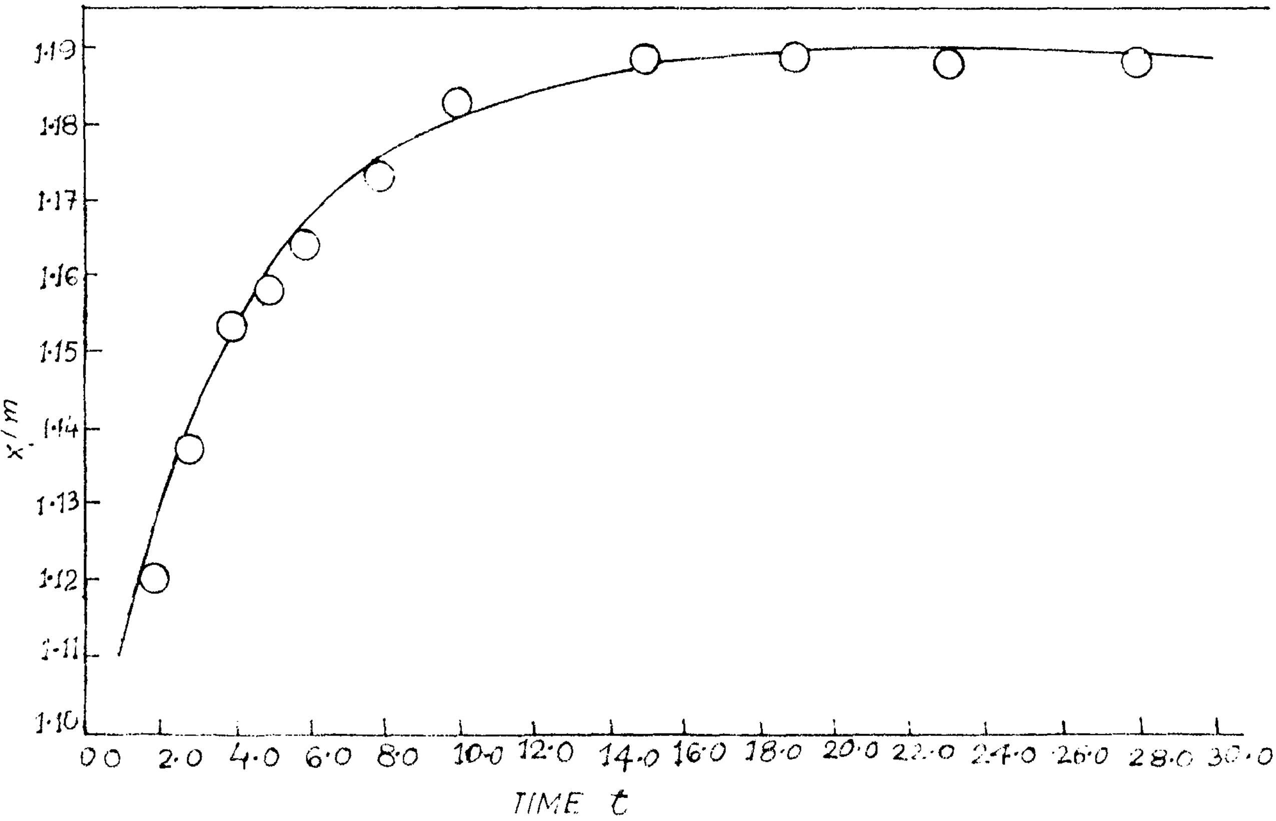


FIGURE:- 3.2.1.2. x/m vs t (LISZI PLOT). FOR 0·18 N IODINE ADSORPTION AT (28°C ± 2°C).

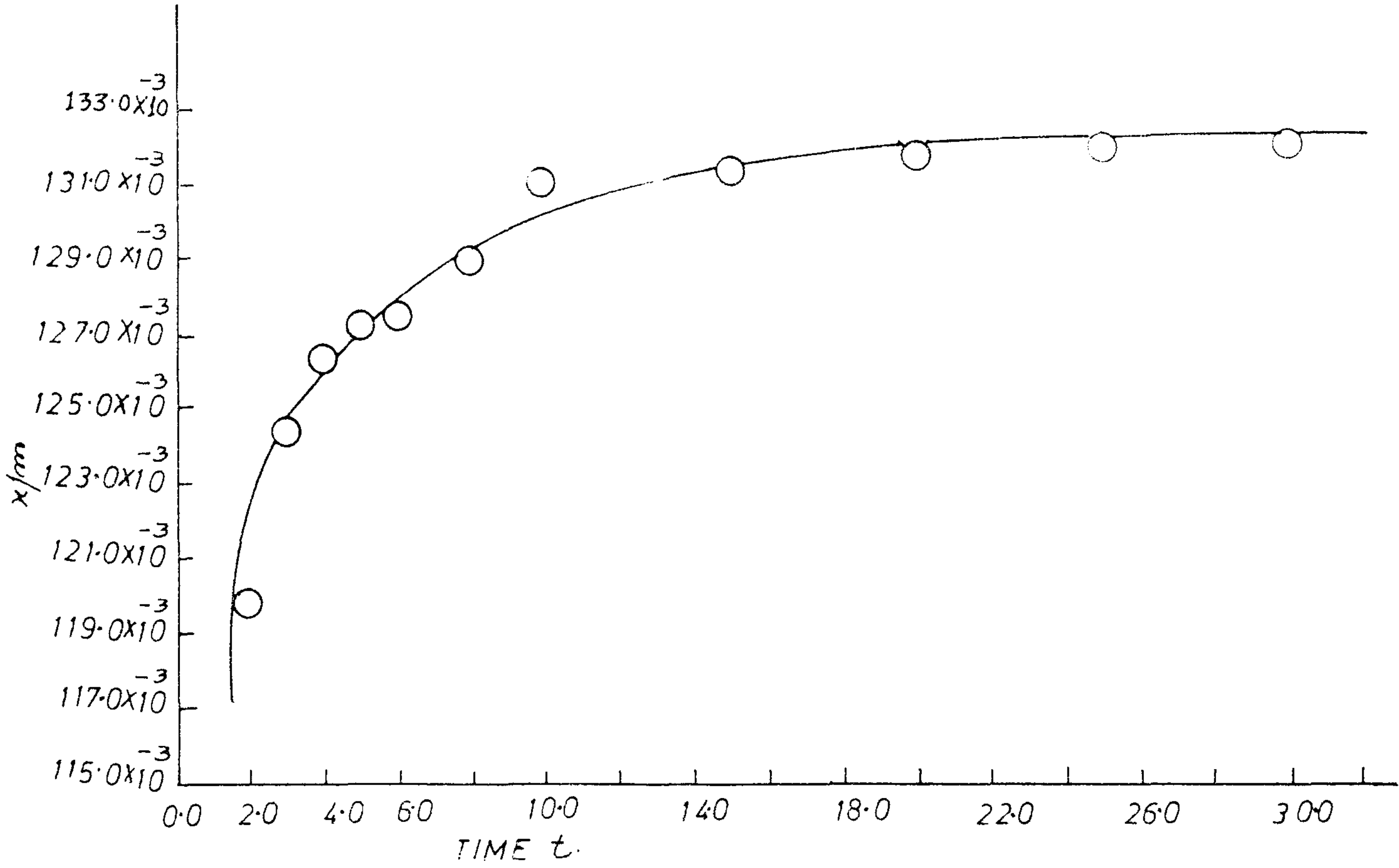


FIGURE :- 3.2.1.4. LISZI PLOT (x/m vs t) FOR (400 mg/l) PHENOL ADSORPTION ON ACTIVE CARBON (E. Merck) AT 28°C ± 2°C.

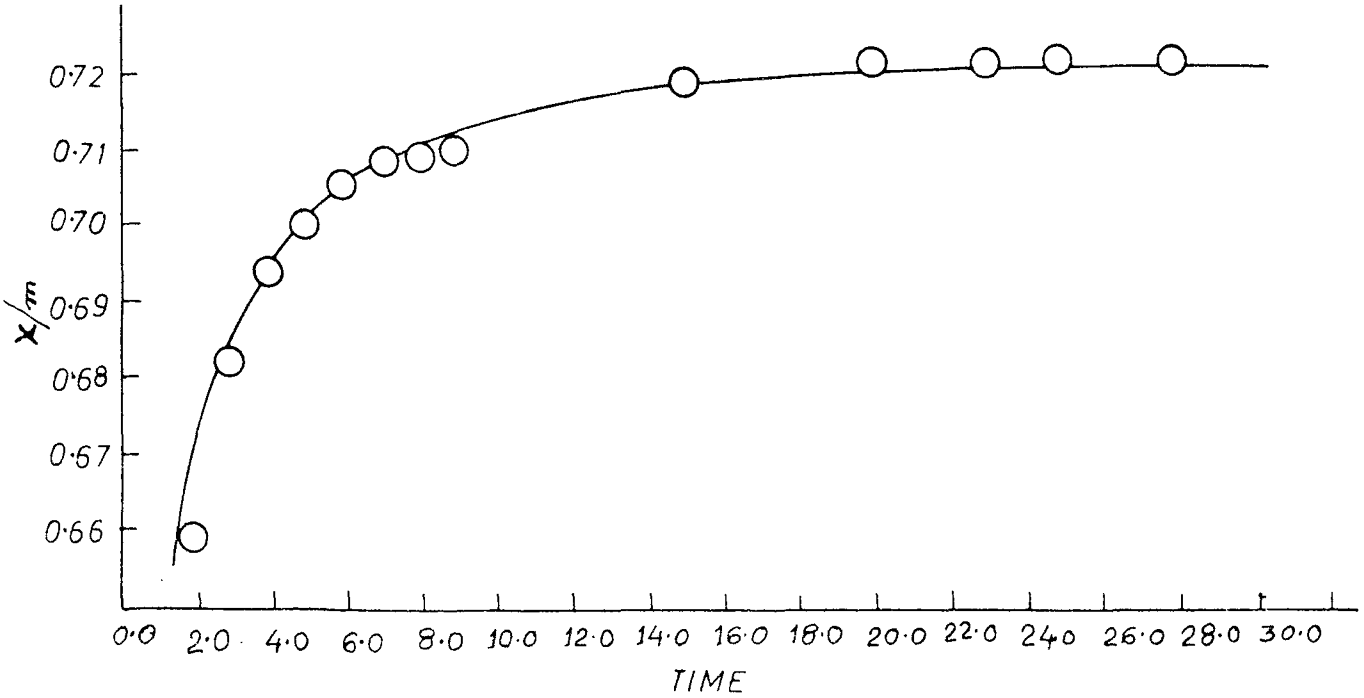


FIGURE :- 3.2.1.3. x/m vs t PLOT FOR 0·6N $KMnO_4$ ADSORPTION ON ACTIVE CARBON (E. Merck) AT 28°C ± 2°C.

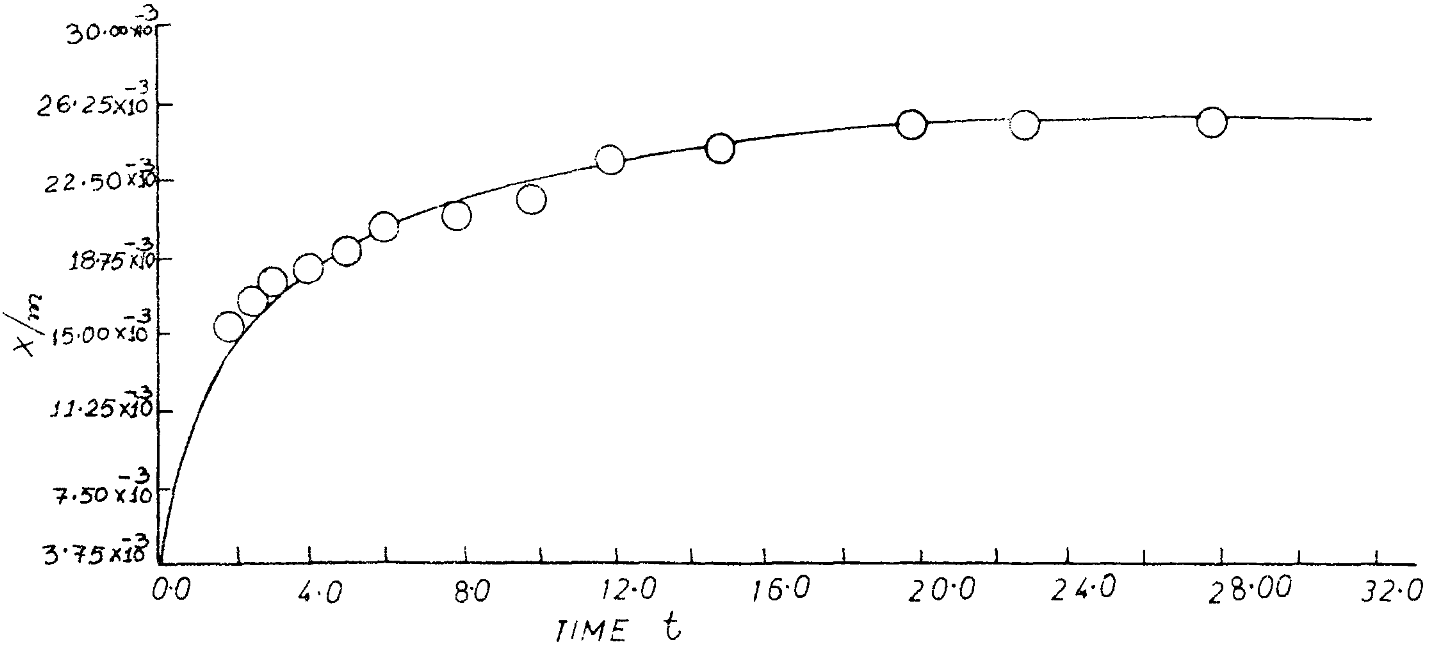


FIGURE:- 3.2.1.5. LISZI PLOT (x/m vs. t) FOR 0·50N $KClO_4$ ADSORPTION ON ACTIVE CARBON AT (28°C+2°C).

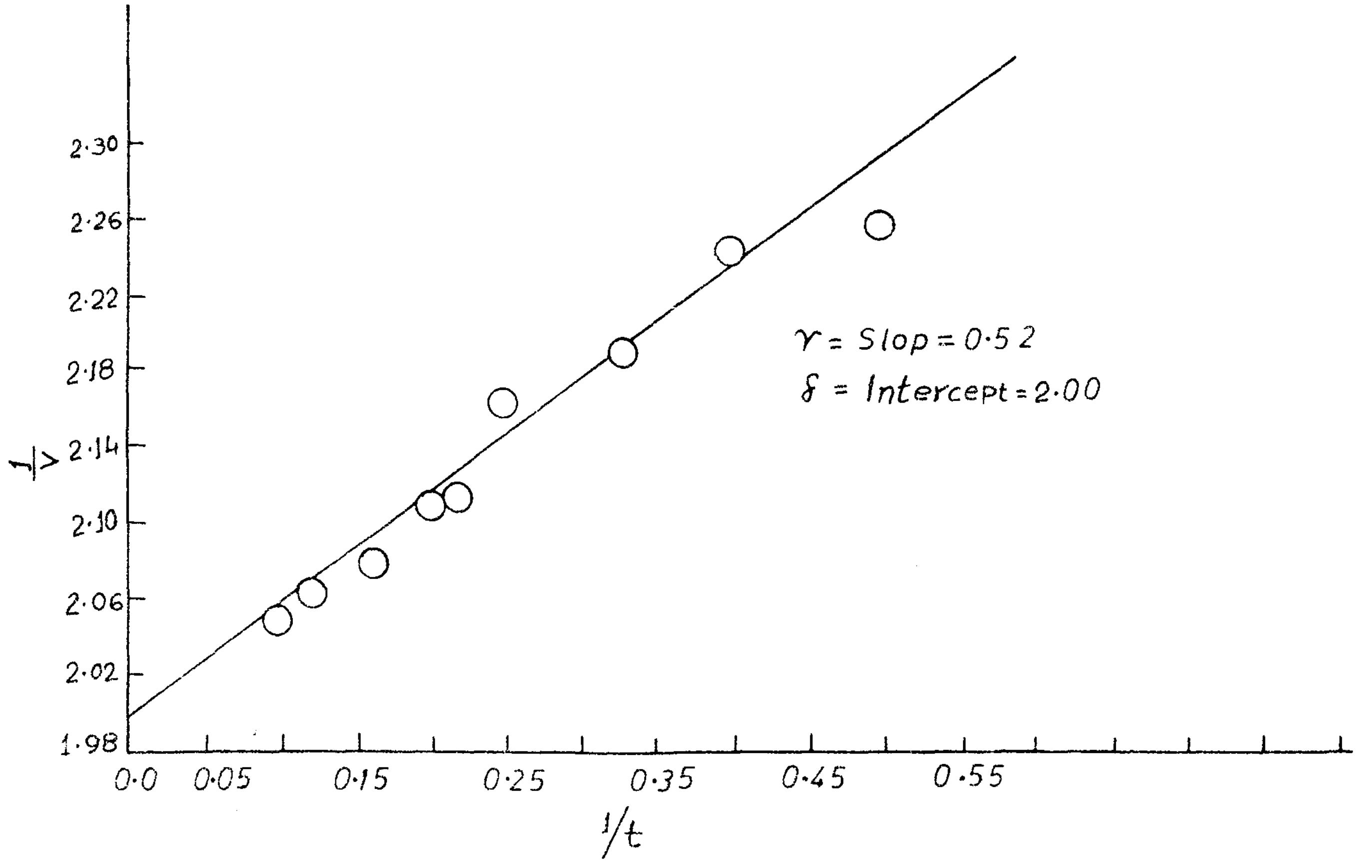


FIGURE:- 3.2.1.6. LISZI PLOT ($1/v$ vs $1/t$) FOR 0·519N CH_3COOH ADSORPTION ON ACTIVE CARBON AT 28°C+2°C .

According to these equations, plots of 1/v against 1/t or t/v against t should give straight lines. The former (1.17a) should provide ' γ ' from the slopes and ' δ ' from the intercepts whereas the latter (1.17b) should give ' δ ' from the slope and ' γ ' from the intercept.

The plots of 1/v against 1/t are shown in the Figs. 3.2.1.6, 3.2.1.7 , 3.2.1.8 , 3.2.1.9 , 3.2.1.10 for iodine, acetic acid, potassium permanganate, phenol and potassium perchlorate. As expected good linearity have been obtained in all these cases. The values of γ and δ obtained from these plots are presented in the tables 3.2.1.1 , 3.2.1.2 , 3.2.1.3, 3.2.1.4 , 3.2.1.5. Plots of t/v vs t (Figs. 3.2.1.11 , 3.2.1.12, 3.2.1.13 , 3.2.1.14 and 3.2.1.15) also has given straight lines as expected with slopes equal to ' δ ' and intercept equal to ' γ '. The values of ' δ ' and ' γ ' obtained from Figs. 3.2.1.6 , 3.2.1.7 , 3.2.1.8 , 3.2.1.9 and 3.2.1.10 agree with the corresponding values from Figs. 3.2.1.11 , 3.2.1.12 , 3.2.1.13 , 3.2.1.14 , 3.2.1.15.

RATE CONSTANTS AND ORDER OF ADSORPTION:

From the values of ' γ ' and ' δ ' as obtained from the plots of i/v vs 1/t and t/v vs t , the order of adsorption and the value of rate constants are found out. At low 't' i.e. when $\delta t << \gamma$, equation (1.17) gives

$$v = \frac{t}{\gamma} \quad \ldots\ldots \quad (1.17c)$$

$$\text{or } \frac{dv}{dt} = \frac{1}{\gamma} = r \quad \ldots\ldots \quad (1.17d)$$

where, 'r' is the initial rate of adsorption. It means that the initial rates of adsorption can be obtained from the reciprocal of

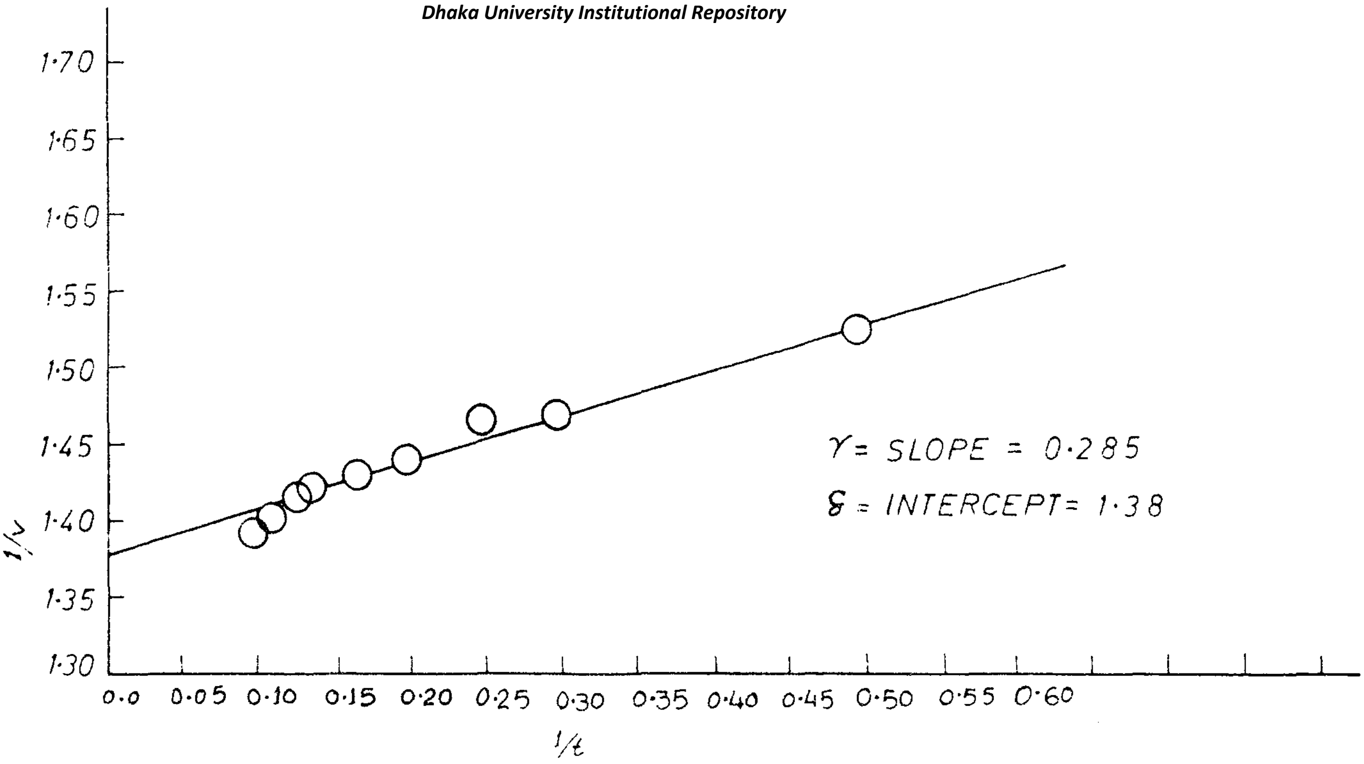


FIGURE:- 3.2.1.8. LISZI PLOT (1/V vs 1/t) FOR 0·60N $KMnO_4$ ADSORPTION ON ACTIVE CARBON AT 28°C ± 2°C.

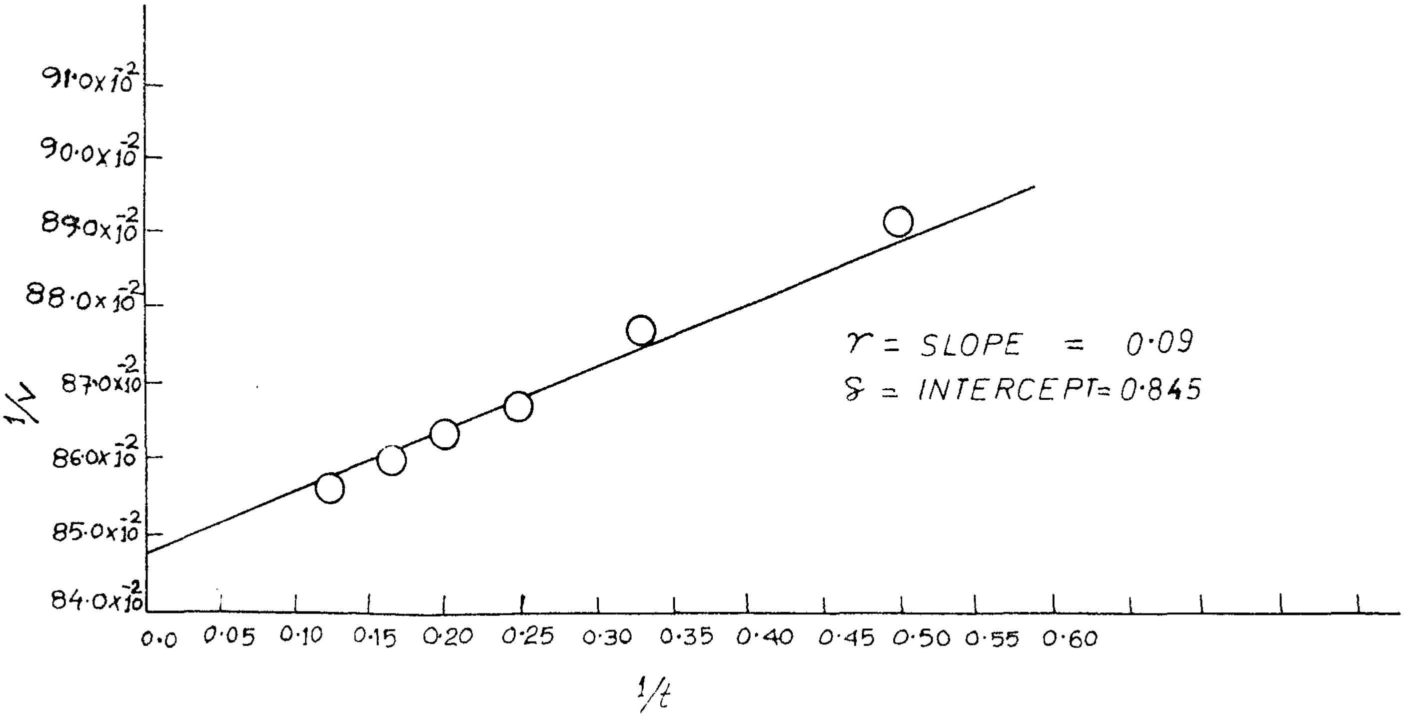


FIGURE:- 3.2.1.7. LISZI PLOT (1/V vs 1/t) FOR 0·18N I_2 ADSORPTION ON ACTIVE CARBON (E.Merck) AT 28°C ± 2°C.

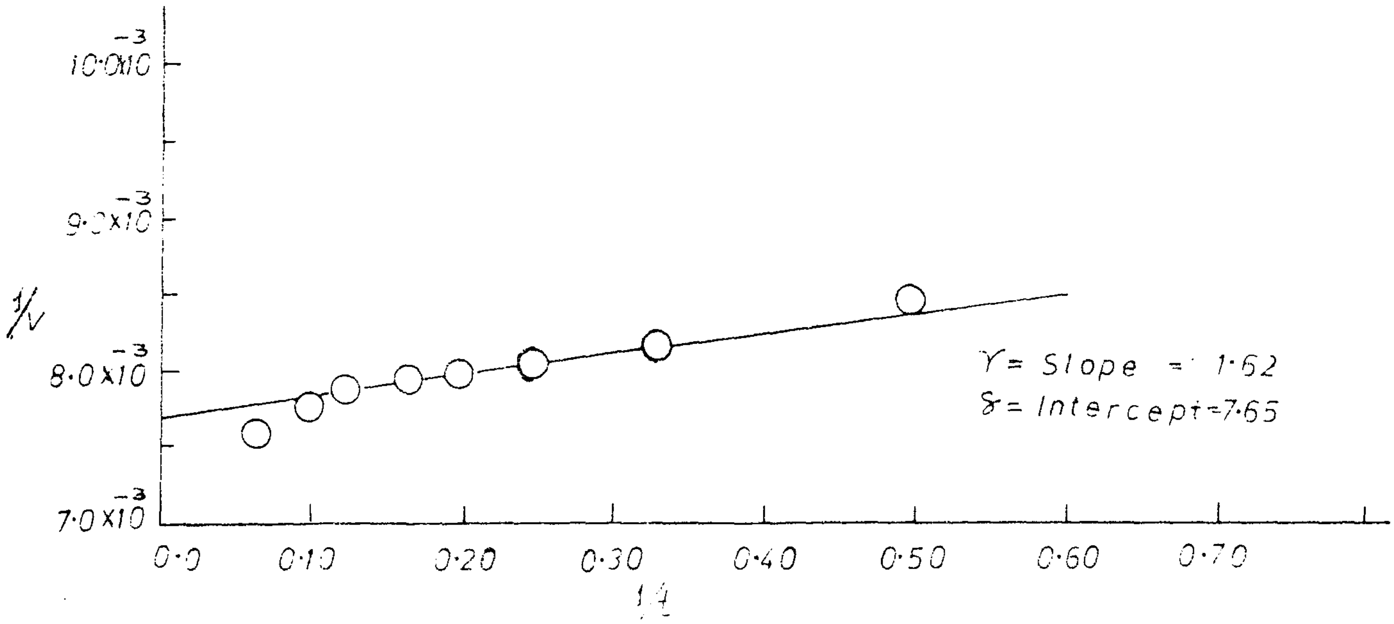


FIGURE:- 3.2.1.9. LISZI PLOT(1/V vs 1/t) FOR 400 mg/litre PHENOL ADSORPTION ON ACTIVE CARBON (E.Merck) AT 28°C±2°C.

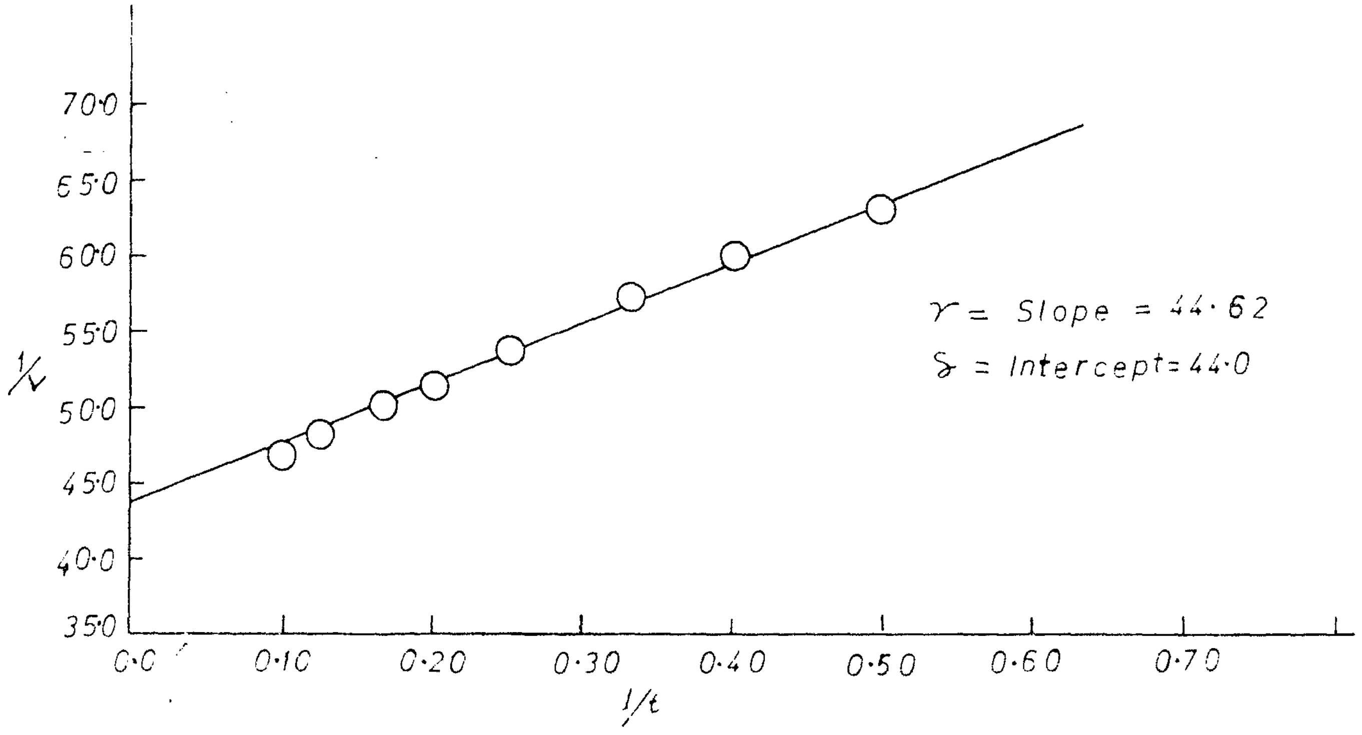


FIGURE:- 3.2.1.10. LISZI PLOT(1/V vs 1/t) FOR 0.50N $KClO_4$ ADSORPTION ON ACTIVE CARBON (E.Merck) AT 28°C±2°C.

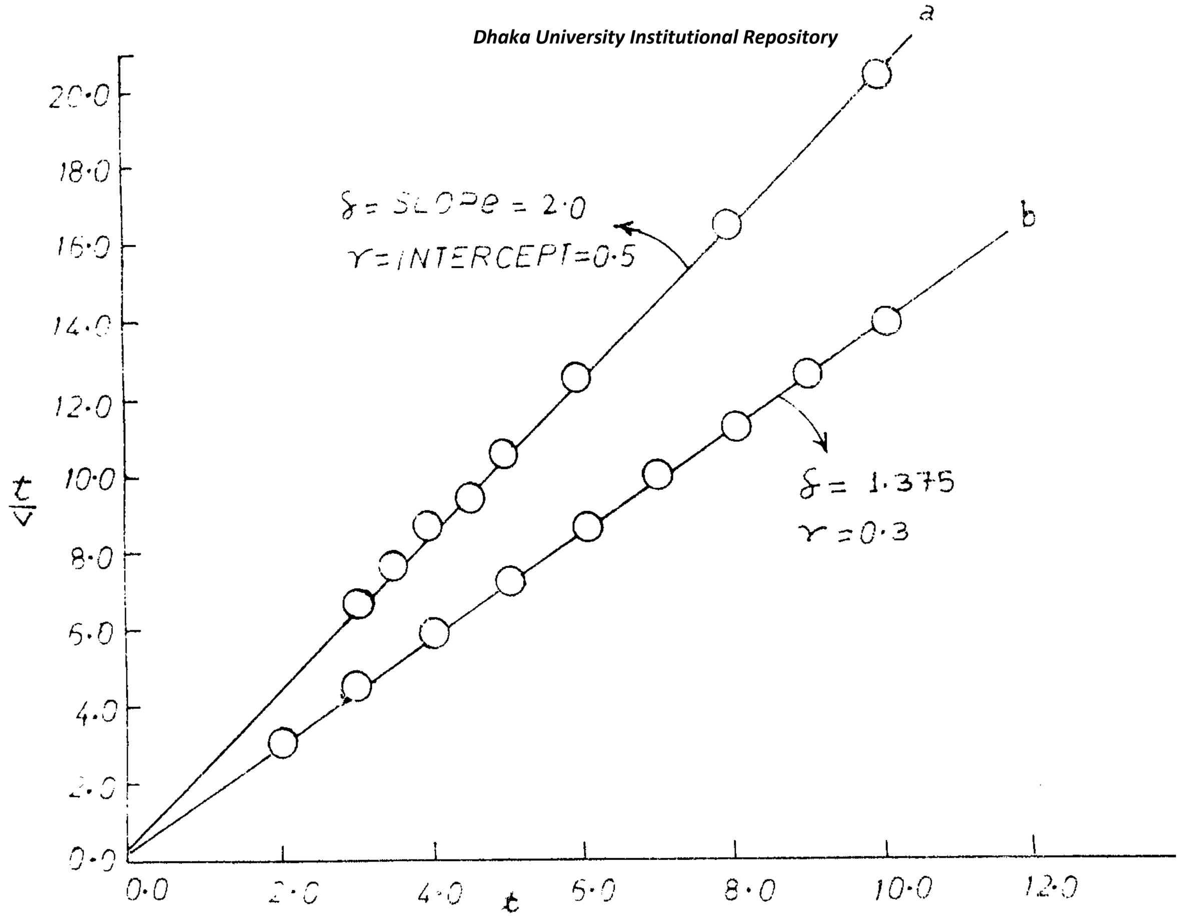


FIGURE:-3.2.1.12 LISZT PLOT(t/V vs t) FOR(a) 0·519N ACETIC ACID AND (b) 0·50N $KMnO_4$ ADSORPTION ON ACTIVE CARBON(E. Merck) AT 28°C ± 2°C.

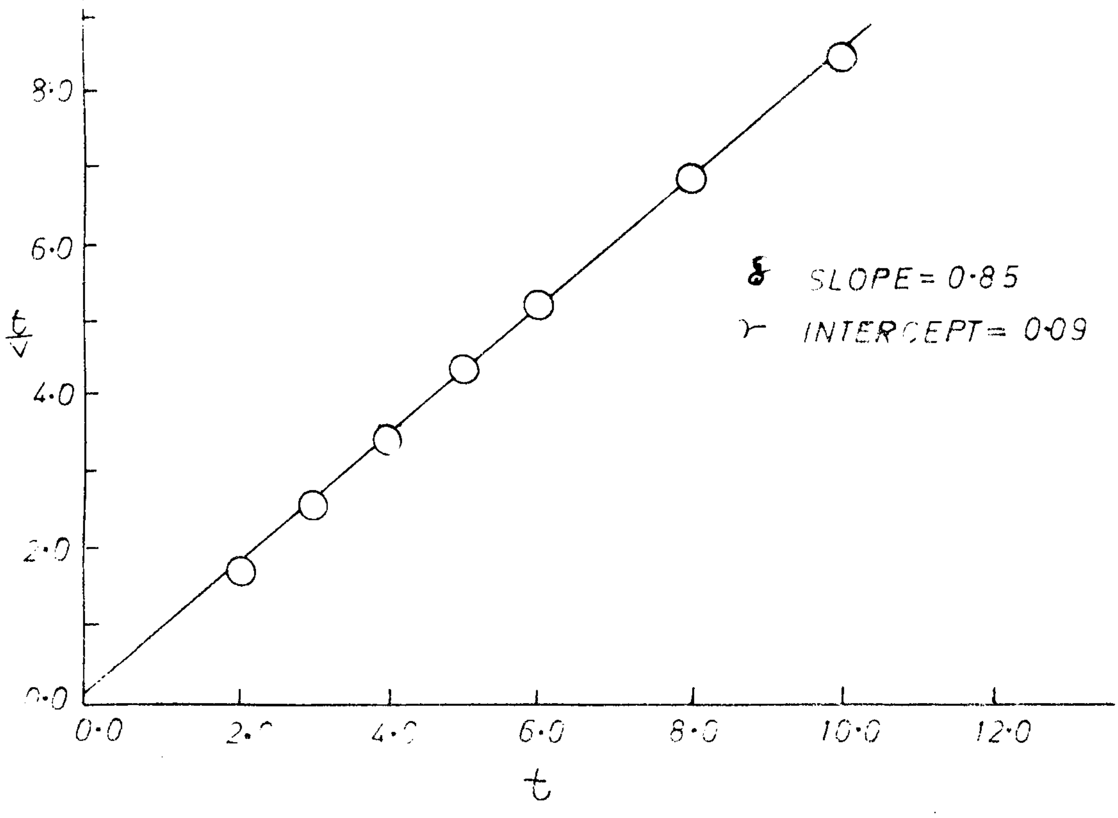


FIGURE:-3·2·1·11 LISZT PLOT(t/V VS t) FOR 0·18N IODINE ADSORPTION ON ACTIVE CARBON (E. Merck) AT 28°C ± 2°C.

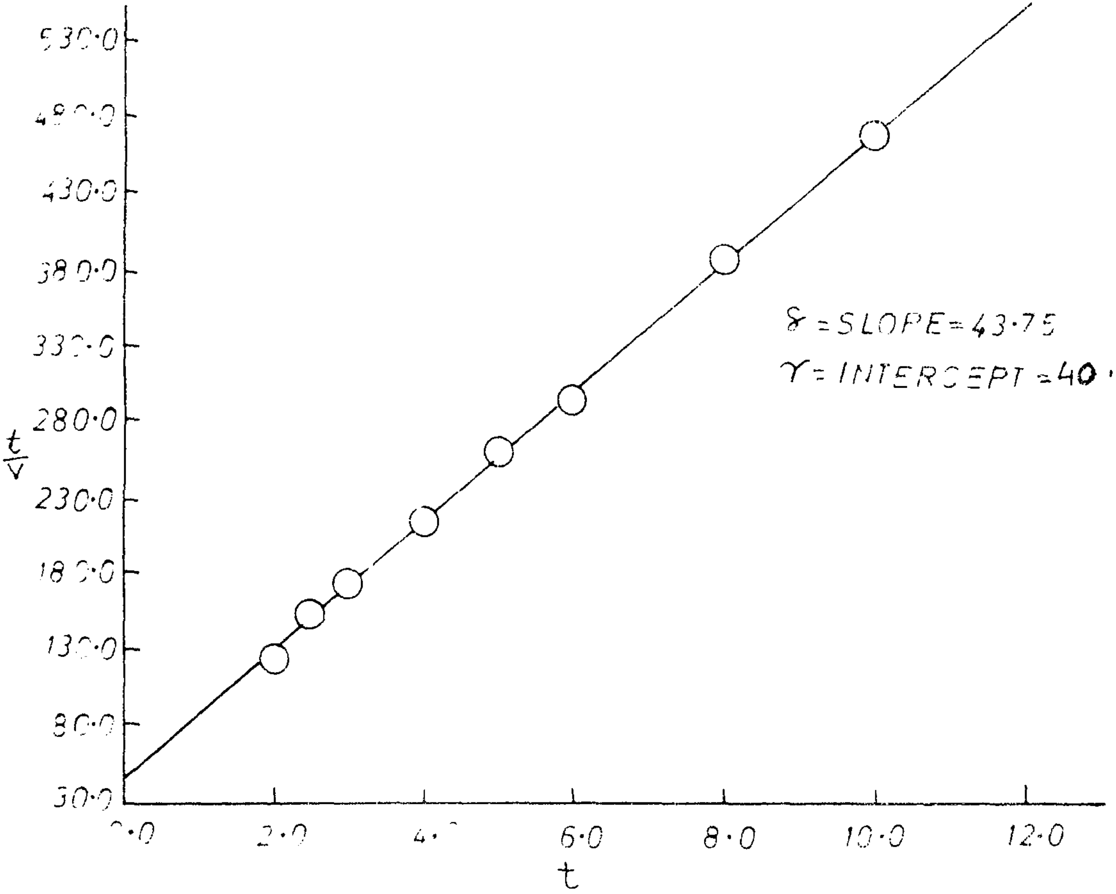


FIGURE:- 3.2.1.14 LISZI PLOT (t/V vs t) FOR 0·5N $KClO_4$ ADSORPTION ON ACTIVE CARBON (E.Merck) AT 28°C±2°C

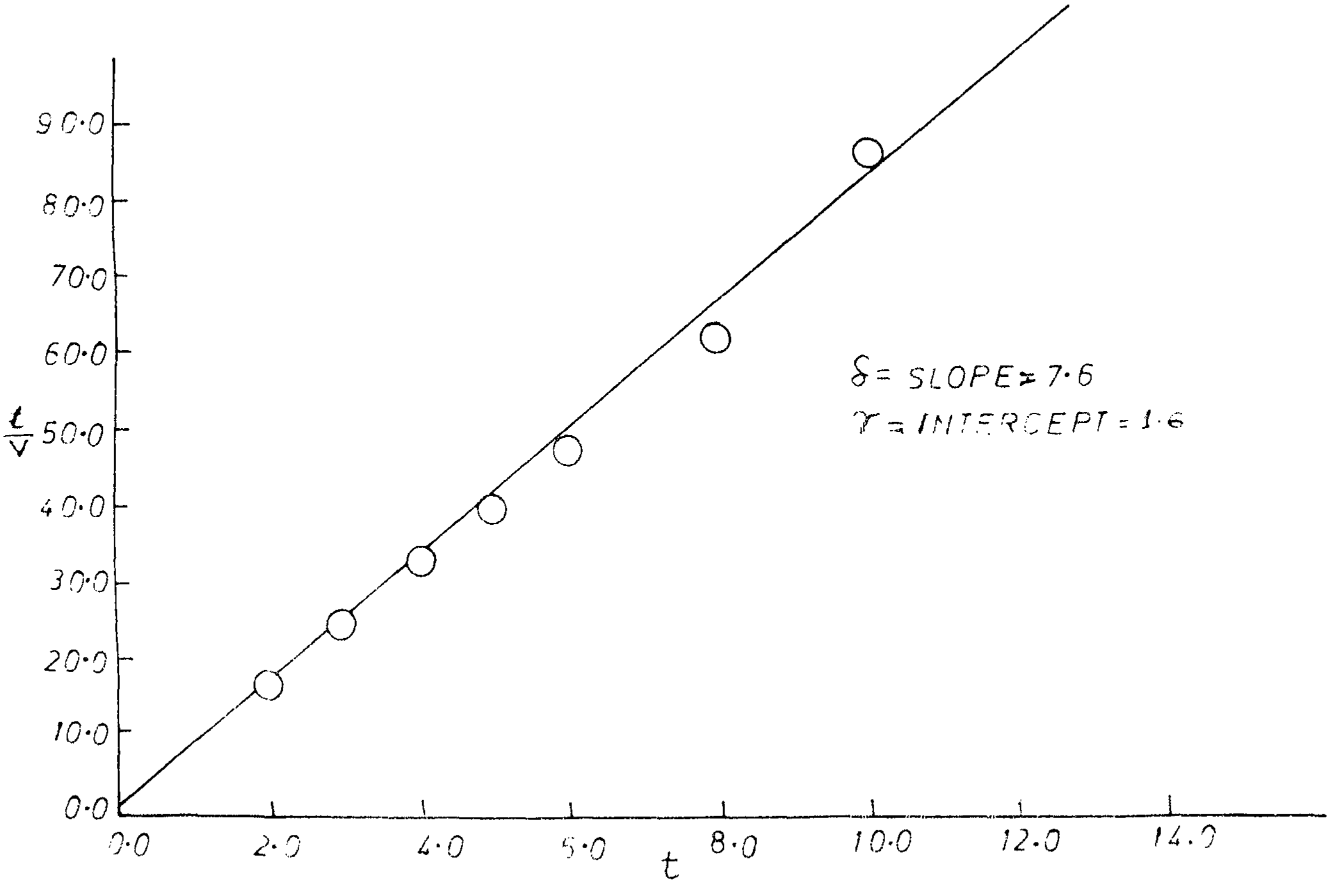


FIGURE:- 3.2.1.13 LISZI PLOT (t/V vs t) FOR 400mg/Litre C_6H_5OH ADSORPTION ON ACTIVE CARBON (E.Merck) AT 28°C±2°C.

the 'γ' values. Now,

rate = r = kc^n, where 'n' is the order of adsorption, and c is the concentration.

$$\text{or } \log r = \log k + n \log c$$

$$\text{or } \log\left(\frac{1}{\gamma}\right) = \log k + n \log c \quad \ldots\ldots \qquad (1.17e)$$

(from (1.17d) where $r = \frac{1}{\gamma}$)

So, a plot of log $\frac{1}{\gamma}$ vs log c gives straight line, the slope of which is the order of adsorption and intercept is the logarithm of rate constants.

At high 't' i.e. when $\gamma \ll \delta t$, equation (1.17) reduces to

$$v_\infty = \frac{1}{\delta} \quad \ldots\ldots\ldots \qquad (1.17\ f)$$

since at high 't' the v-t curves levels off, $\frac{1}{\delta}$ represents the limiting adsorption.

ACTIVATION ENERGY: The activation energy of adsorption has been found out by applying the Arrhenious equation,

$$k = Ae^{-Ea/RT}$$

$$\text{i.e. } k = \text{the rate constant} = Ae^{-Ea/RT}$$

$$\text{or } \ln k = \ln A - Ea/RT$$

$$\text{or } 2.303 \log k = 2.303 \log A - {}^{Ea}/2.303\ RT$$

so, from the plots of log k vs 1/T , which has given a straight line, the slope is equal to ${}^{-Ea}/2.303\ R$ and from there, the value of activation energy Ea is calculated.

3.2.2 ADSORPTION KINETICS FOR ACETIC ACID AND IODINE.

In order to understand reaction (i.e. adsorption) mechanism and to calculate activation energy, order of adsorption,

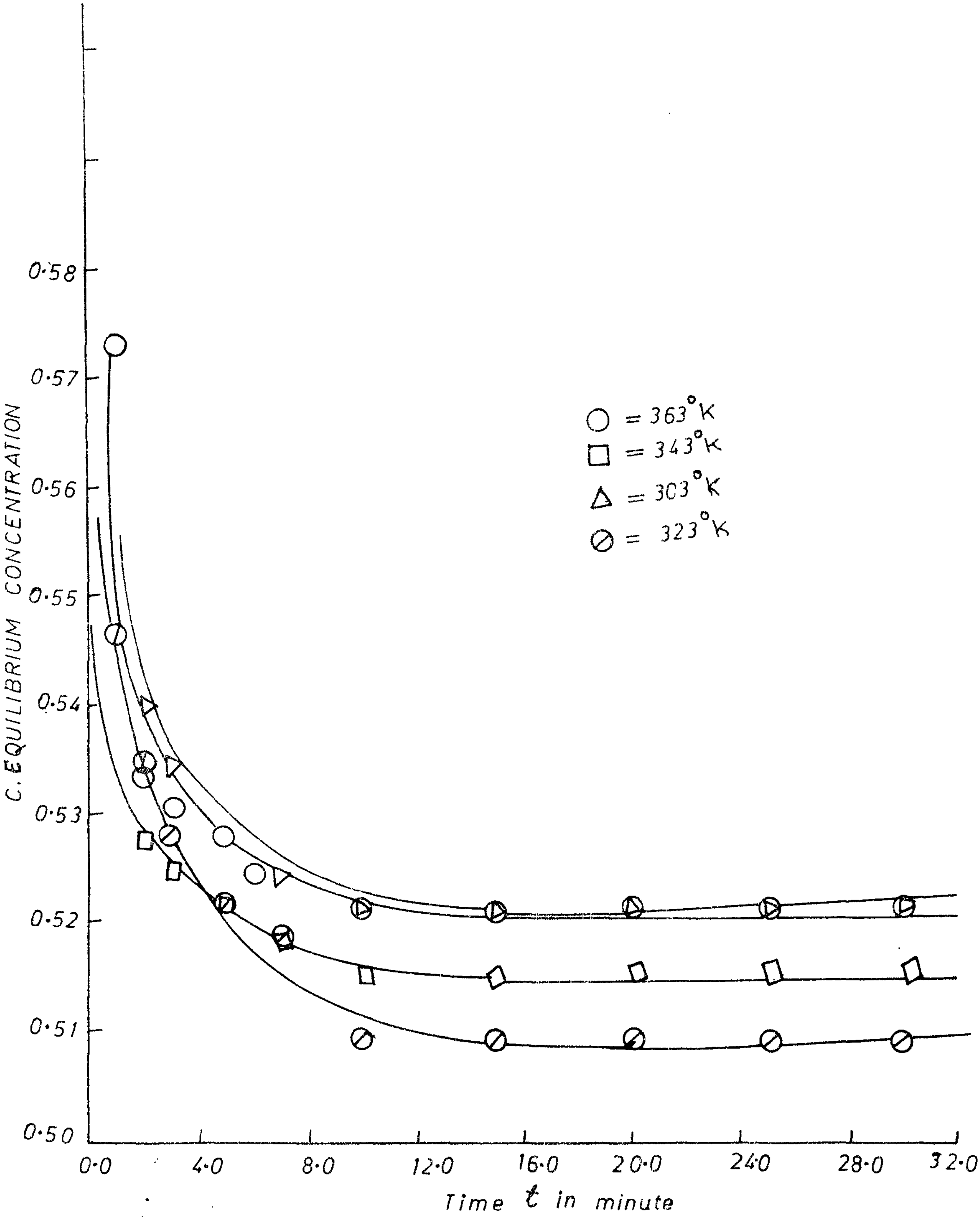


FIGURE:– 3.2.2.1. CONCENTRATION VS TIME PLOTS FOR THE ADSORPTION OF ACETIC ACID ON ACTIVATED CARBON (STEAM).

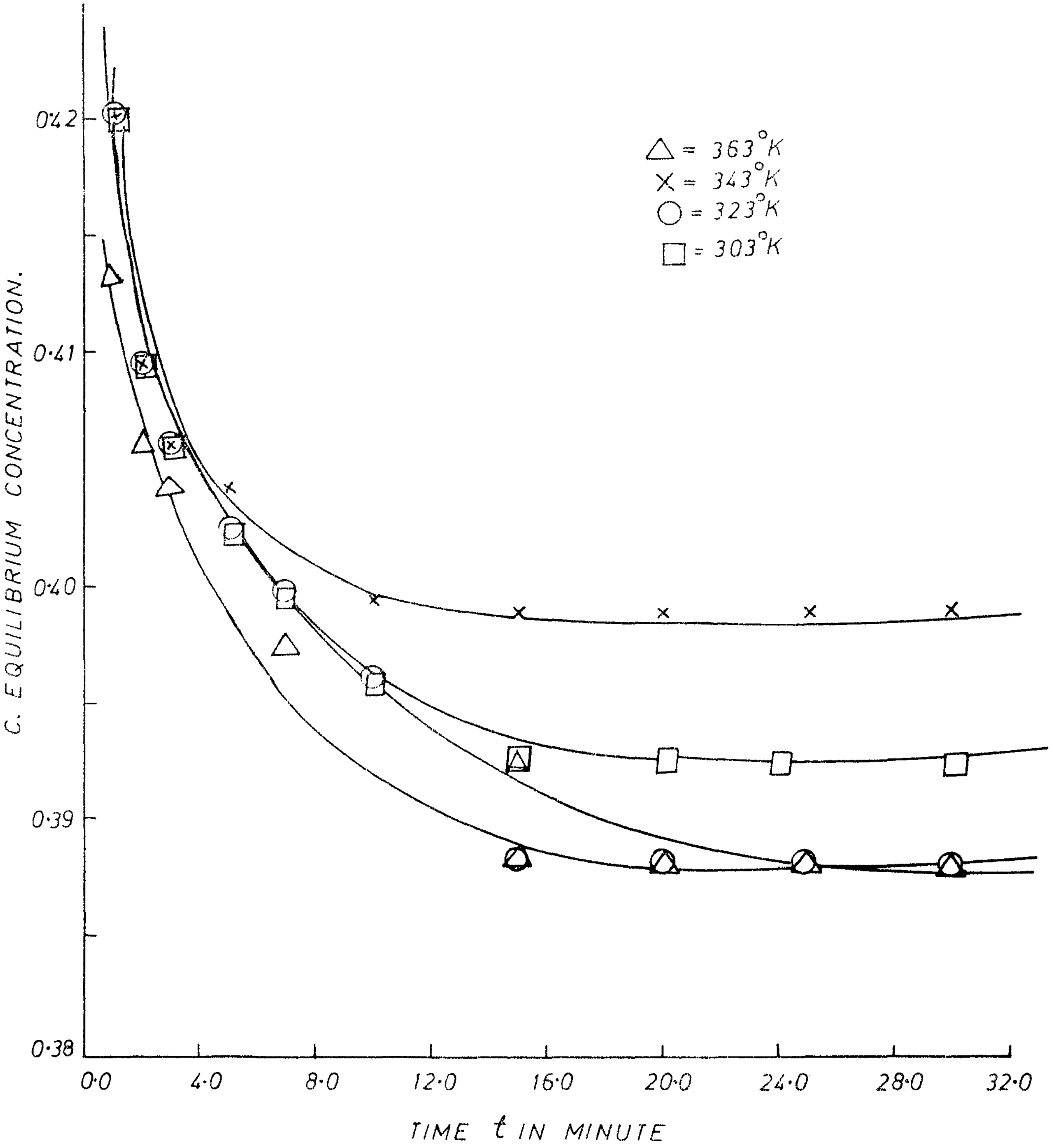


FIGURE :- 3.2.2.2. CONCENTRATION VS TIME PLOT FOR I_2 ADSORPTION ON ACTIVATED CARBON (STEAM).

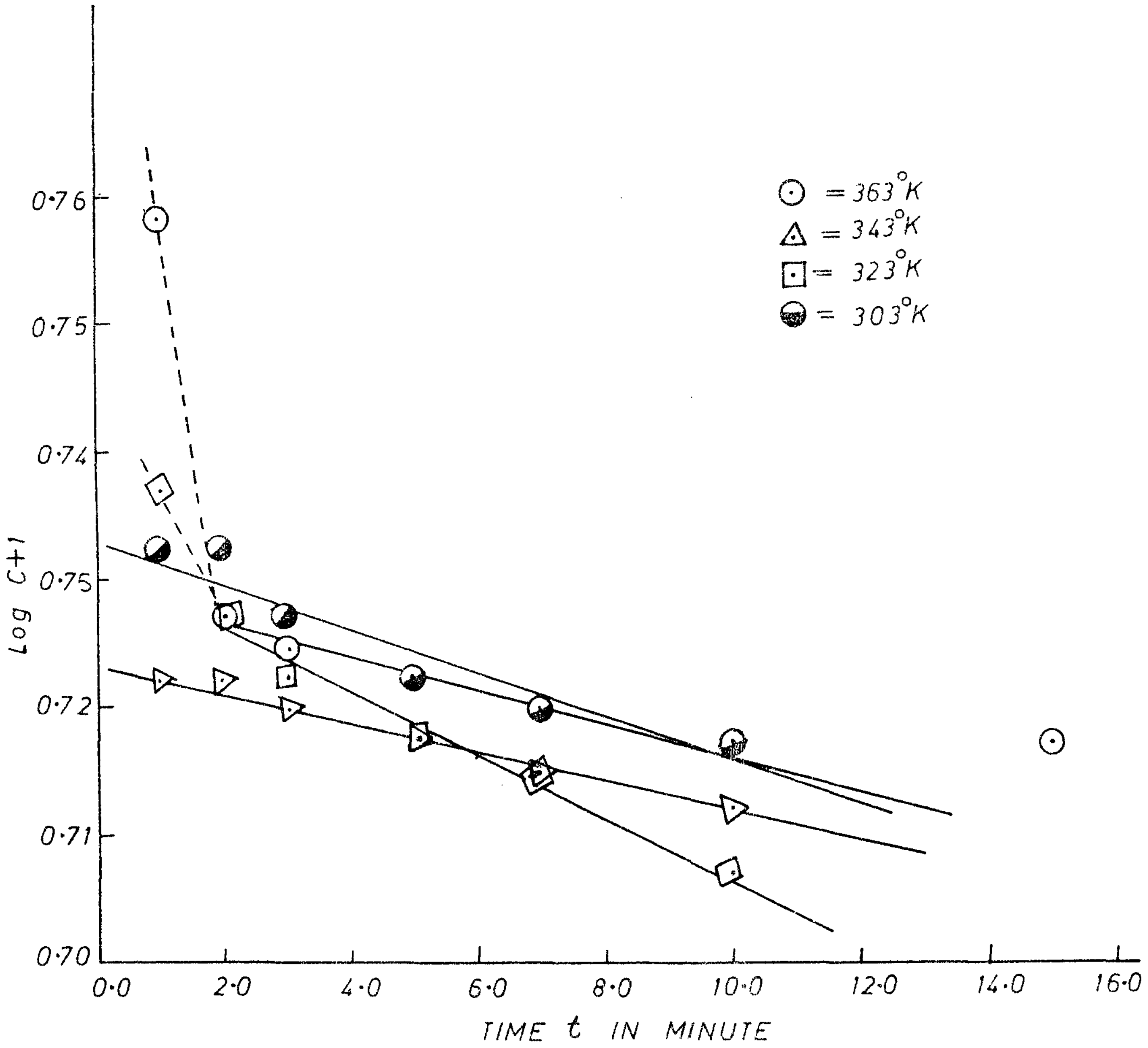


FIGURE:- 3.2.2.1.1. FIRST ORDER KINETIC PLOT (Log C vs t) FOR ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON. STIPPLED CURVE SIGNIFY DEVIATION.

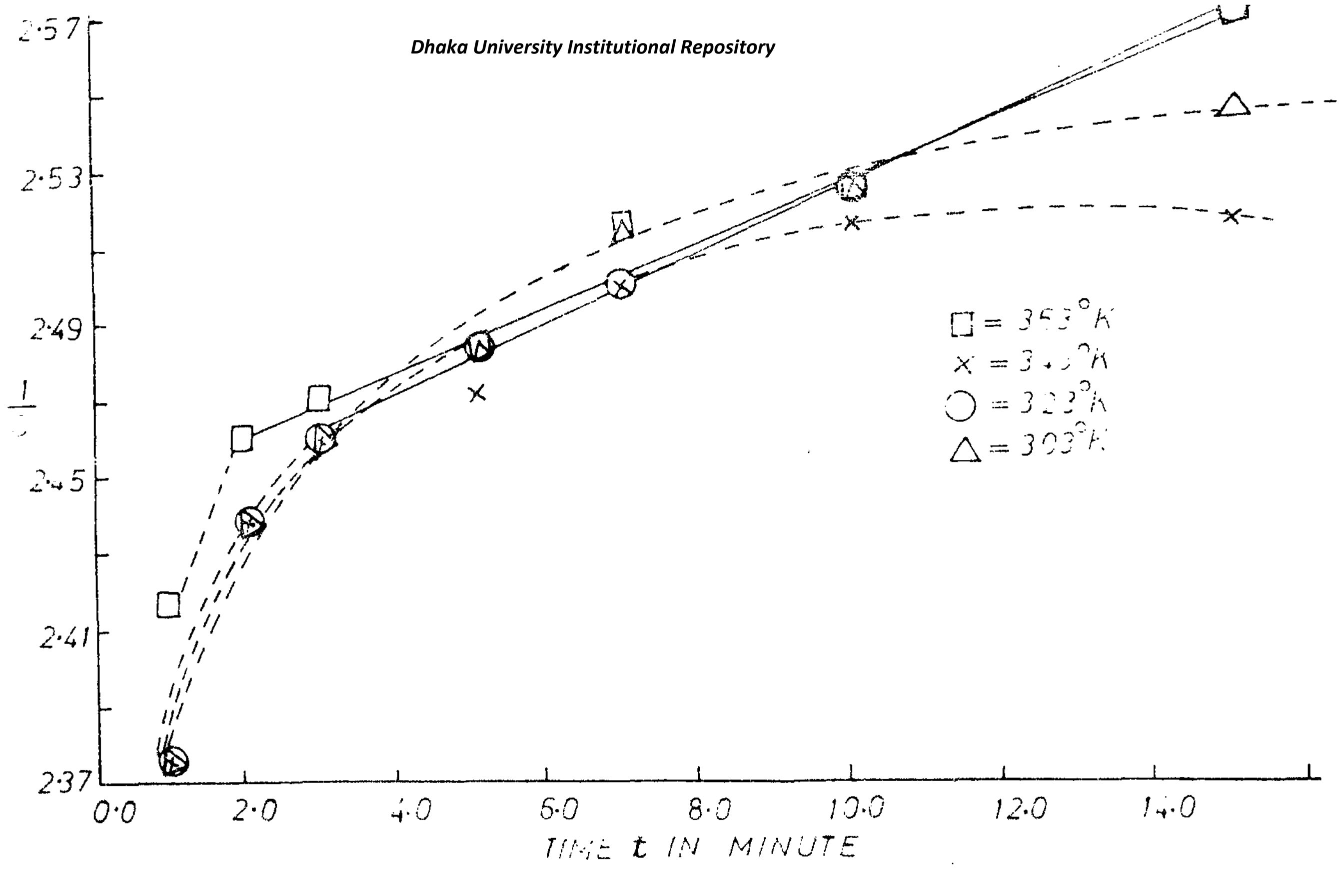


FIGURE:- 3.2.2.2.2 SECOND ORDER KINETIC PLOT ($^1/C$ vs t) FOR (0·538N) I_2 ADSORPTION ON ACTIVATED CARBON (STEAM).
STIPPLED CURVE SIGNIFY DEVIATION.

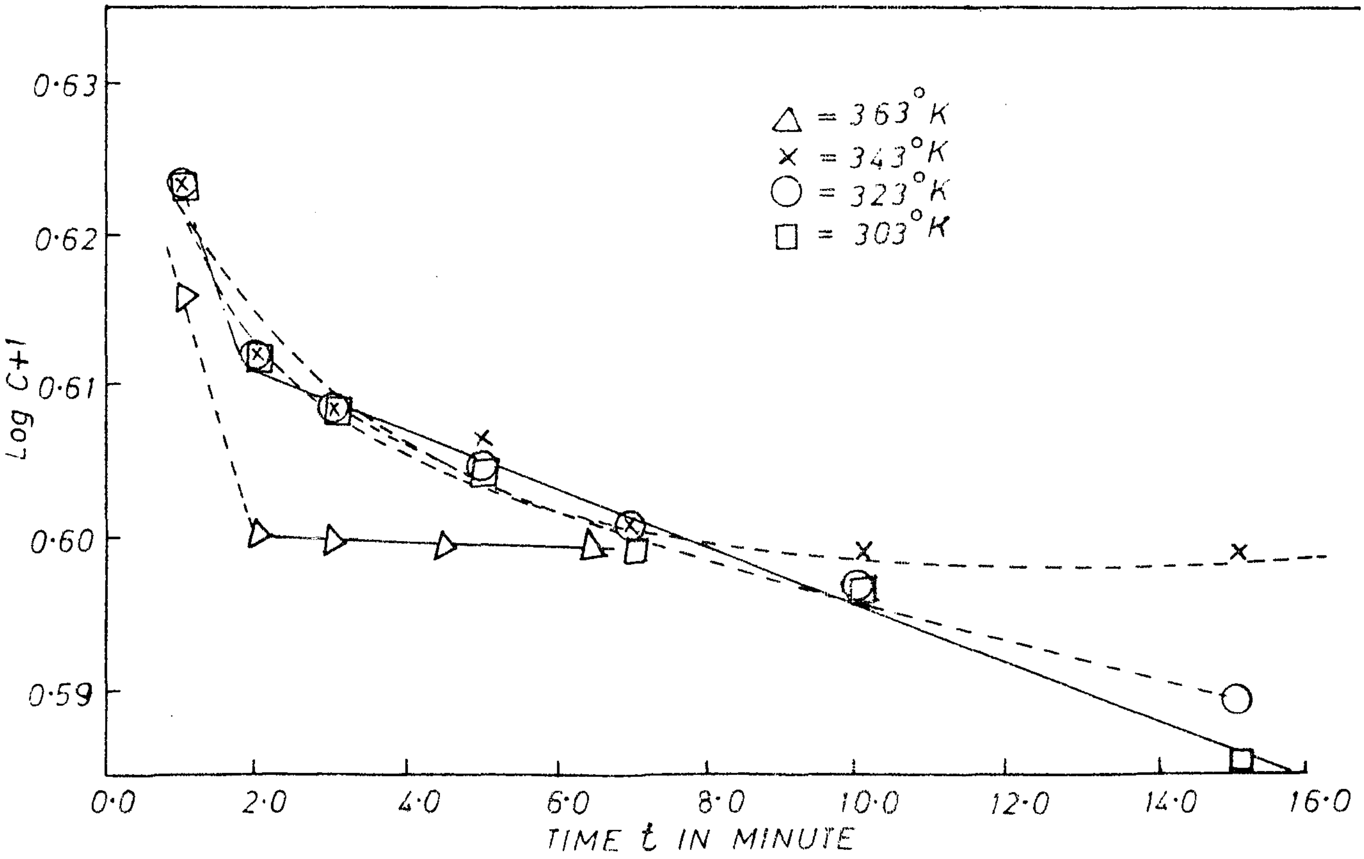


FIGURE:-3.2.2.2.1 FIRST ORDER KINETIC PLOT (Log C vs t) FOR (0·538N) I_2 ADSORPTION ON ACTIVATED CARBON (STEAM).
STIPPLED CURVE SIGNIFY DEVIATION.

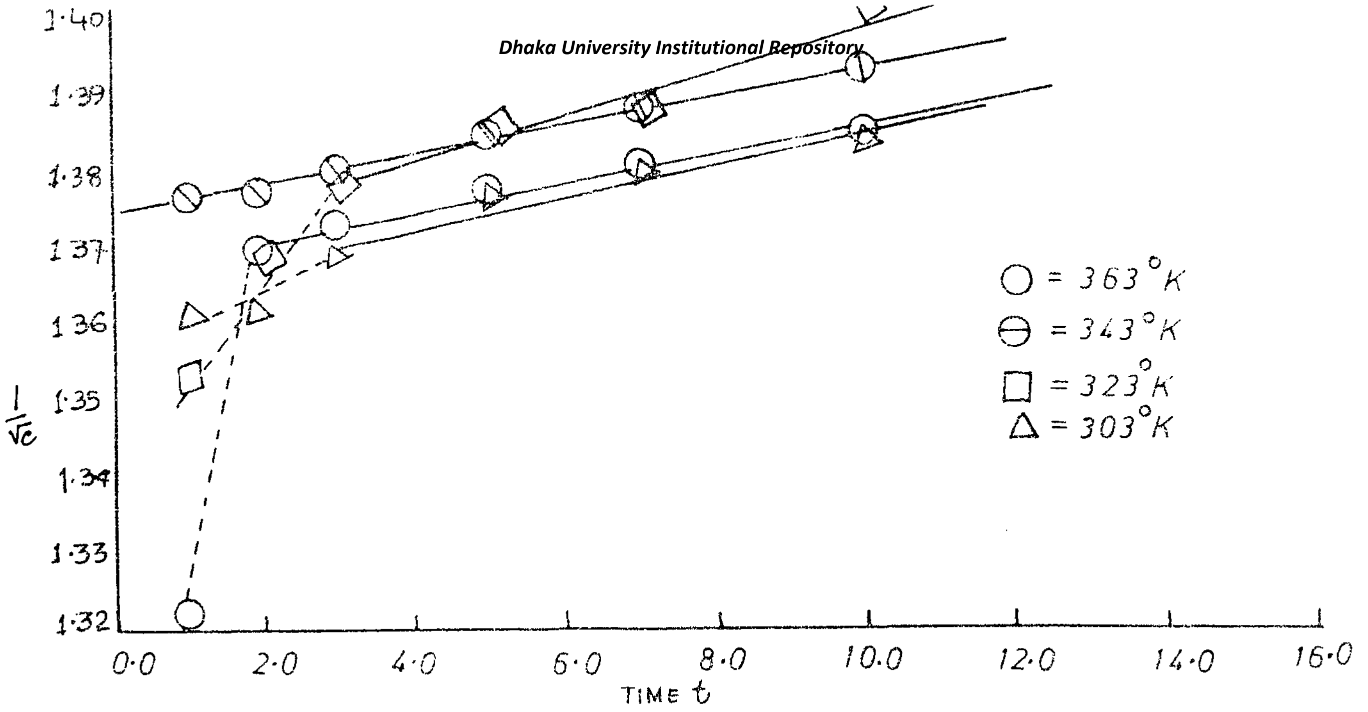


FIGURE:- 3.2.2.1,3. KINETIC PLOT OF ORDER 1·5 ($1/\sqrt{c}$ vs t) FOR ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON. STIPPLED CURVE SIGNIFY DEVIATION.

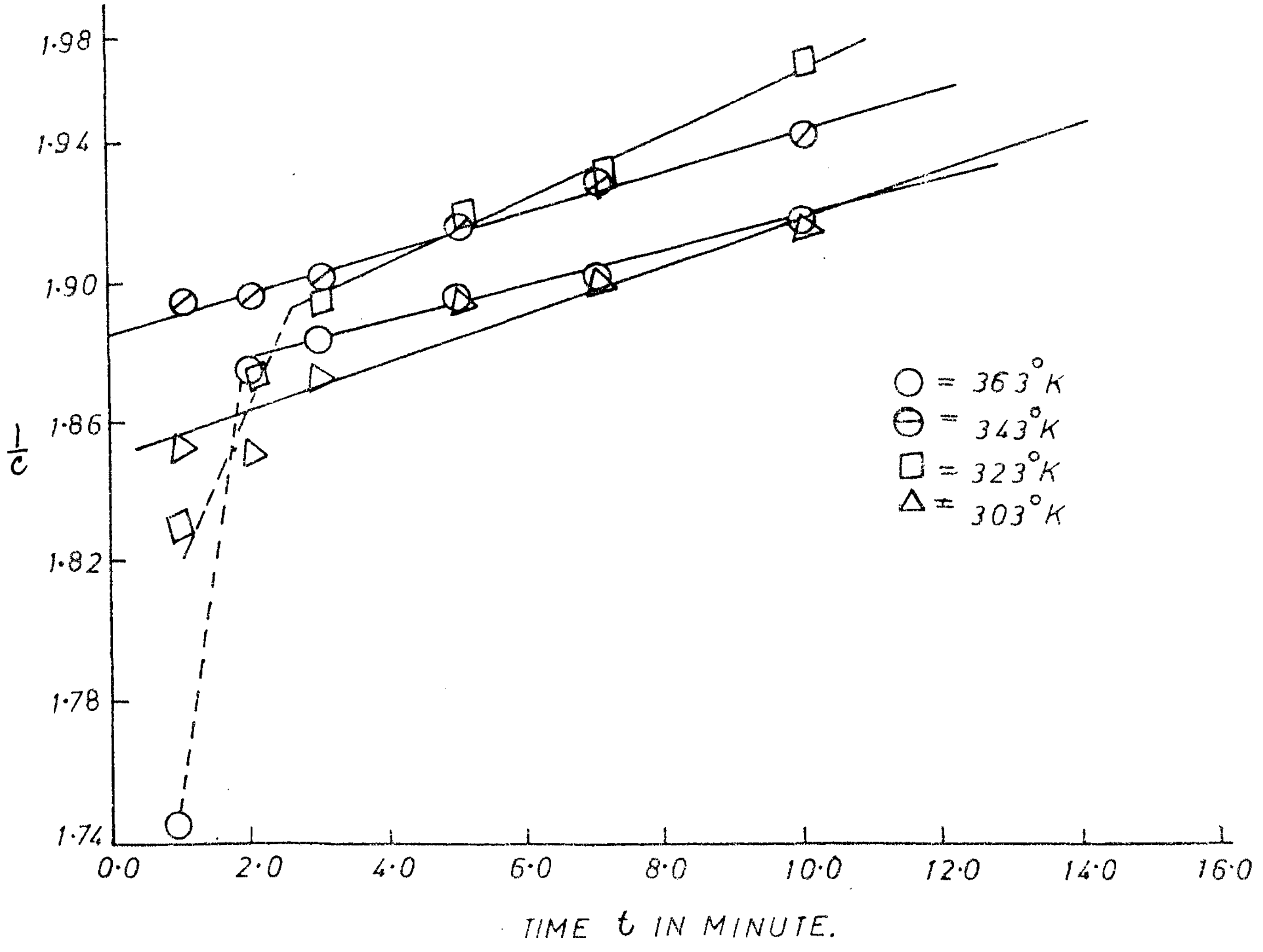


FIGURE:-3,2,2,1,2. SECOND ORDER KINETIC PLOT ($1/c$ vs t) FOR ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON. (STIPPLED CURVE SIGNIFY DEVIATION).

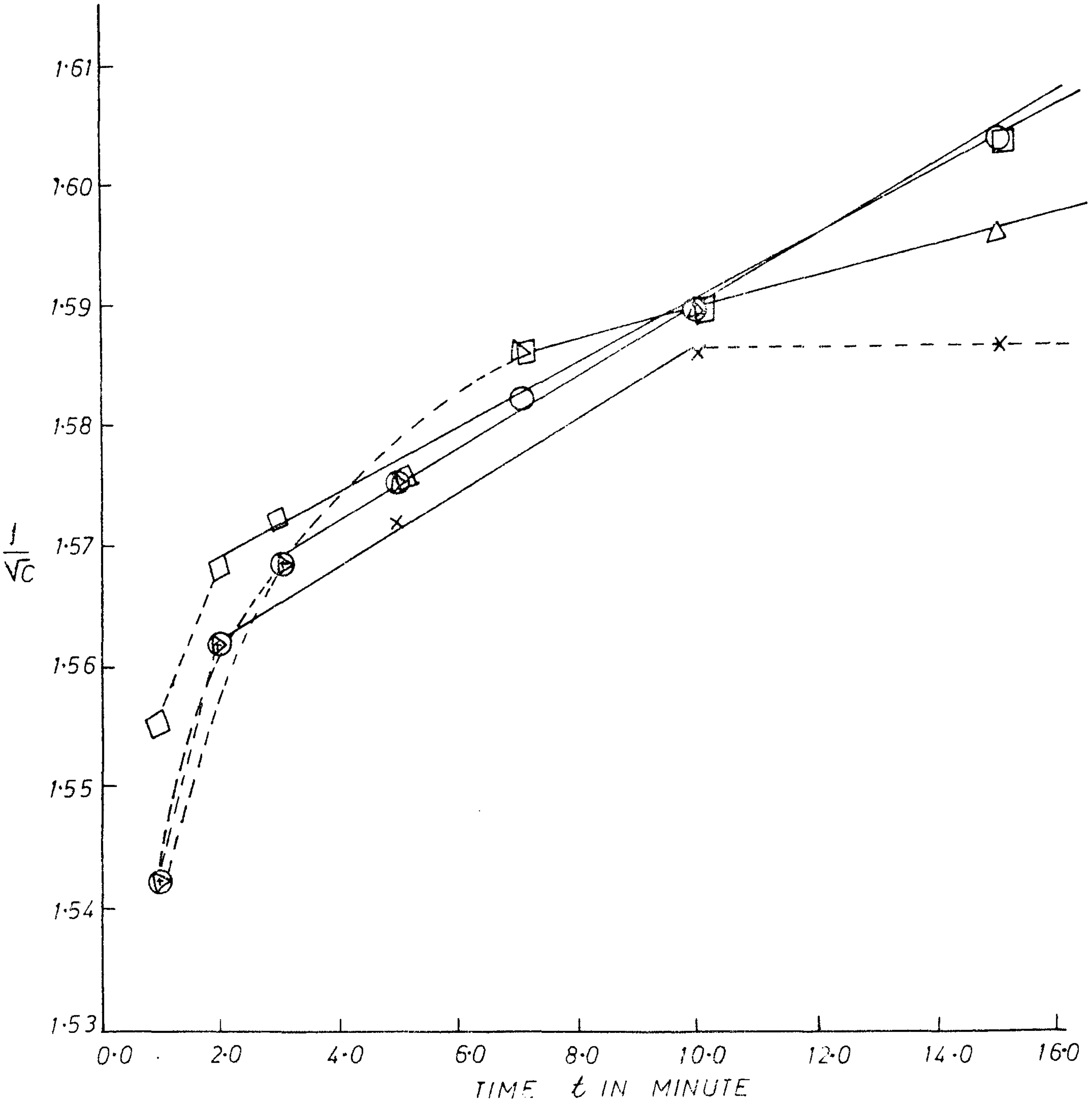


FIGURE:- 3.2.2.2.3. KINETIC PLOT OF ORDER 1·5 ($1/\sqrt{C}$ vs. t) FOR (0·538N) I_2 ADSORPTION ON STEAM ACTIVATED CARBON. STIPPLED CURVES SIGNIFY DEVIATION.

rate constants, we have confined our work to the adsorption of acetic acid and iodine only.

The kinetics of adsorption of acetic acid and iodine on activated carbon (steam activated) have been investigated by measuring the decrease in the concentration of adsorbate(CH_3COOH or I_2) with time within the temperature range 303^oK - 363^oK. The relevant data are recorded in Table 3.2.2.1 and Table 3.2.2.2 (Appendix II). Typical concentration-time plots are shown in Figures 3.2.2.1 and 3.2.2.2 .

For the purpose of finding out the order of reaction, the adsorption of acetic acid or iodine on activated carbon is regarded as chemical reactions between acetic acid and iodine molecule and the surface sites of the adsorbent (activated carbon) and the following graphical methods have been adopted.

(i) log c is plotted against time (Figs. 3.2.2.1.1 and 3.2.2.2.1) to test whether the adsorption is a reaction of first order with respect to either CH_3COOH or I_2.
(ii) 1/c is plotted against time (Figs. 3.2.2.1.2 and 3.2.2.2.2) in order to test whether adsorption of CH_3COOH or I_2 on carbon followed a second order rate equation with respect to CH_3COOH or I_2.

(iii) $1/\sqrt{c}$ vs t is plotted (Figs. 3.2.2.1.3 and 3.2.2.2.3) to test whether the adsorption of iodine or acetic acid is a reaction of 1.5 order with respect to CH_3COOH or I_2.

It is seen from the Figures 3.2.2.1.1 , 3.2.2.1.2 , 3.2.2.1.3 , 3.2.2.2.1 , 3.2.2.2.2 , 3.2.2.2.3 that the points do not

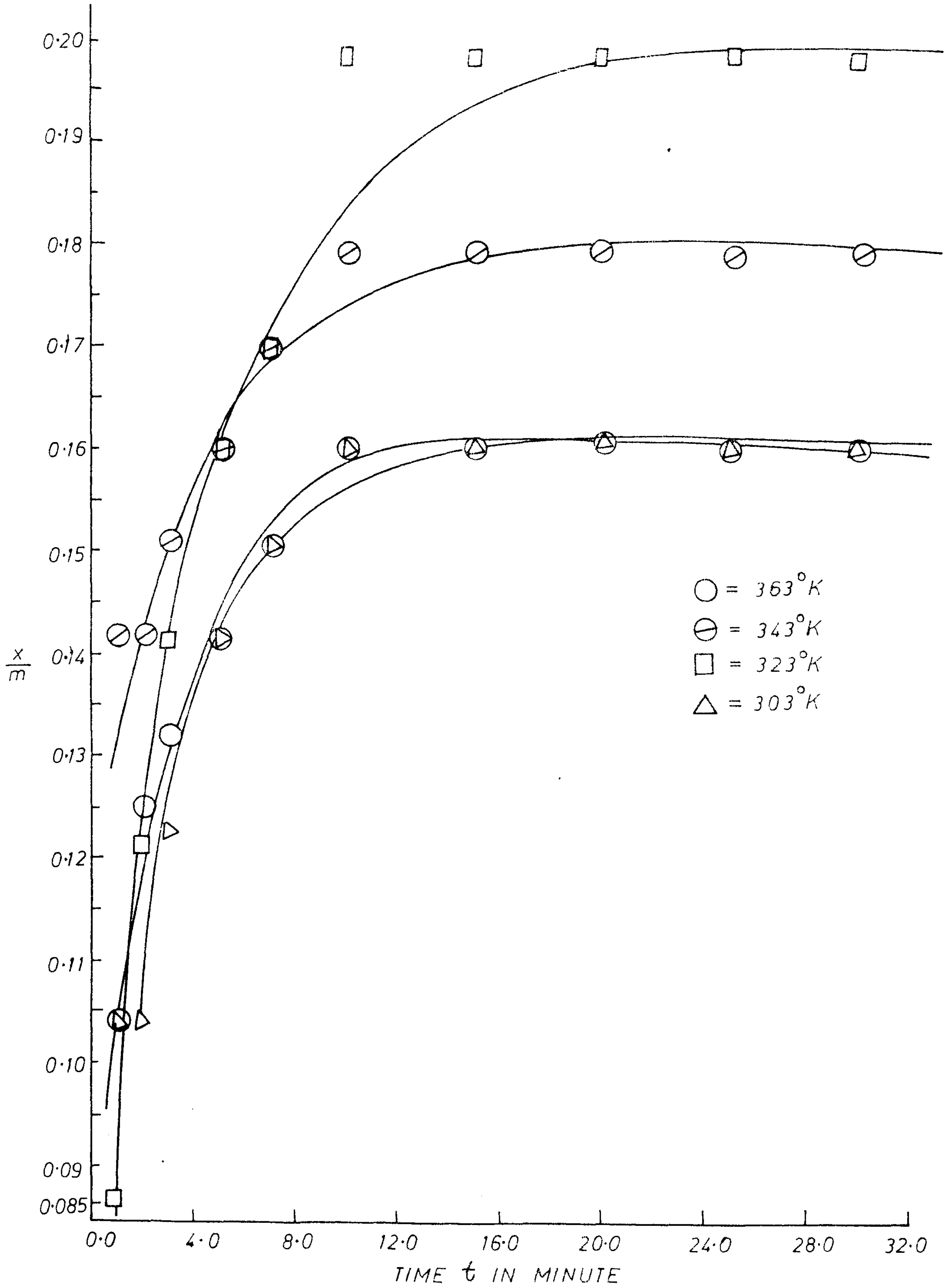


FIGURE:- 3.2.3.1. LISZI (x/m vs t) PLOT FOR 0·575 CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

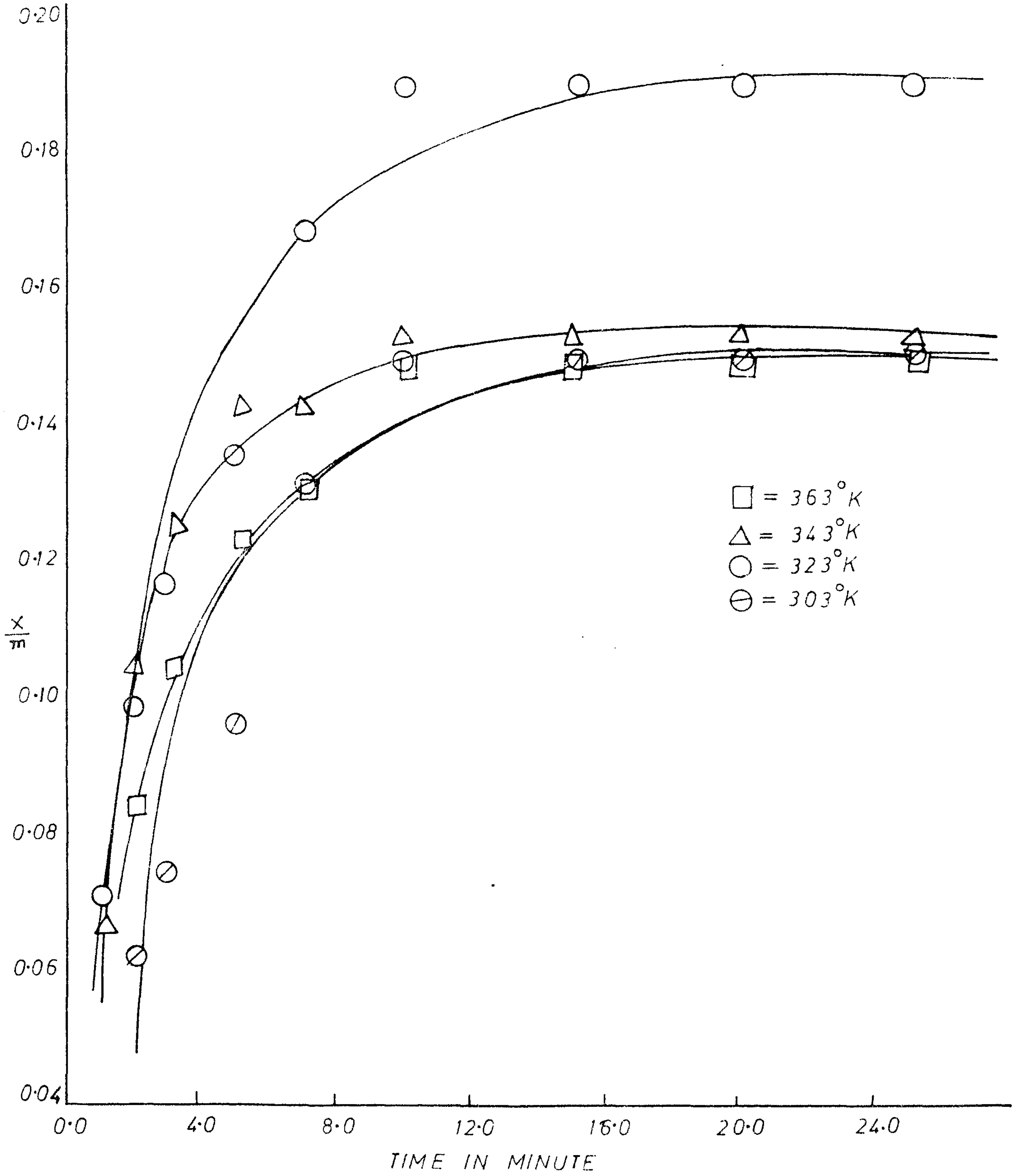


FIGURE:- 3,2,3,2, LISZI PLOT (x/m vs t) FOR 0·446N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

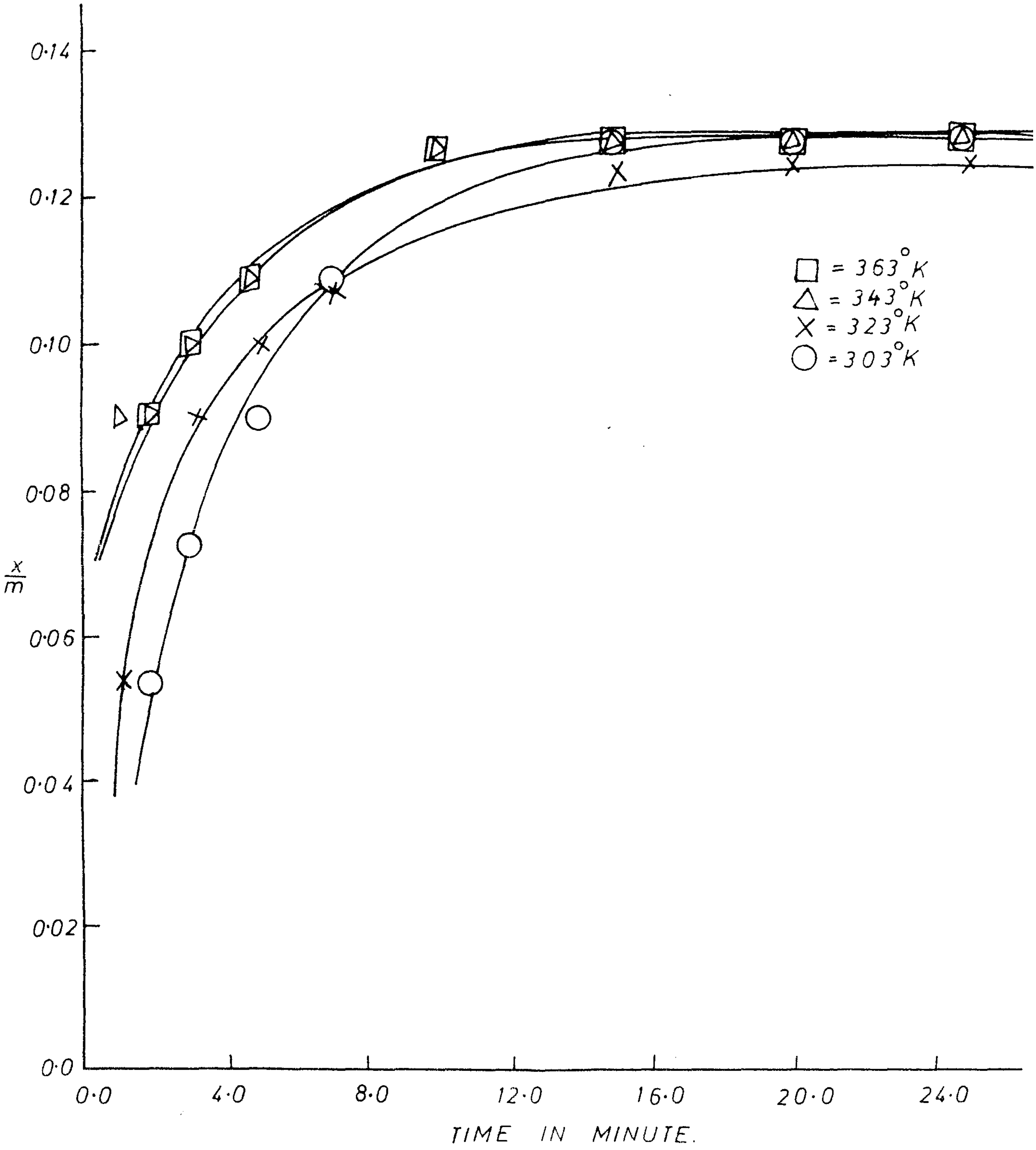


FIGURE:-3.2.3.3. LISZI PLOT (x/m vs t) FOR 0·358 N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

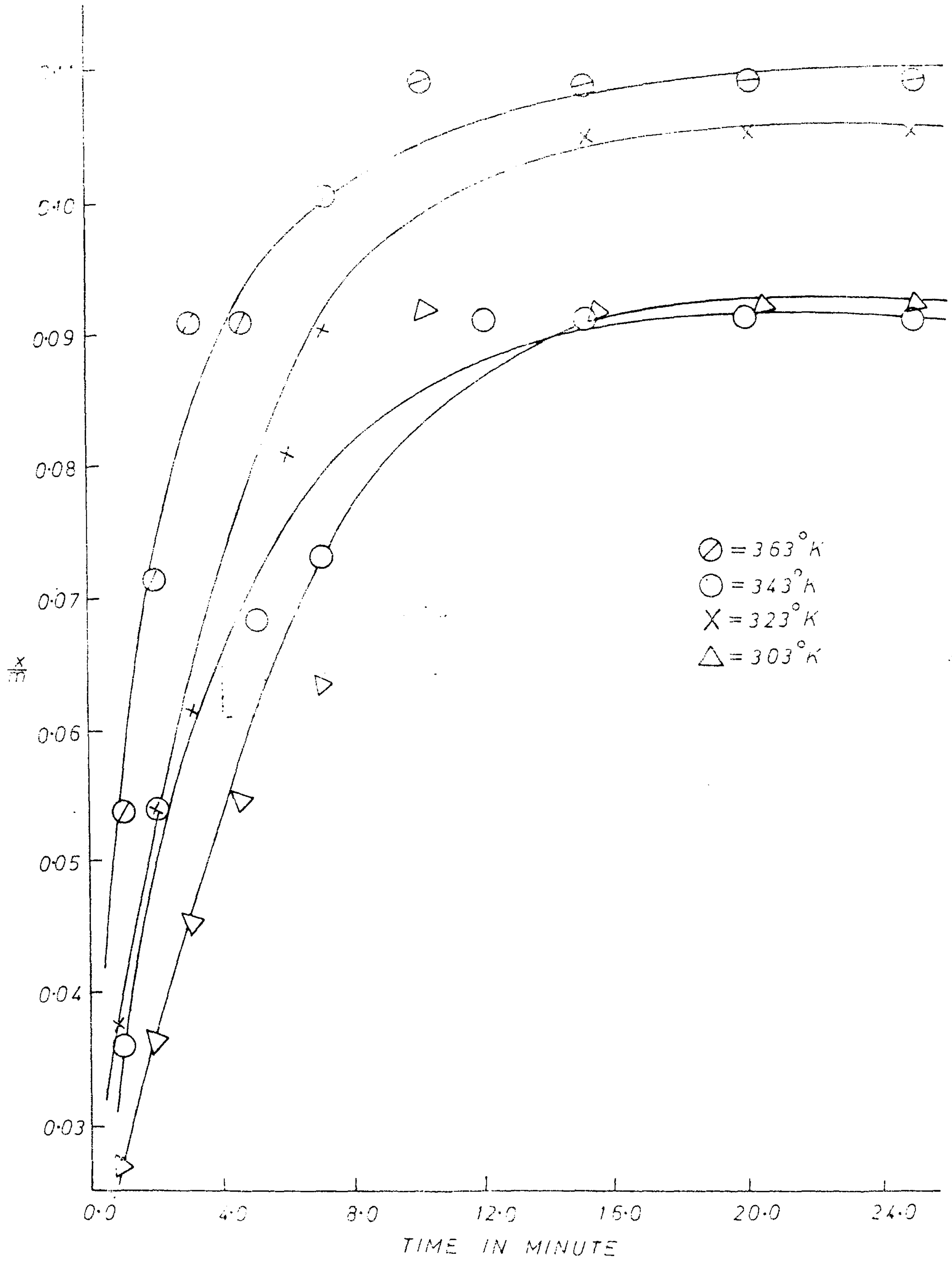


FIGURE:- 3.2.3.4. LISZI PLOT(x/m vs t) FOR 0·243N CH_3COOH ADSORPTION ON ACTIVATED CARBON (STEAM).

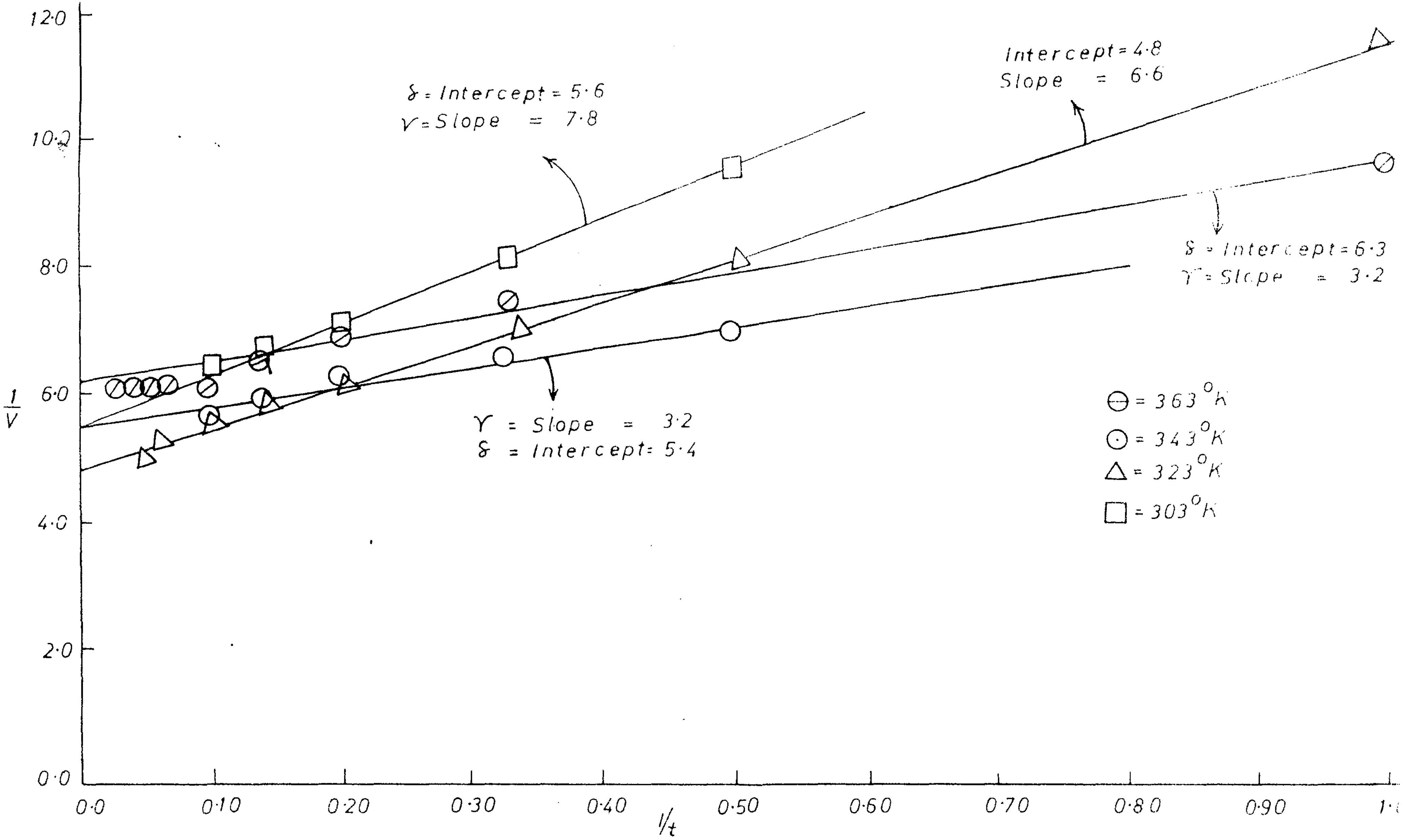


FIGURE:- 3.2.3.5. LISZI PLOT($1/V$ vs $1/t$) FOR 0·575N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

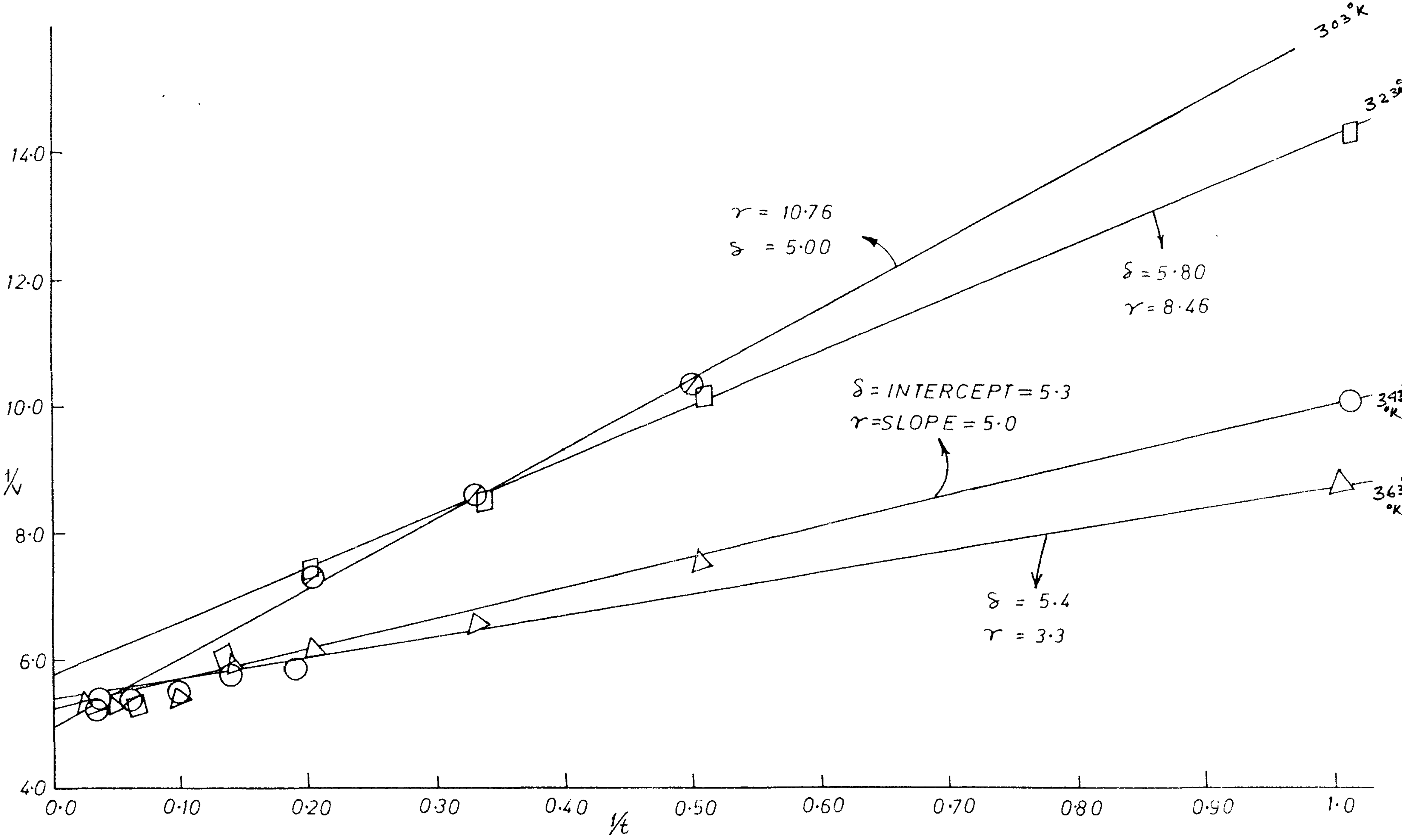


FIGURE:- 3.2.3.6. LISZI PLOT(1/v vs 1/t) FOR 0·446N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON

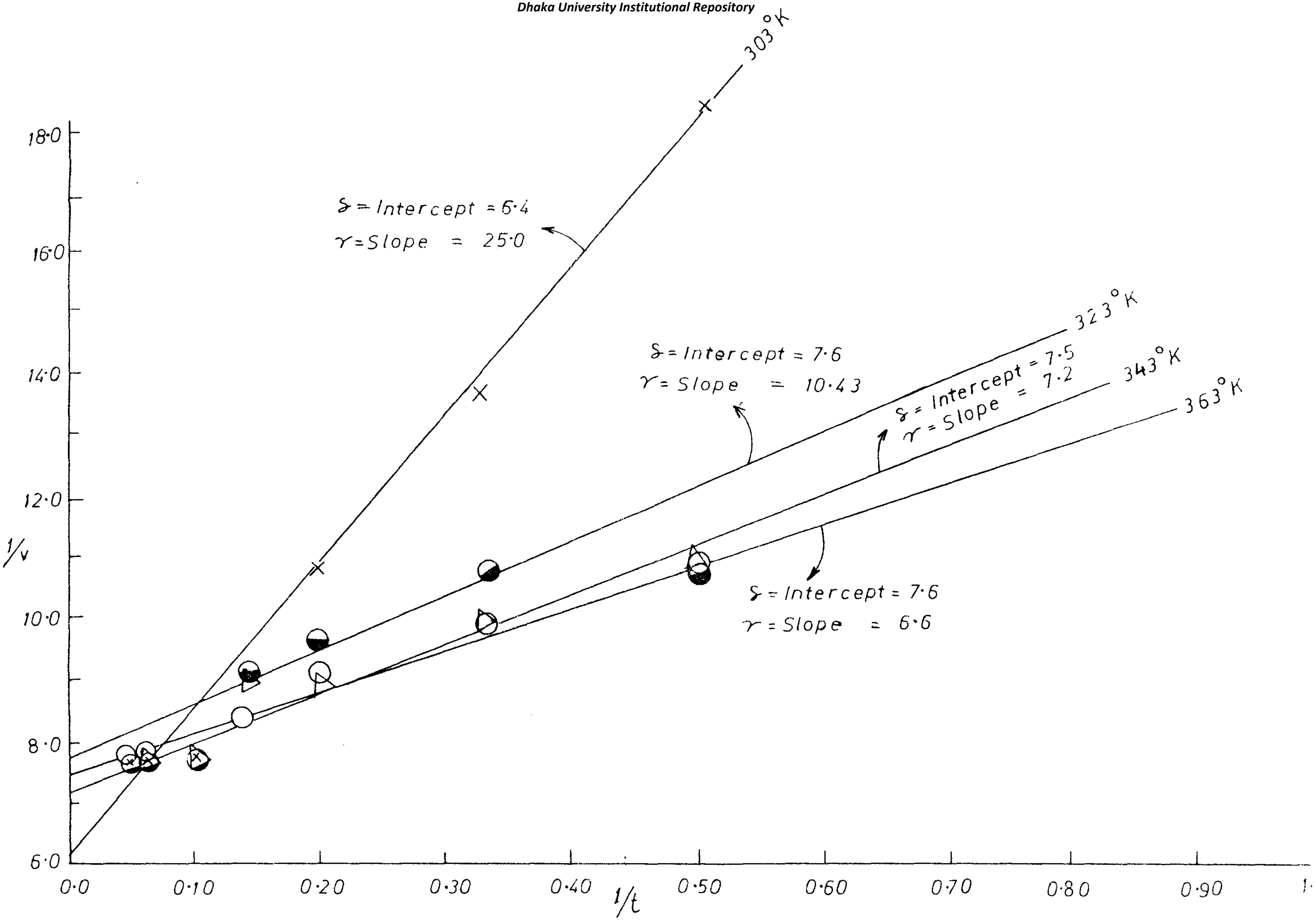


FIGURE:- 3.2.3.7. LISZI PLOT(1/v vs 1/t) FOR 0·358 N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBO

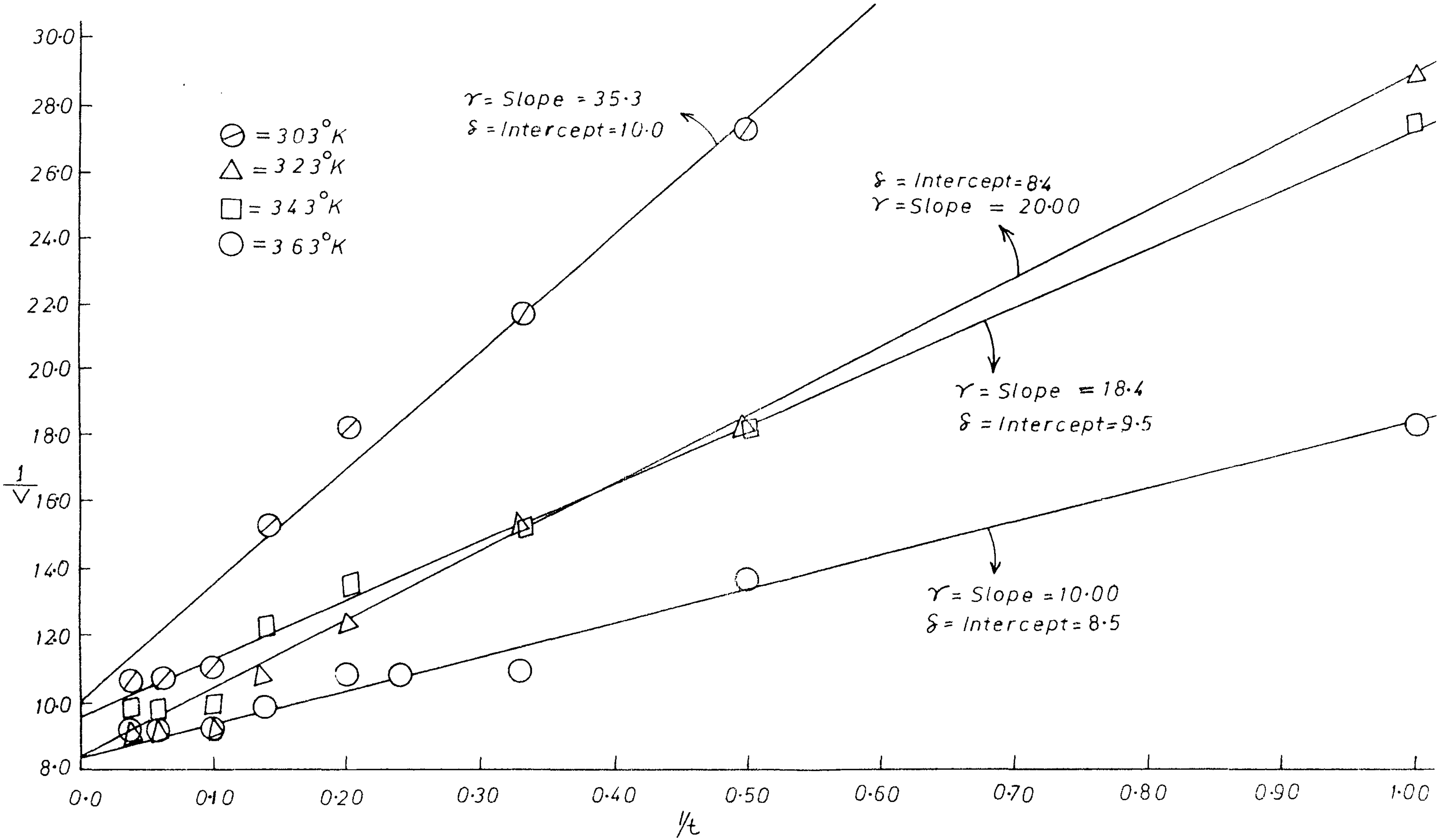


FIGURE :- 3.2.3.8. LISZI PLOT ($\frac{1}{V}$ vs $1/t$) FOR 0·243 N ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON.

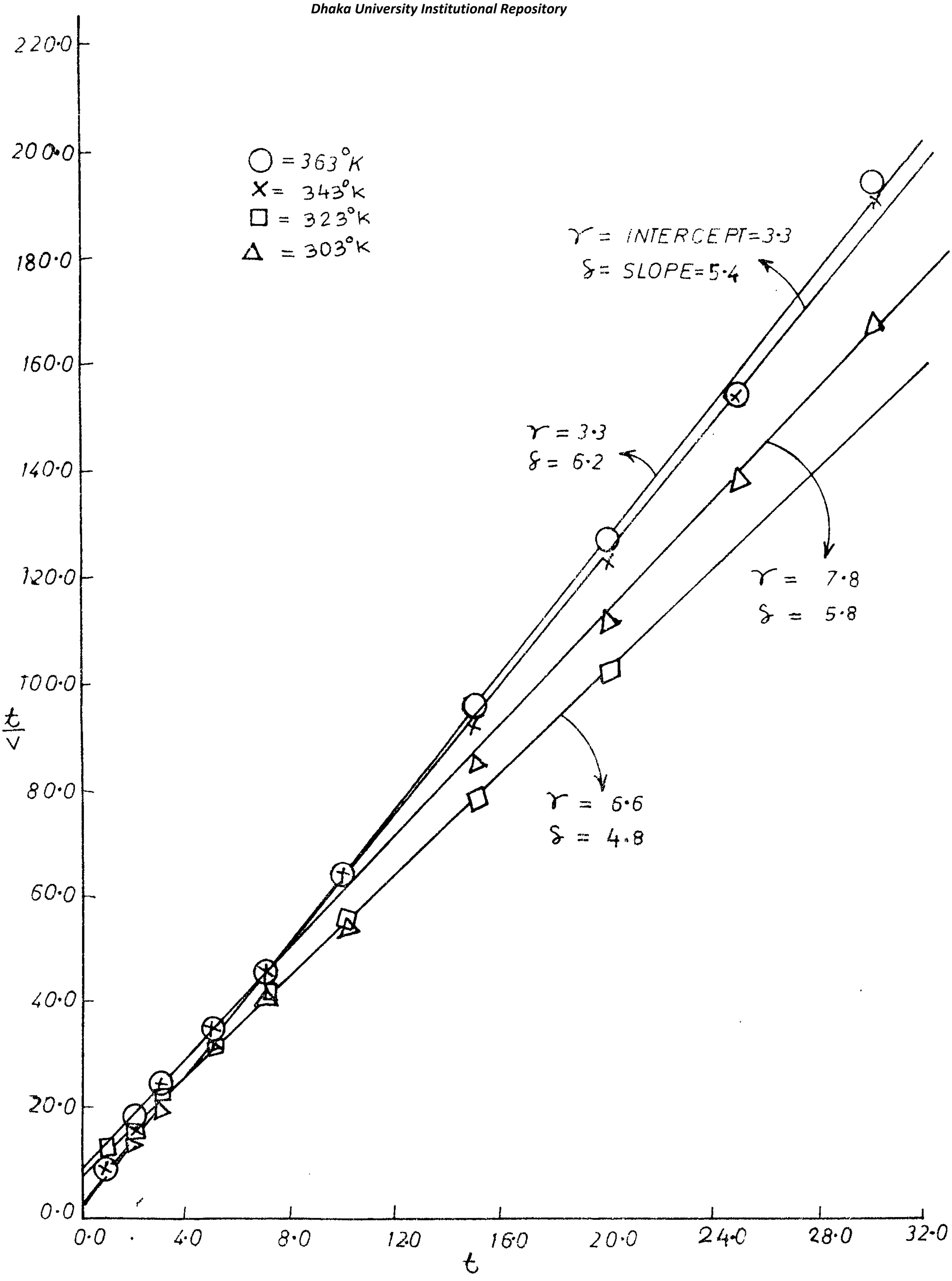


FIGURE:- 3,2,3,9. LISZI PLOT (t/v vs t) FOR ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON.

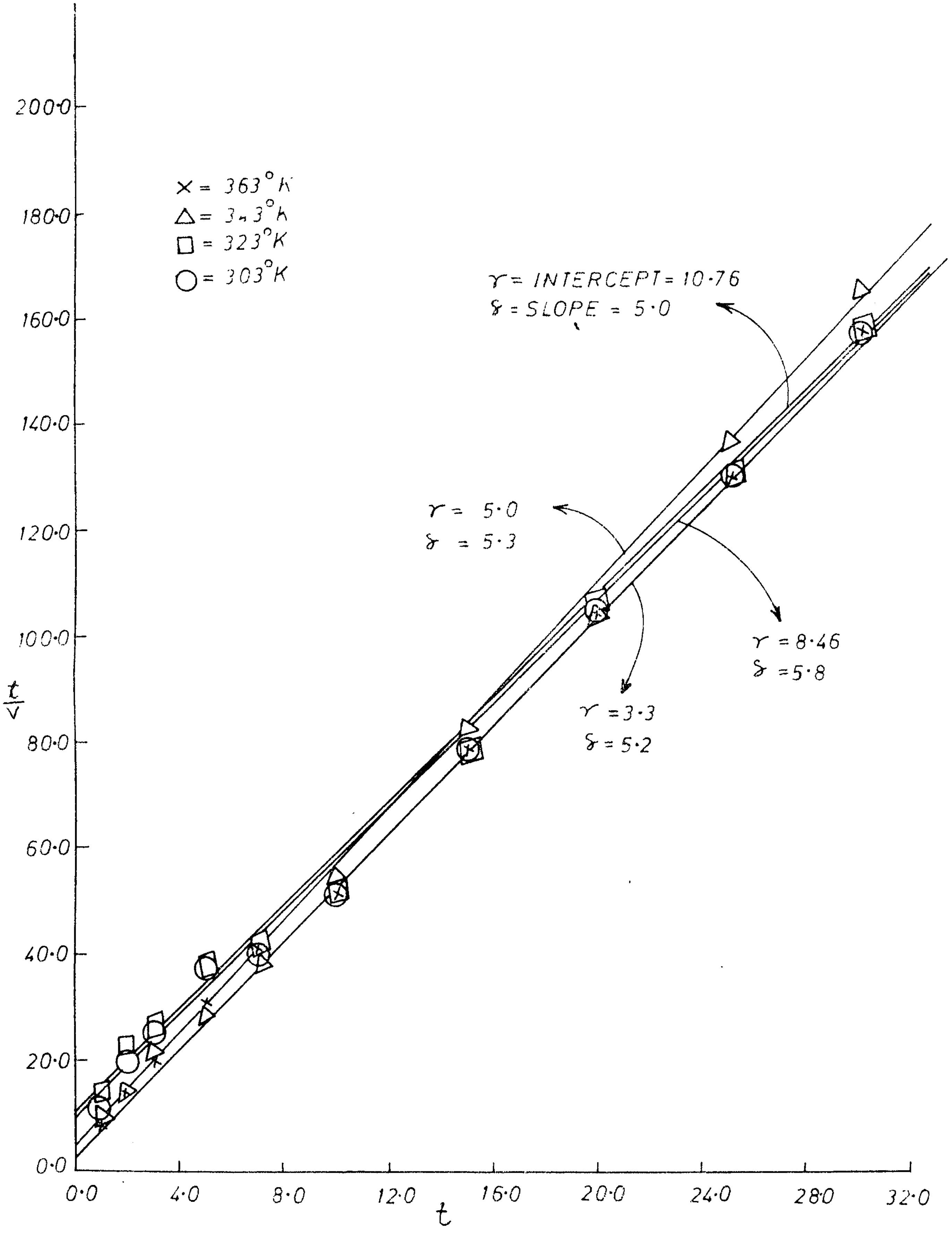


FIGURE:- 3.2.3.10 LISZI PLOT (t/v vs t) FOR 0·446N ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON.

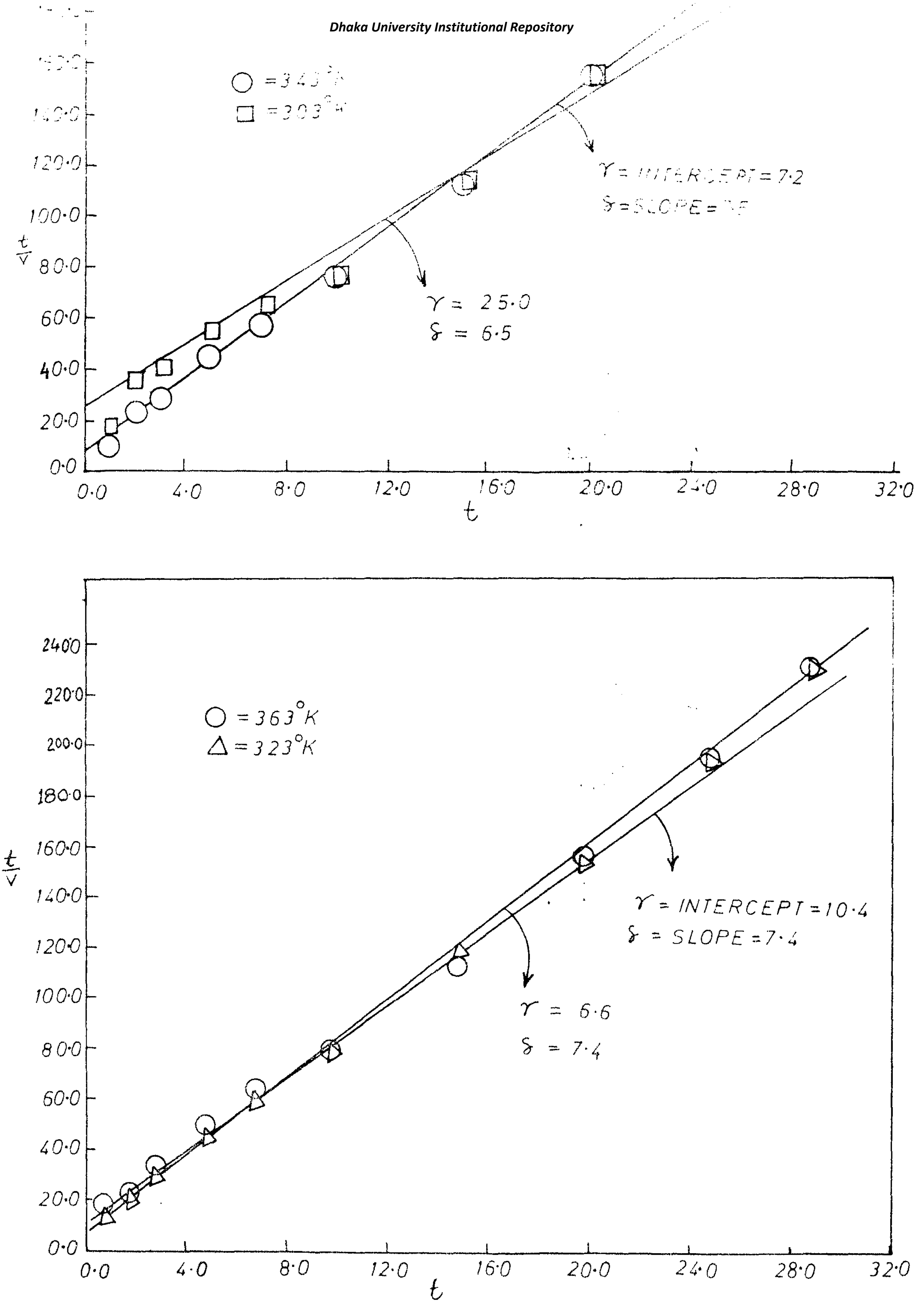


FIGURE:- 3.2.3.11. LISZI PLOT ($\frac{t}{v}$ vs t) FOR 0·358N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

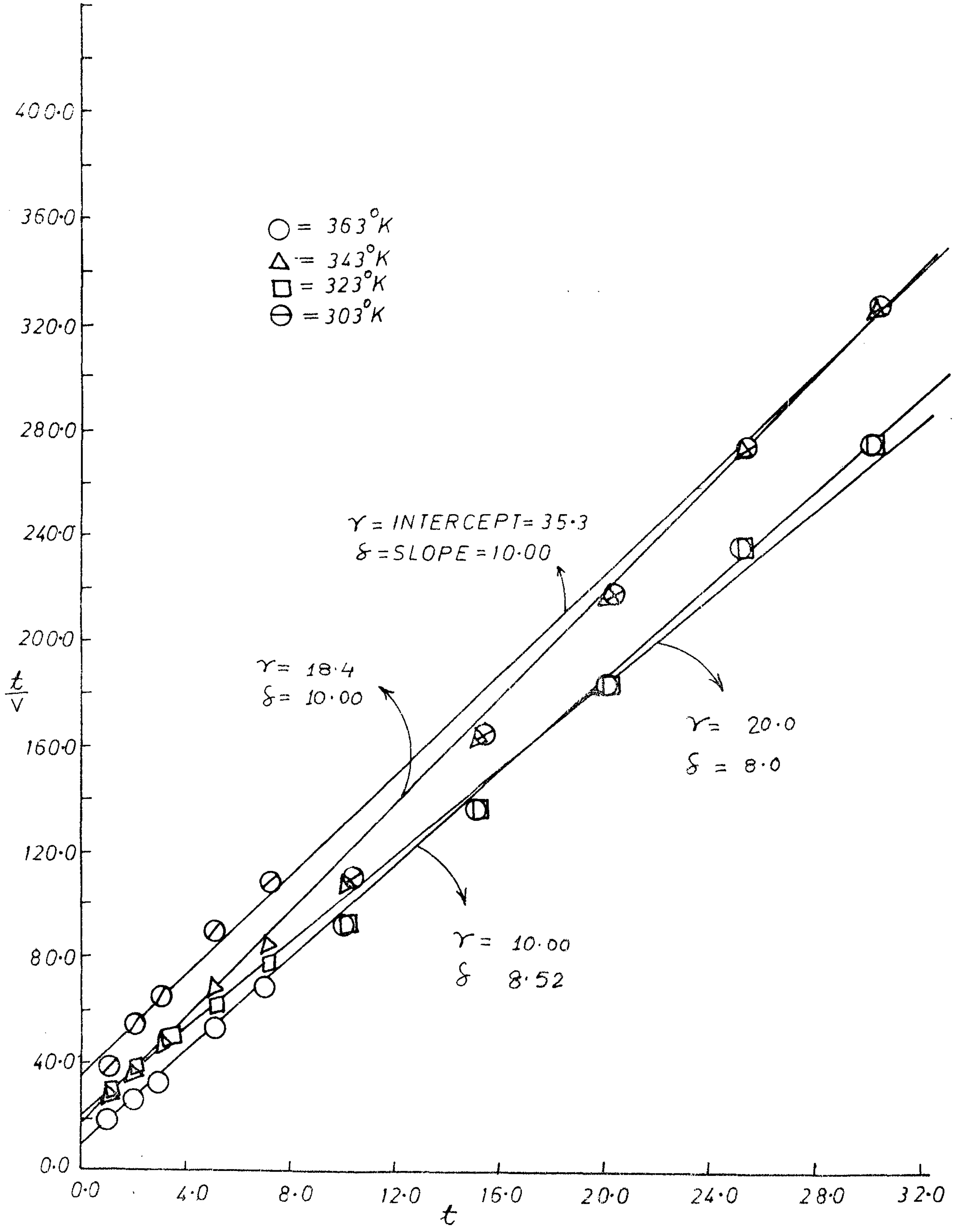


FIGURE:- 3.2.3.12. LISZI PLOT (t/V vs t) FOR 0·243N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

fall on straight lines over the whole period of time in which the adsorption of CH_3COOH or I_2 has taken place. It is clear therefrom that the kinetics of adsorption of I_2 and acetic acid cannot be described by conventional rate equations. This is not unexpected because the reaction rate is dependent on both the concentration and the activities of the surface sites in addition to the concentration of the adsorbates. As adsorption proceeds, the concentration of surface site decreases.

3.2.3 ACETIC ACID ADSORPTION: As the conventional rate equation cannot describe the adsorption kinetics we applied Liszi equation (1.17). Adsorptions of acetic acid solution on steam activated carbon have been investigated at 363^oK, 343^oK, 323^oK and 303^oK at the atmospheric pressure. The kinetic data are presented in Tables 3.2.3.1 (a-d), 3.2.3.2 (a-d), 3.2.3.3 (a - d), 3.2.3.4 (a - d) (Appendix II). Typical v-t plots are shown in Figs. 3.2.3.1, 3.2.3.2, 3.2.3.3 and 3.2.3.4 . Other Liszi plots, i.e. 1/v vs 1/t and t/v vs t are shown in Figures 3.2.3.5, 3.2.3.6, 3.2.3.7, 3.2.3.8 and 3.2.3.9 , 3.2.3.10 , 3.2.3.11, 3.2.3.12 respectively. From the values of γ and δ as have been obtained from these plots, the order of adsorption and the value of the rate constants are found out by least square analysis and presented in Tables 3.2.3.5 , 3.2.3.6 and 3.2.3.7 (Appendix II). The plots of log $\frac{1}{\gamma}$ vs log c are shown in Fig. 3.2.3.13. Values for initial rate and limiting adsorption as have been obtained from the γ and δ values are recorded in Table 3.2.3.5 . Arrhenious plot to determine the activation energy is shown in Fig. 3.2.3.14. The value of activation energy 'Ea' is calculated from the slope of the log k vs 1/T plot which is found

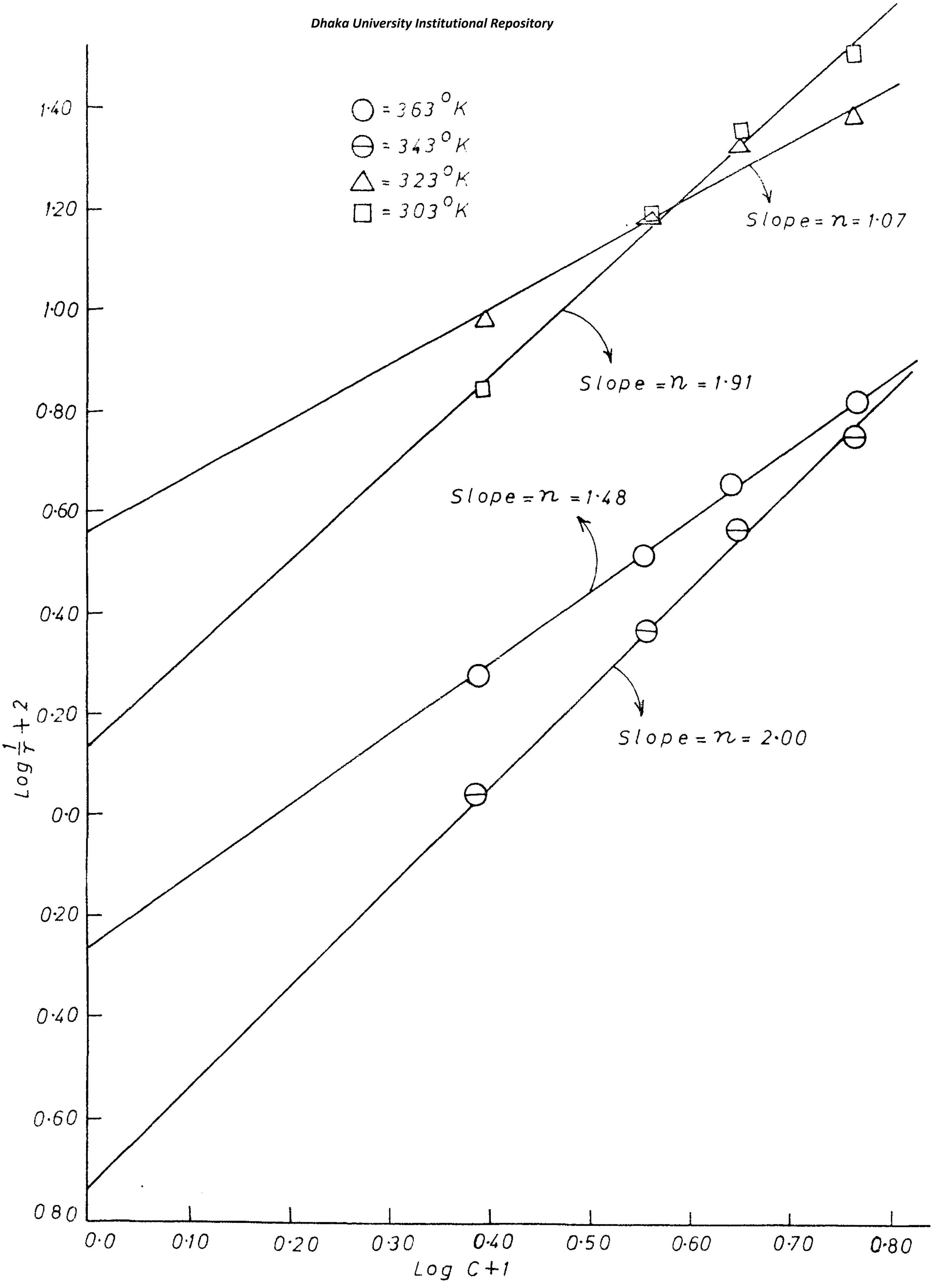


FIGURE:- 3.2.3.13. ORDER PLOT (Log $\frac{1}{r}$ vs Log C) FOR ACETIC ACID ADSORPTION ON STEAM ACTIVATED CARBON.

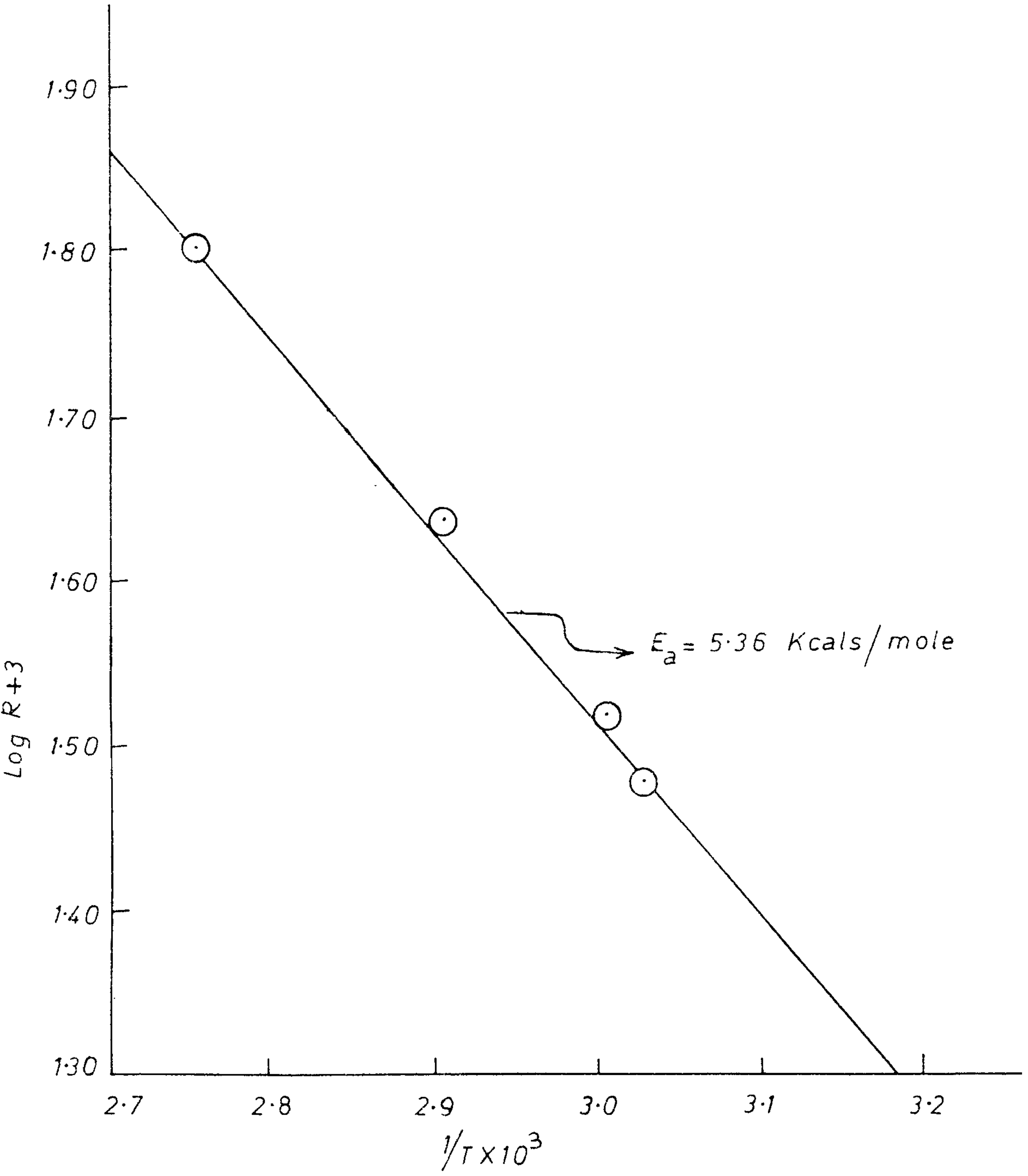


FIGURE:- 3.2.3.14. ARRHENIUS PLOT (Log k vs 1/T) FOR CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON out by the least square analysis and presented in Table 3.2.3.7 (Appendix II).

It is seen from the curves (Figs. 3.2.3.1-14) that the adsorption of CH_3COOH on activated carbon obeys the Liszi equation. The value of γ as obtained from the graphs shows that the initial rate increases with increasing temperature as well as increasing the initial concentration of the adsorbate. The activation energy for acetic acid adsorption at the temperature ranges $303^{o}K$ - $363^{o}K$ is 5.36 KCals/mole. The value is quite low and indicates that the process of adsorption of acetic acid on activated carbon is mostly Vander Waals' type of adsorption i.e. physical adsorption which is also reflected by the low value obtained for heat of adsorption. The value of activation energy (Ea) is comparable to the literature value 1.6 KCals/mole and 2.2 KCals/mole for phenol and 2,4-dinitrophenol.

From the value of the order of adsorption at different temperatures, it can be suggested that the process of adsorption of acetic acid on carbon surface does not follow a simple mechanism at all instances. In most instances there might be a transition from first order to a second order mechanism via some intermediate order. Such a change of mechanism may follow different sequences at the low and high temperatures, approximately corresponding to the temperature ranges covered by the two adsorption processes proposed earlier (section 3.1.2.1 Adsorption isobars). The trend is gradual change of order from 1.00 to 2.00 while there is a departure of the first order mechanism at the higher temperature ($343^{o}K$, $363^{o}K$) which may be predominated by a second order process with occasional change over to an intermediate order.

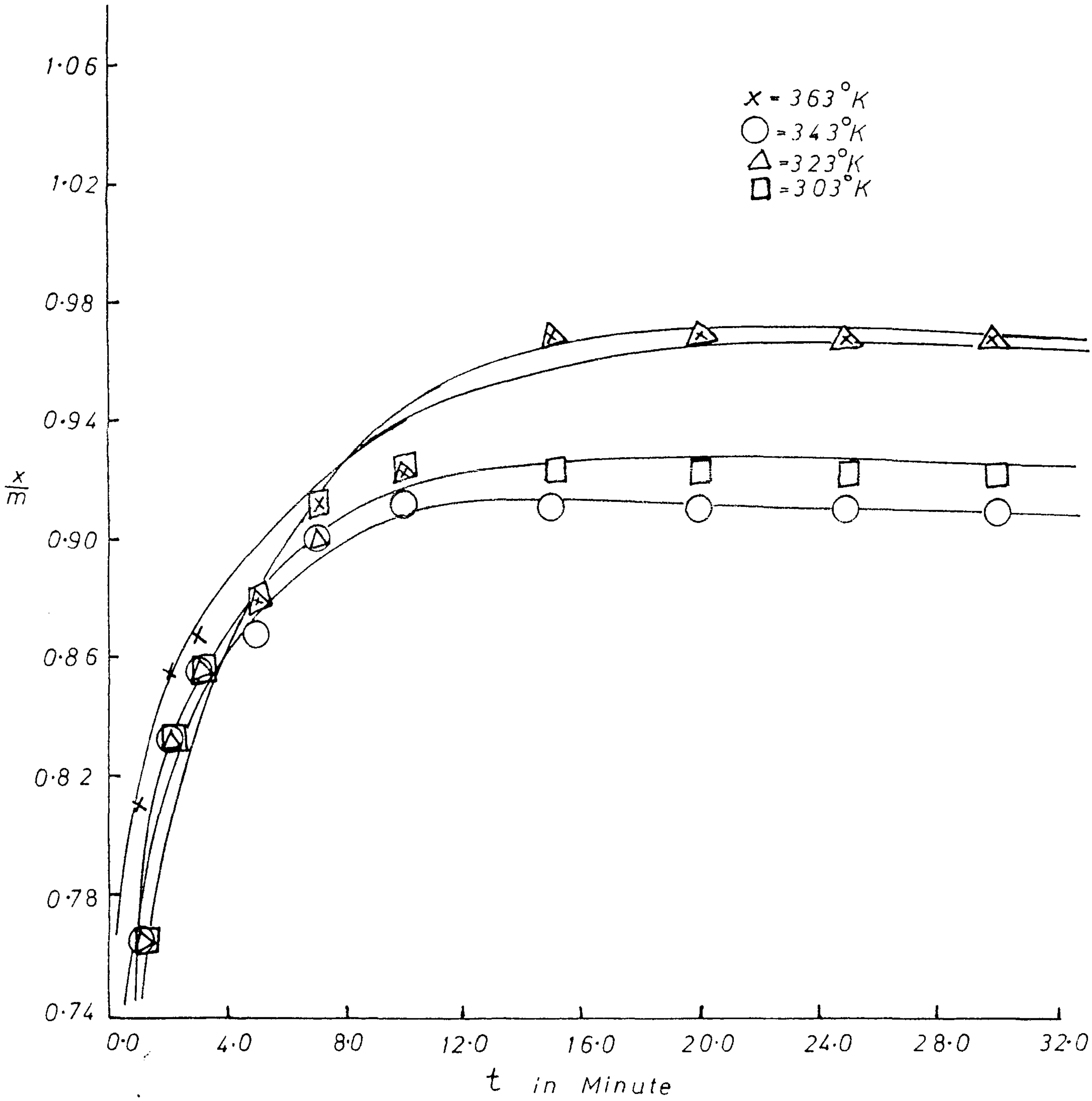


FIGURE:- 3.2.4.1. LISZI PLOT (x/m vs t) FOR 0·538N I_2 ADSORPTION ON ACTIVATED CARBON.

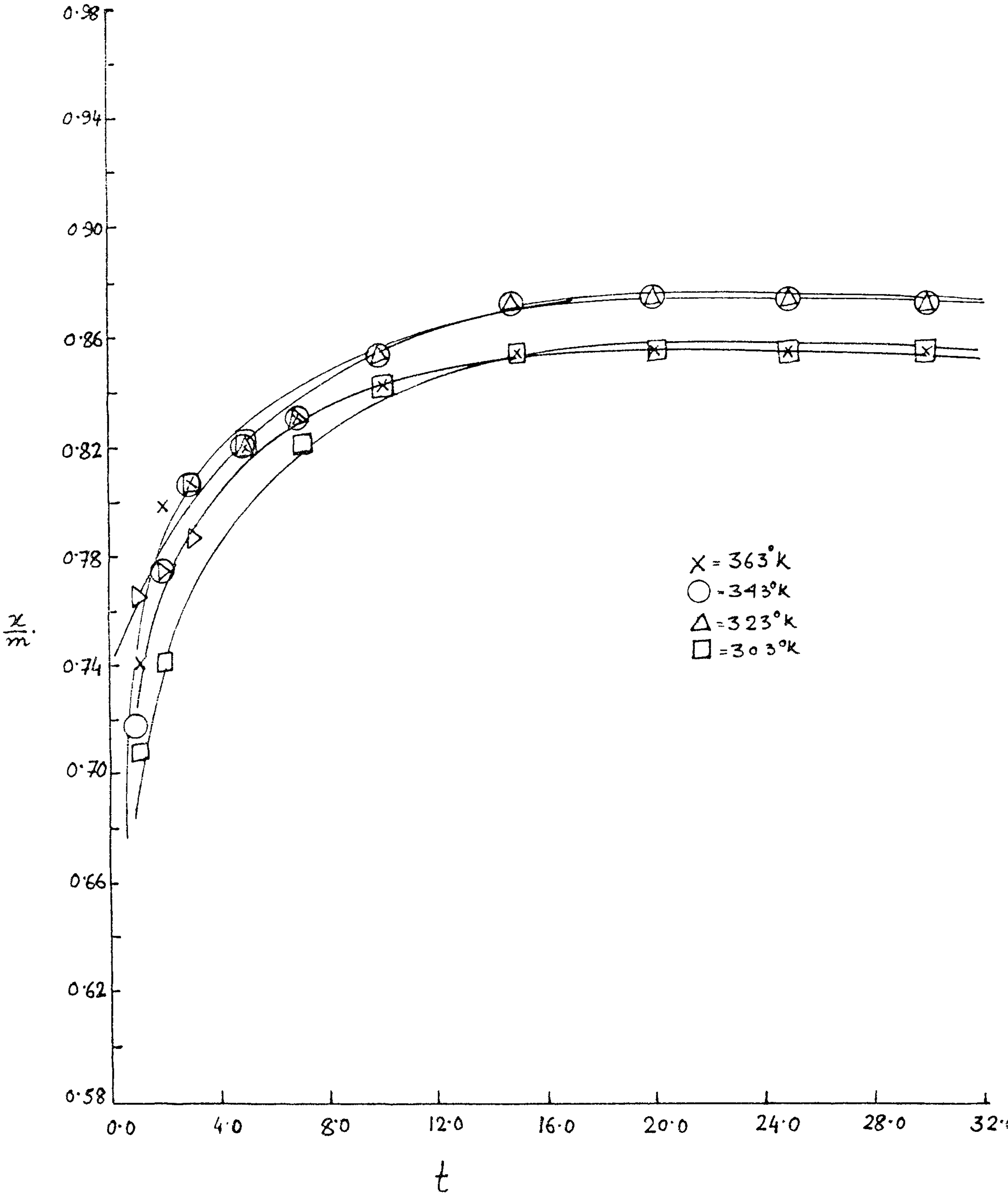


Figure. 3.2.4.2. LIS21 PLOT (x/m vs t) FOR 0·49N I_2 ADSORPTION ON ACTIVATED CARBON.

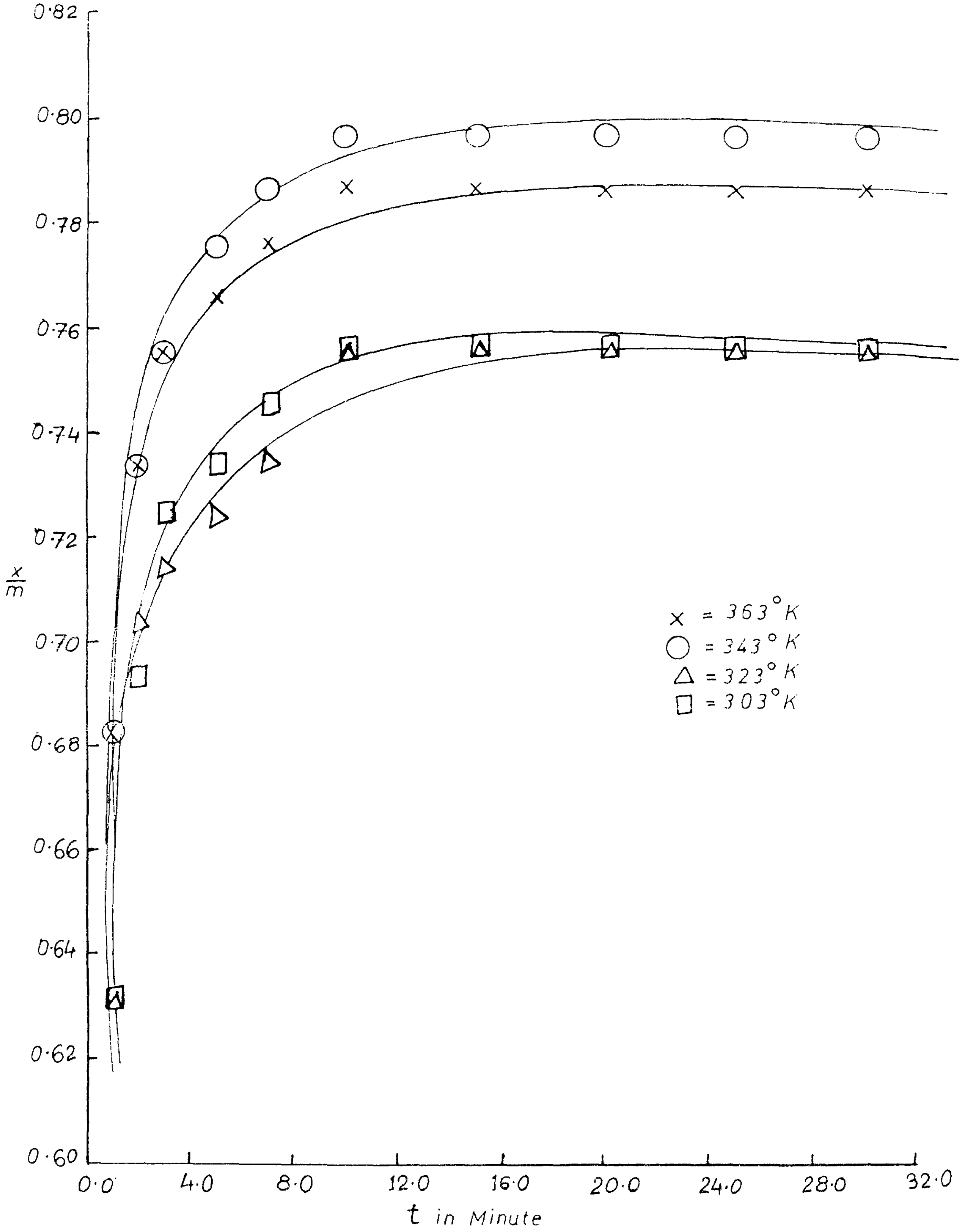


FIGURE:- 3.2.4.3- LISZI PLOT ($\frac{x}{m}$ vs t) FOR 0·36N I_2 ADSORPTION ON ACTIVATED CARBON.

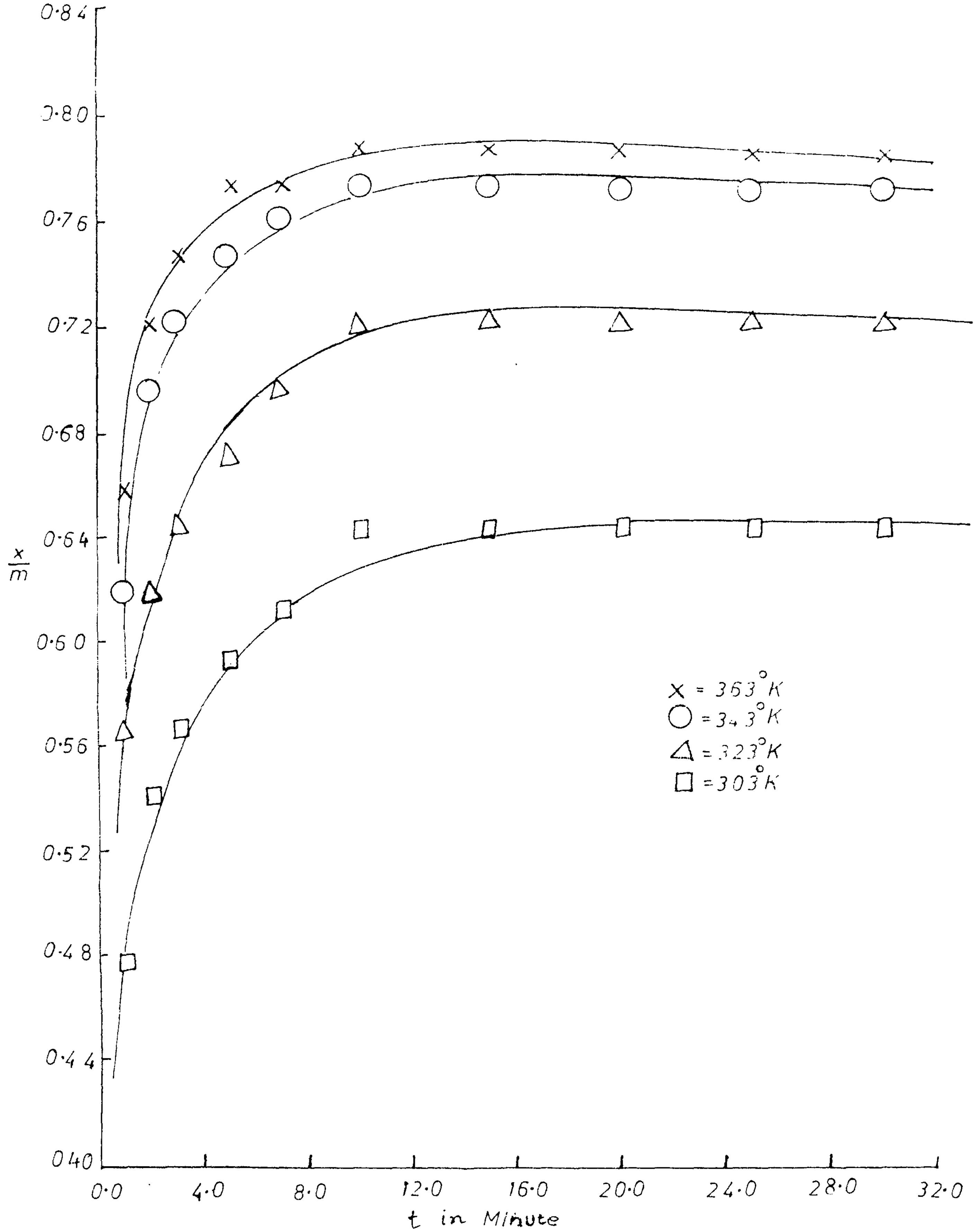


FIGURE:- 3.2.44. LISZI PLOT (x/m vs t) FOR 0·264 N I_2 ADSORPTION ON ACTIVATED CARBON.

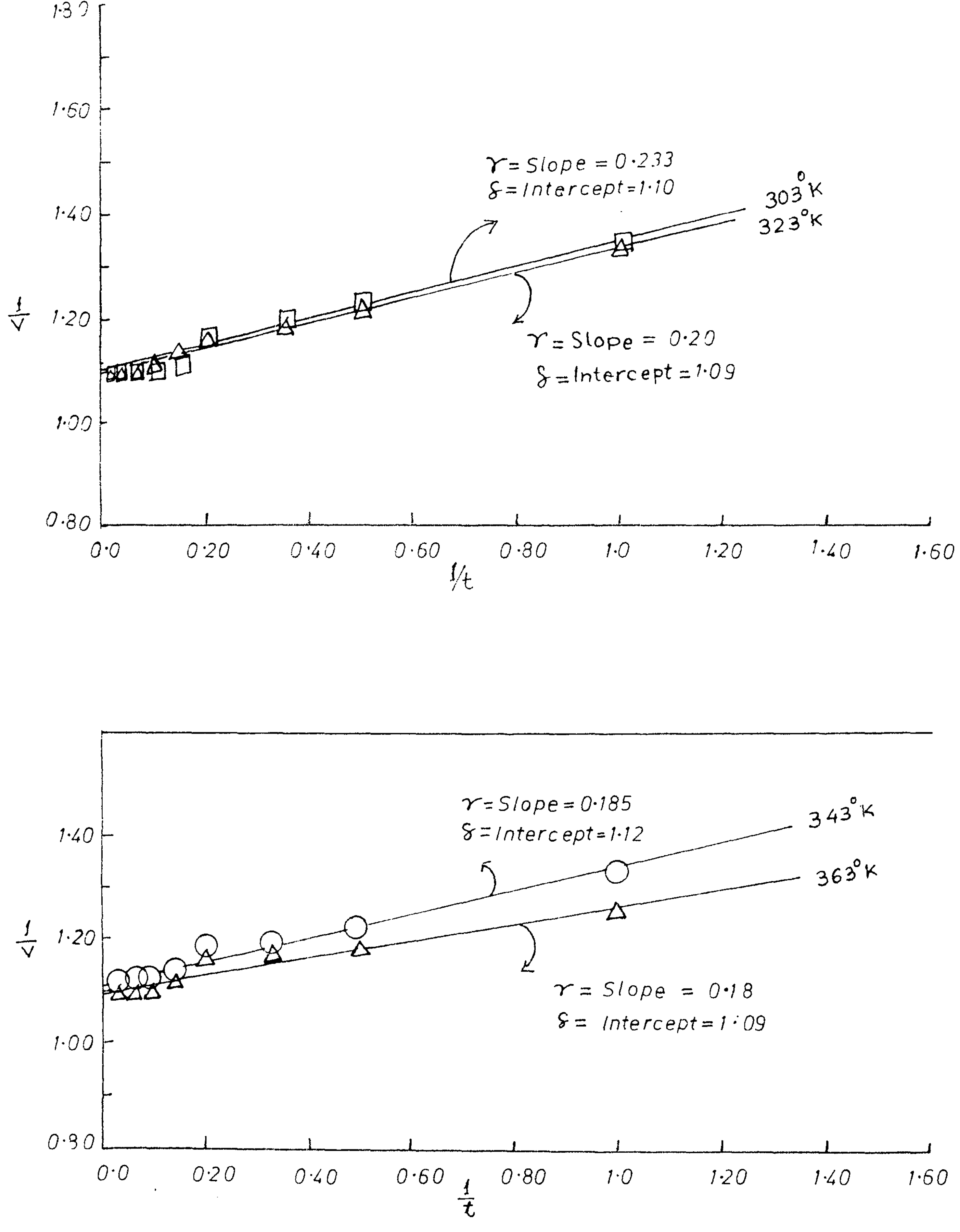


FIGURE:- 3.2.4.5 LISZI PLOT (1/V vs 1/t) FOR 0·538 N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

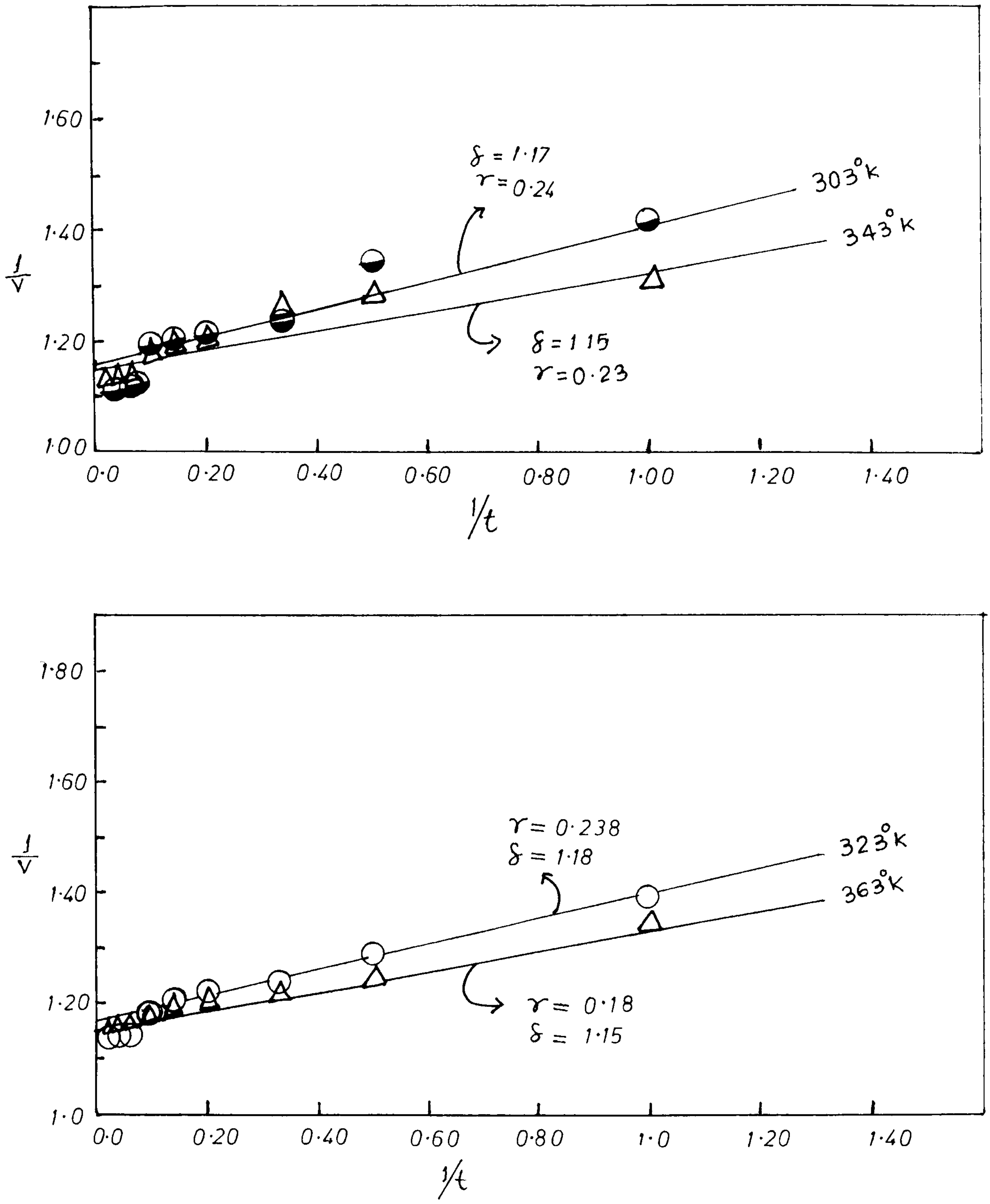


FIGURE:- 3.2.4.6. LISZI PLOT (1/V vs 1/t) FOR 0·49 N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

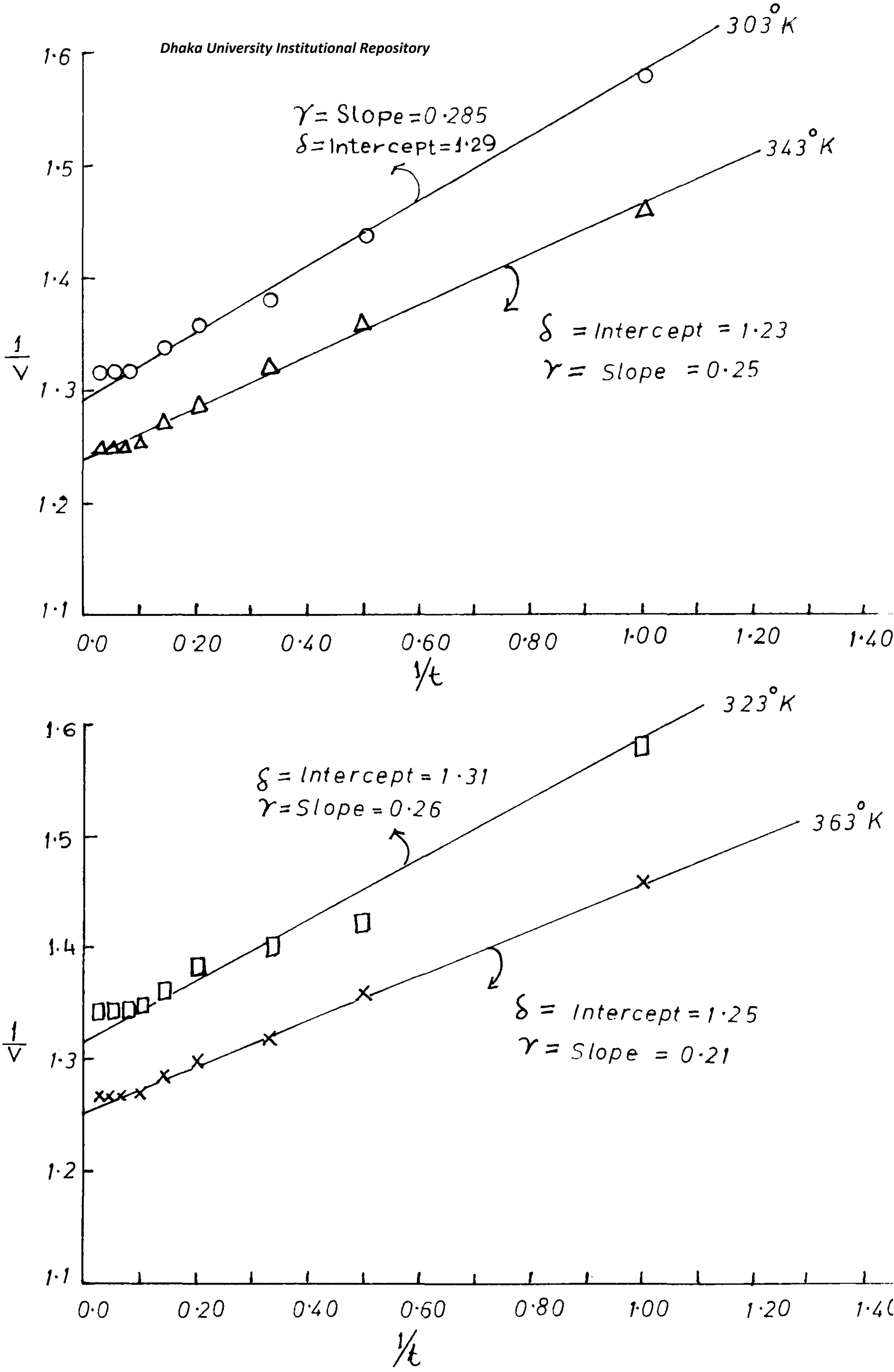


FIGURE:- 3.2.4.7. LISZI PLOT ($1/V$ vs $1/t$) FOR 0·36N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

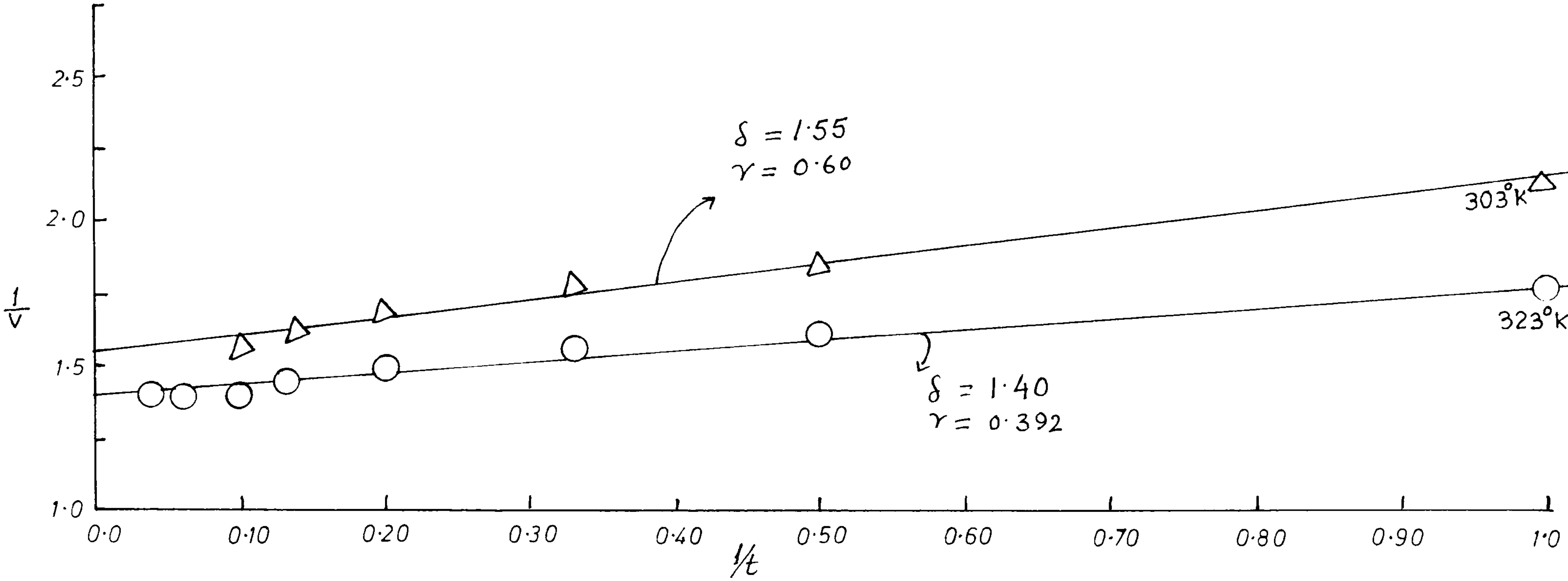


FIGURE:- 3.2.4.8 (a) LISZI PLOT (1/V vs 1/t) FOR 0·264N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

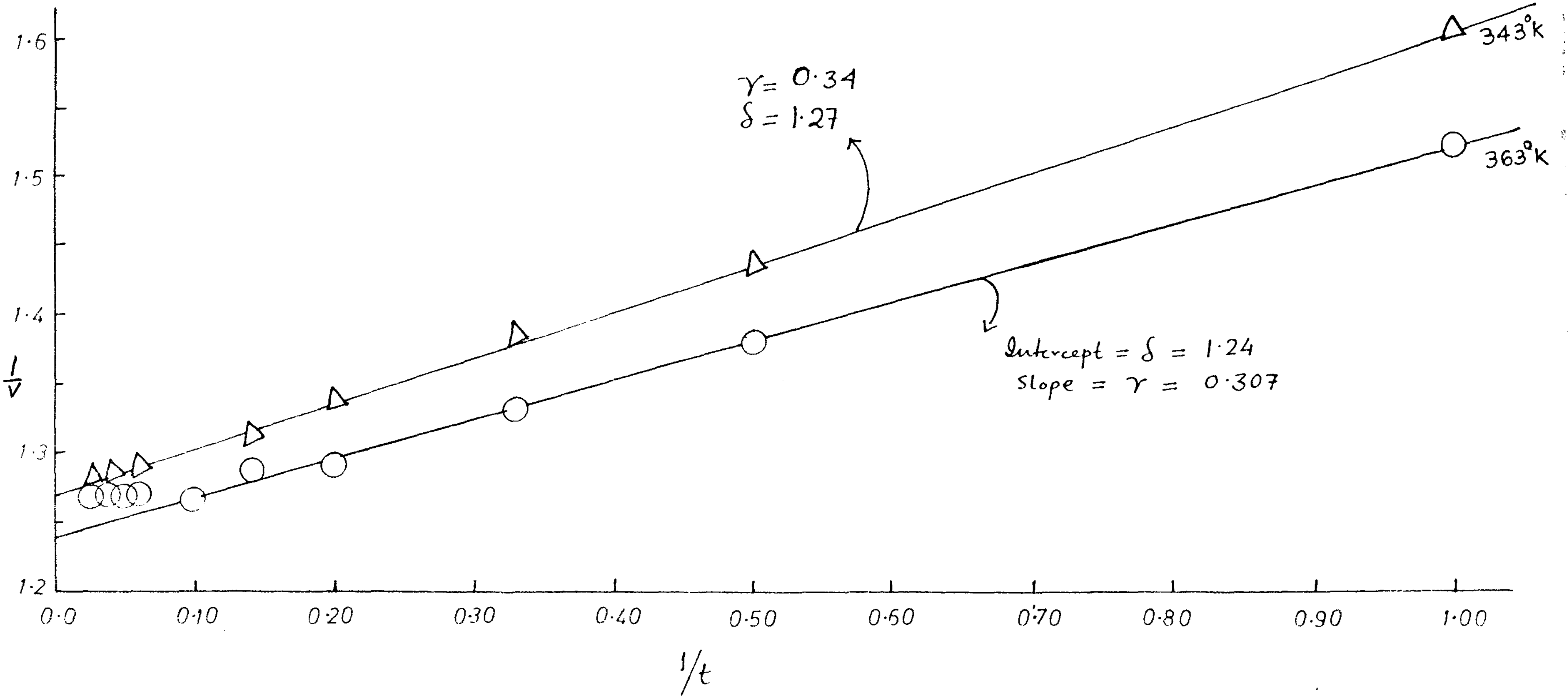


FIGURE:- 3.2.4.8 (b) LISZI PLOT ($1/V$ vs $1/t$) FOR 0·264 N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

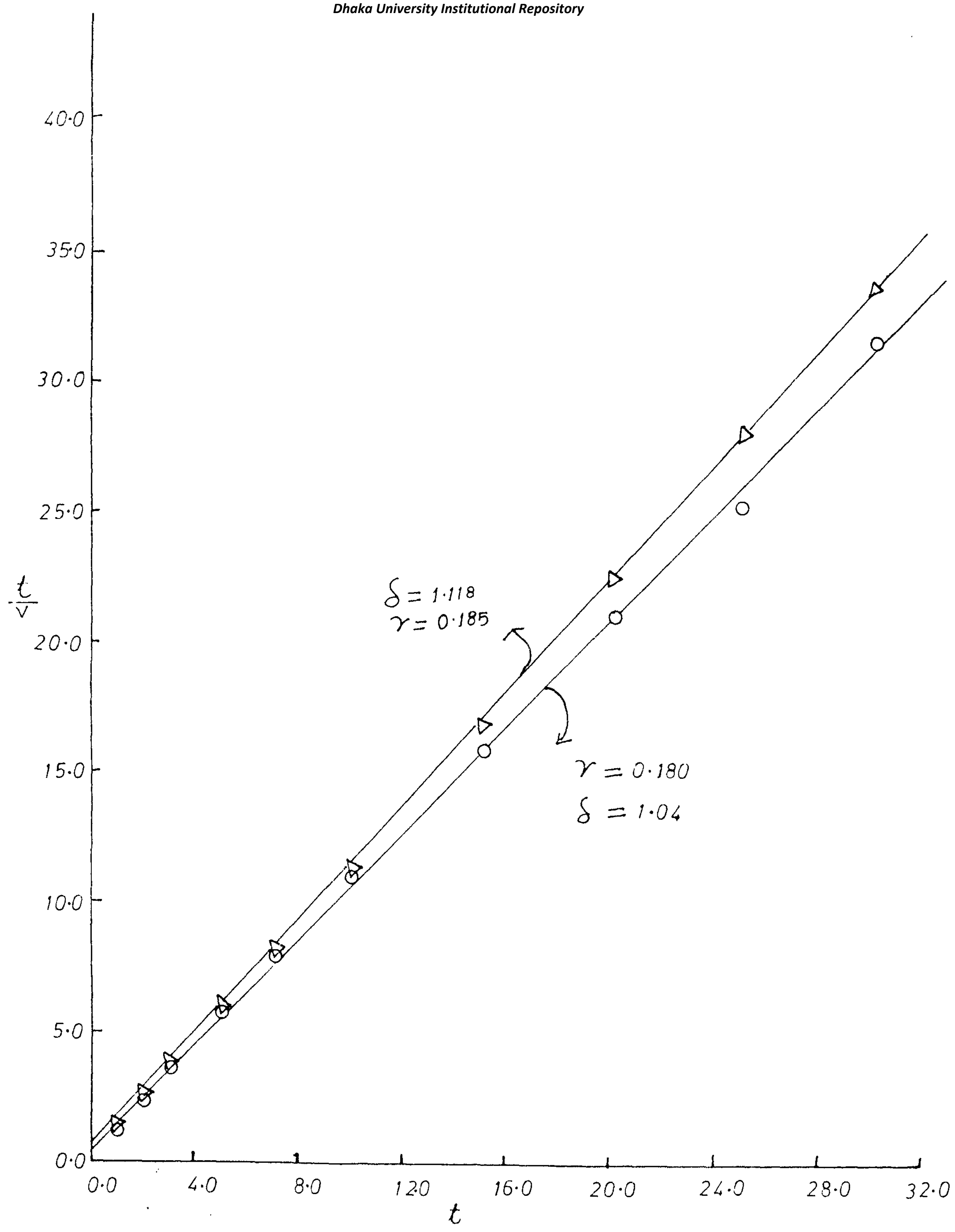


FIGURE:- 3.2.4.9 (a) LISZI PLOT (t/v vs t) FOR 0·538 N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

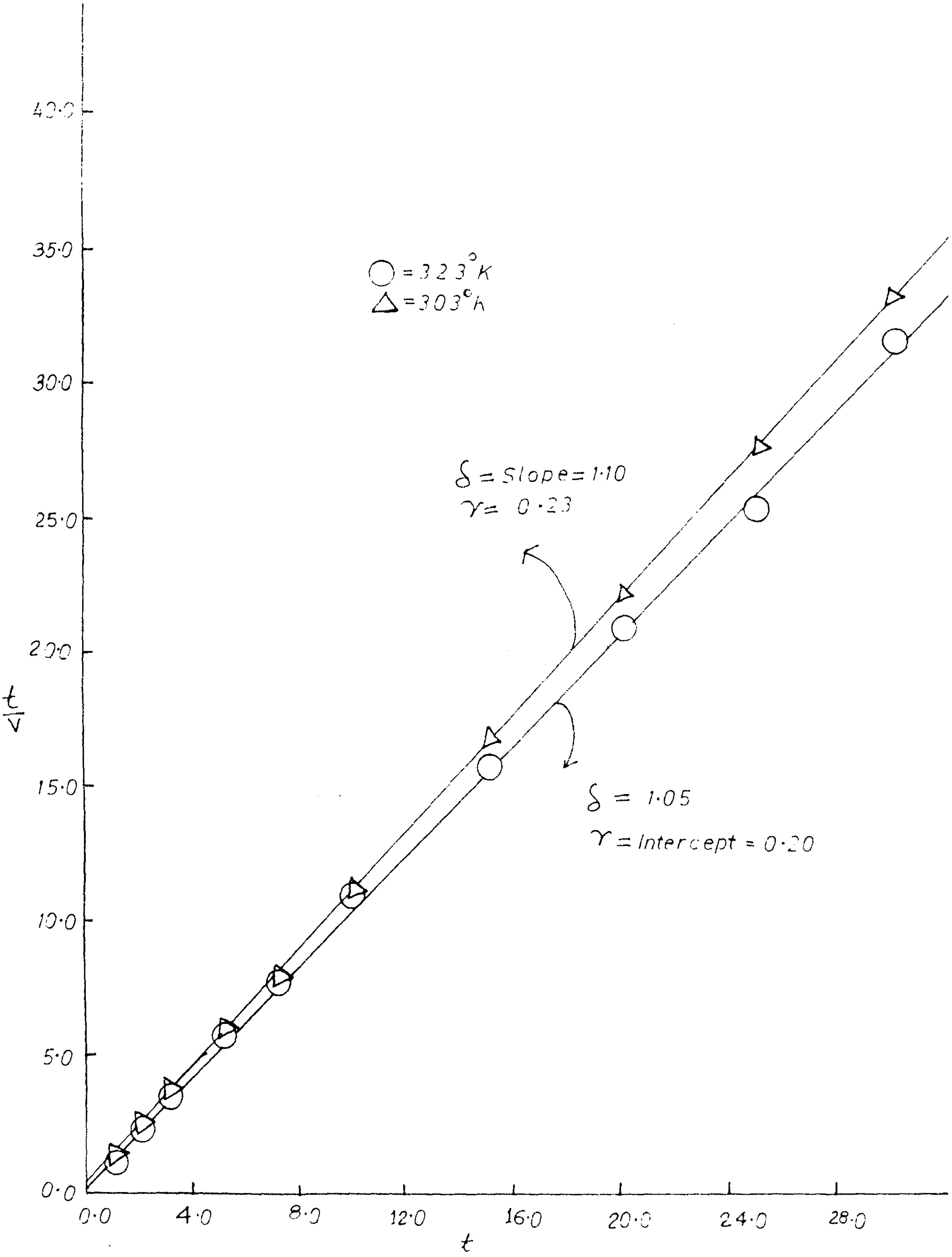


FIGURE 3·2.4.9 (b) LISZI PLOT (t/V vs t) FOR 0·538N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

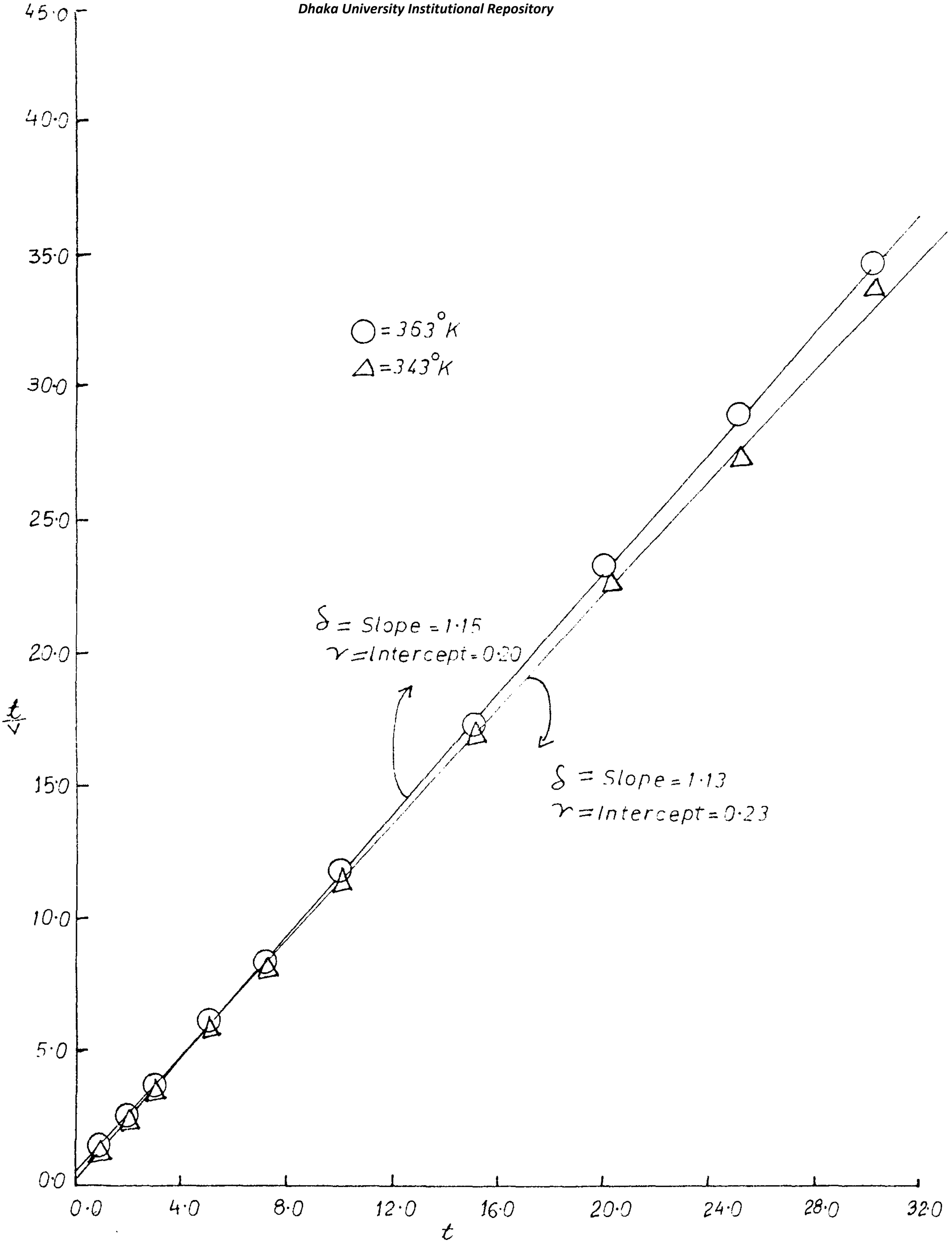


FIGURE:- 3.2.4.10 (a) LISZI PLOT (t/V vs t) FOR 0·49N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

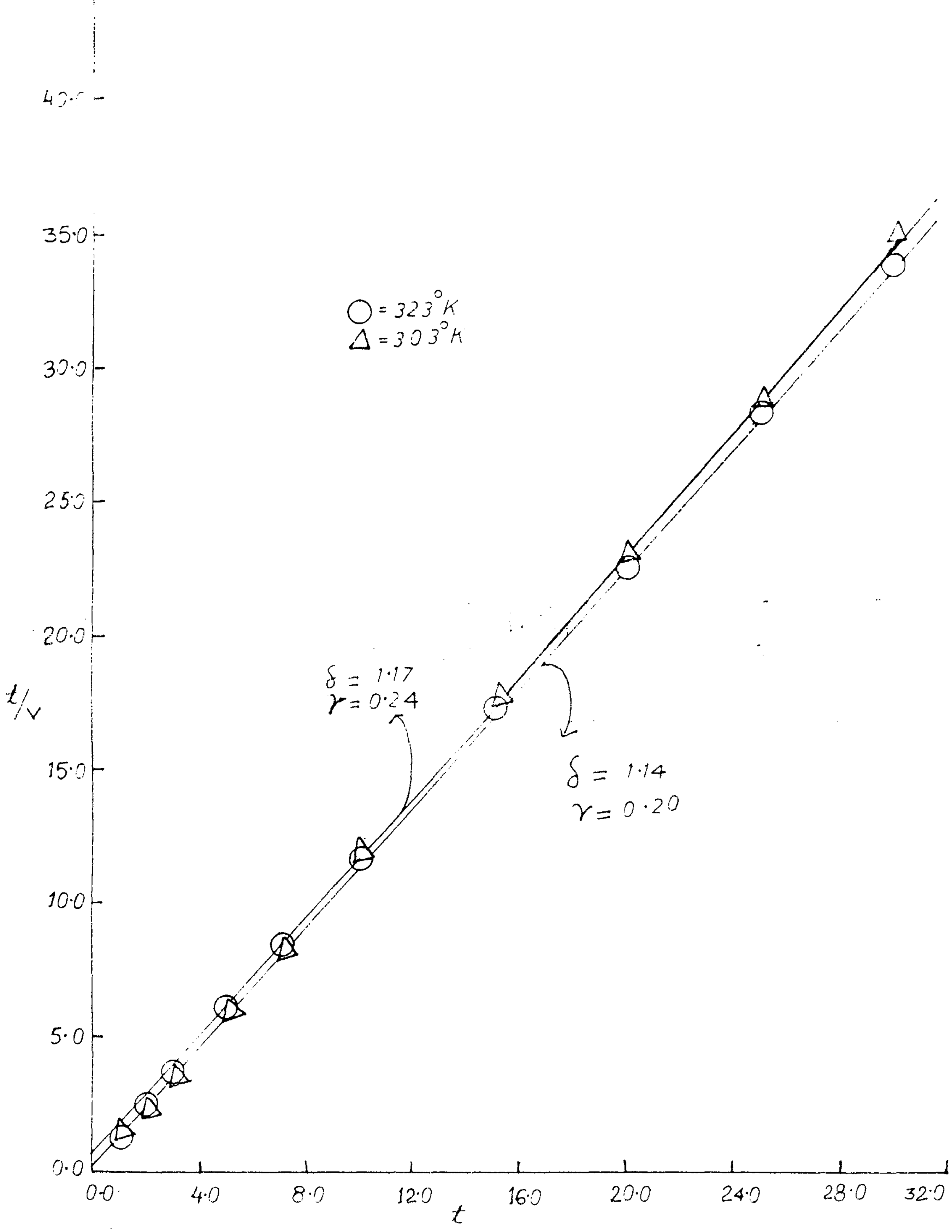


FIGURE:-3.2.4.10(b) LISZT PLOT (t/v vs t) FOR 0·43N I_2 ADSORPTION ON STEAM ACTIVATED CARBON

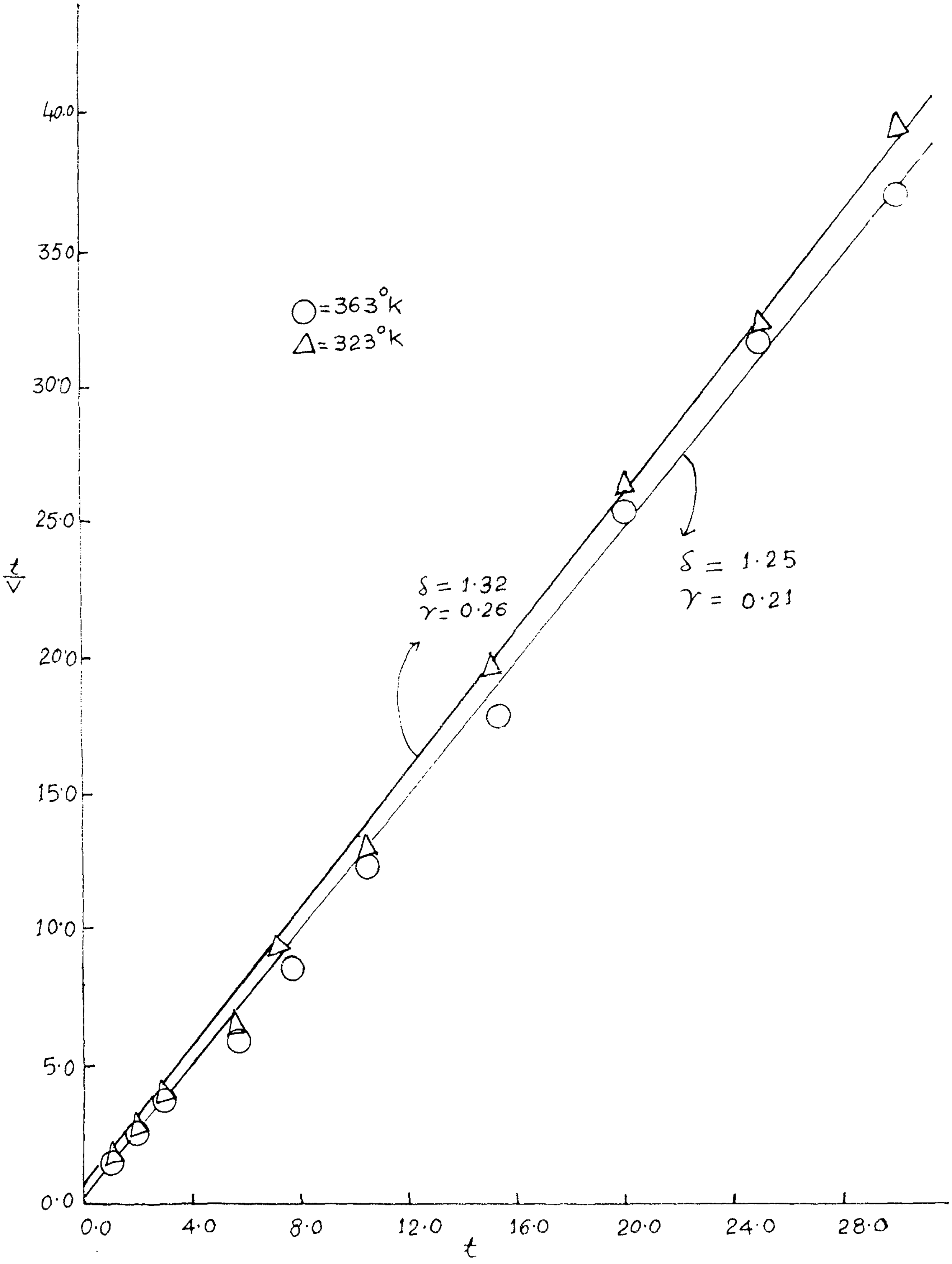


FIGURE:- 3.2.4.11 (a) LISZI PLOT (t/V vs t) FOR 0·36N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

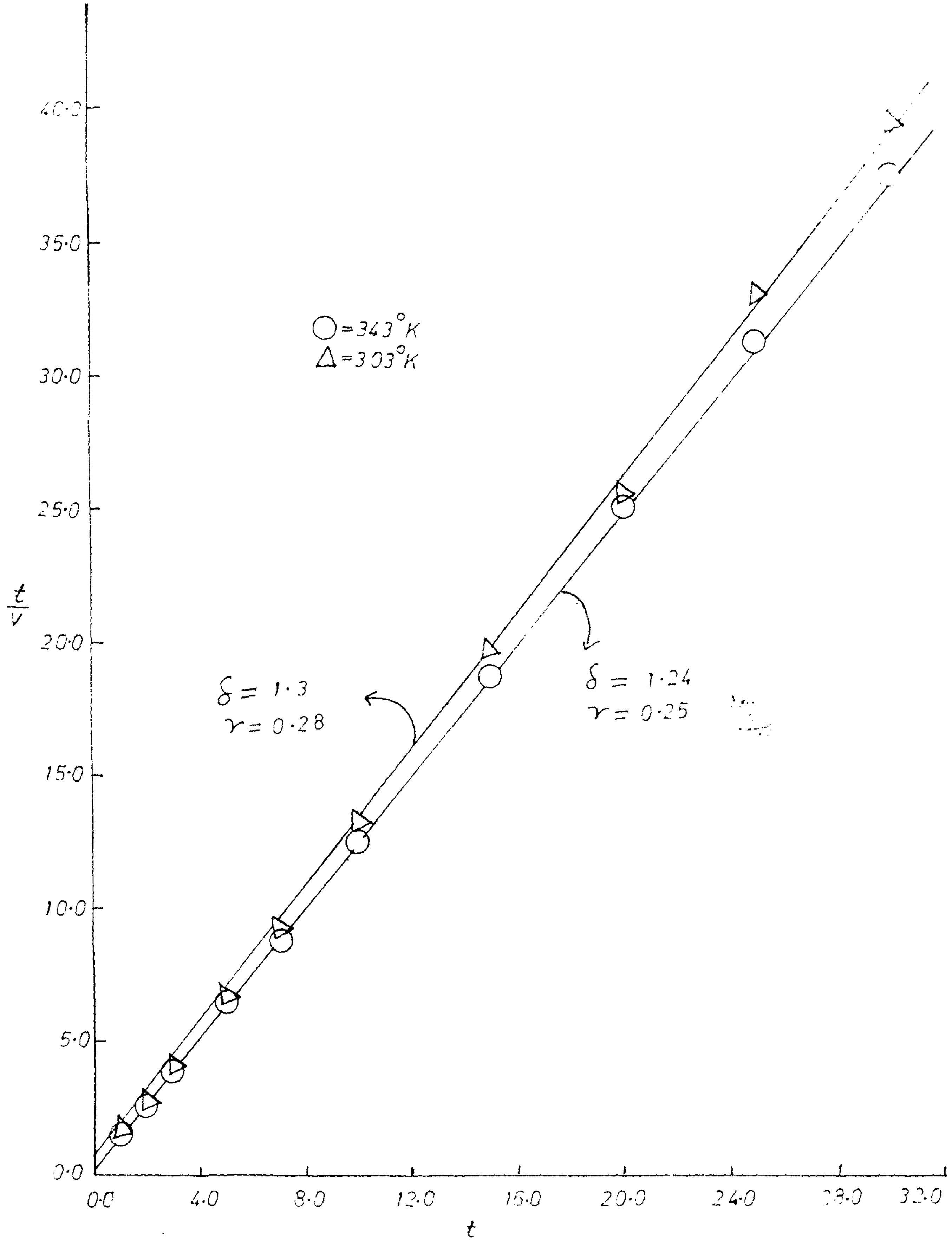


FIGURE:-3.2.4.11 (b) LISZI PLOT (t/v vs t) FOR 0.36 N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

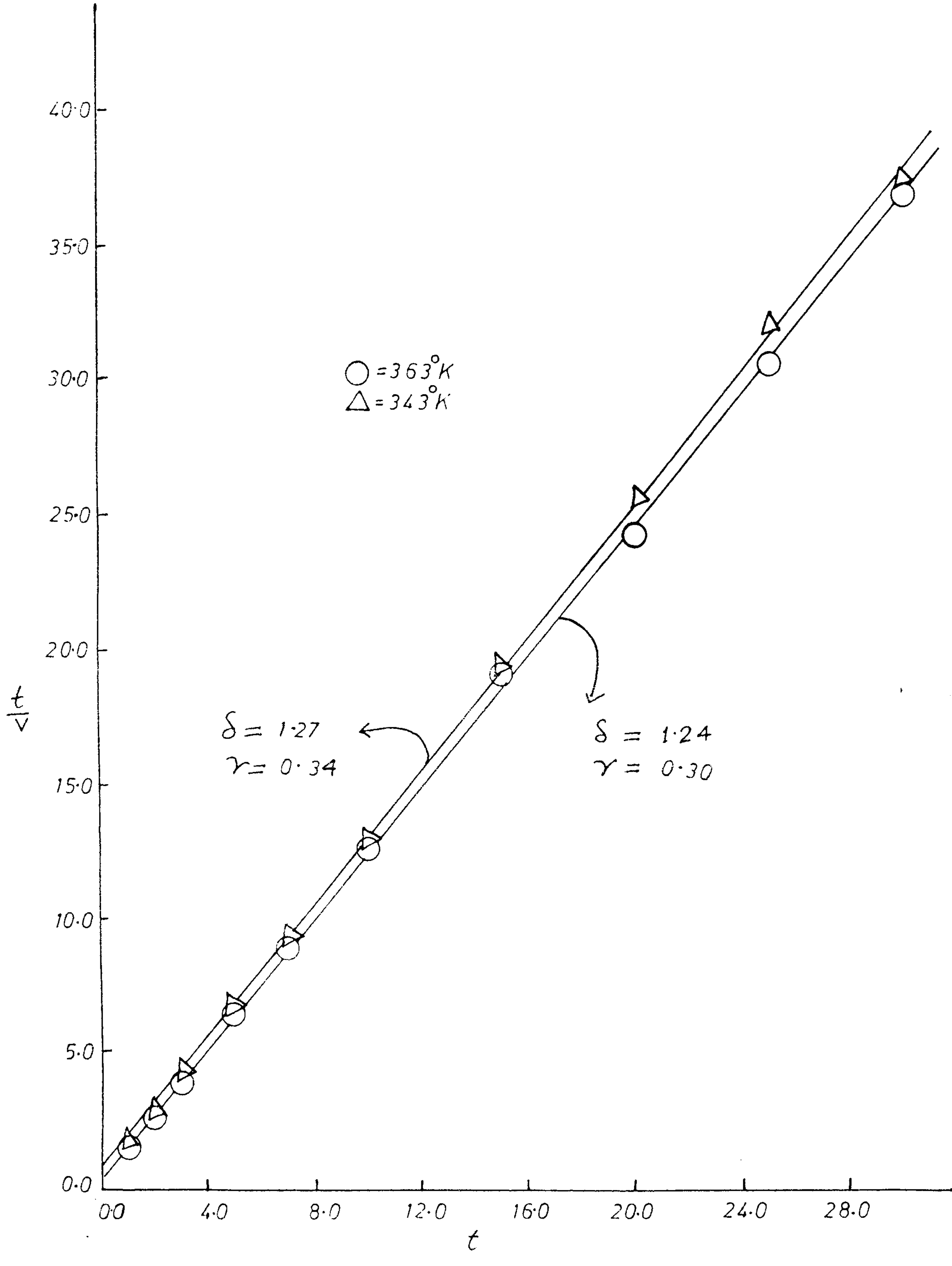


FIGURE:-3.2.4.12(a) LISZI PLOT(t/v vs t) FOR 0·264N I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

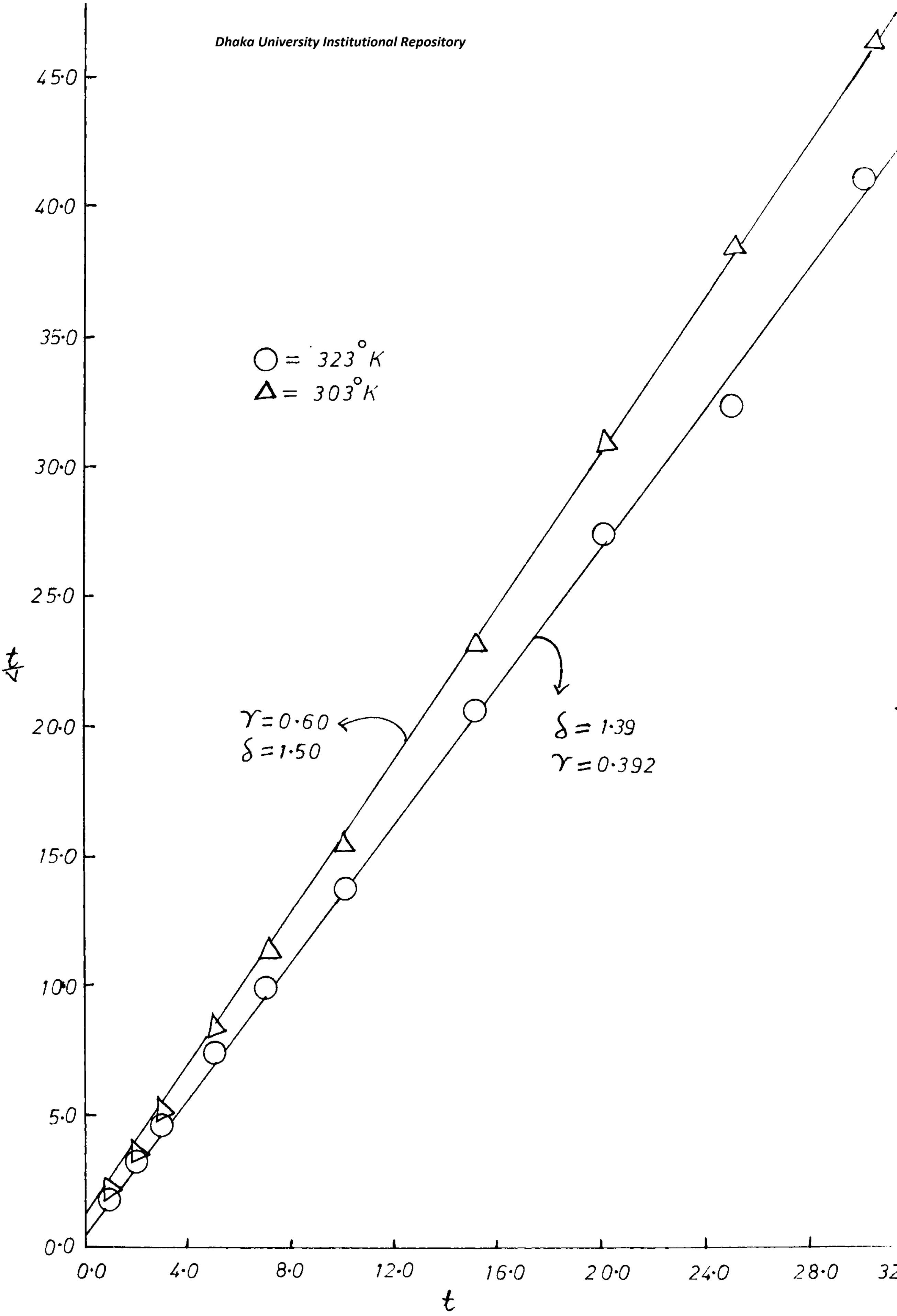


FIGURE:- 3.2.4.12 (b) LISZI PLOT (t/v vs t) FOR 0·264 N I_2 ADSORPTION
ON STEAM ACTIVATED CARBON.

3.2.4 IODINE ADSORPTION: Adsorption of iodine on activated carbon has been investigated at temperature range 303°K - 363°K and at the atmospheric pressure. The kinetic data, the variation of iodine adsorption with time are given in Table 3.2.4.1(a-d), 3.2.4.2(a-d), 3.2.4.3 (a-d), 3.2.4.4 (a-d) (Appendix II). These data are used to draw the v-t plots. Typical examples are shown in Figs. 3.2.4.1 , 3.2.4.2 , 3.2.4.3 , 3.2.4.4 . Plots of 1/v vs 1/t and t/v vs t have been drawn (Figs. 3.2.4.5-8, 3.2.4.9-12) to get the values of the two constants 'γ' and 'δ' . The values are given in Table 3.2.4.5 (Appendix II). From the values of 'γ' at different temperatures and concentrations, the values for the orders of adsorption are found out by plotting log $1/\gamma$ vs log c as shown in Fig. 3.2.4.13. The value of the initial rates and limiting adsorption are recorded in Table 3.2.4.5. The order of adsorption as calculated are found to vary from 0.66 to 1.2 as the temperature is decreased from 363°K to 303°K and shown in Table 3.2.4.6 . The results are calculated by the least square analysis method. The activation energy is calculated from the Arrhenius plot (Fig. 3.2.4.14) and it has been found that the activation energy increases with decrease of temperature. The value of activation energy calculated at four different temperature 363°K, 343°K, 323°K and 303°K are 0.4358, 0.6650, 1.64 and 2.74 KCals/mole respectively. The values obtained are too low and indicates that the adsorption of iodine on carbon surface is mostly of Vander Waals' type. It is also evident from the shape of the adsorption isotherms as shown in the previous chapter (section 3.1.1.2). The value of activation energy is comparable to the literature value as mentioned in case of acetic

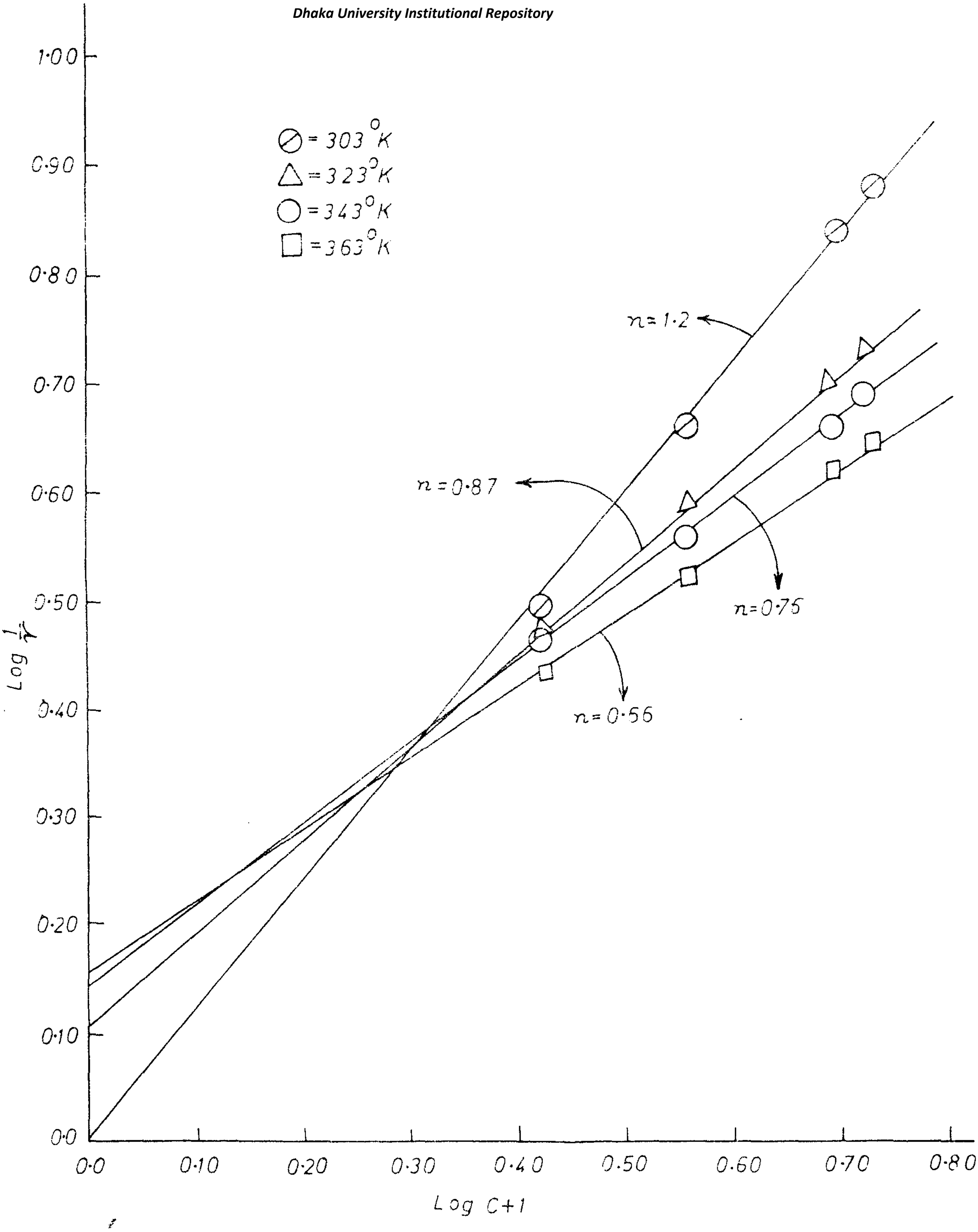


FIGURE: 3.2.4.13. ORDER PLOT (Log $\frac{1}{\gamma}$ vs Log C) FOR I_2 ADSORPTION ON STEAM ACTIVATED CARBON

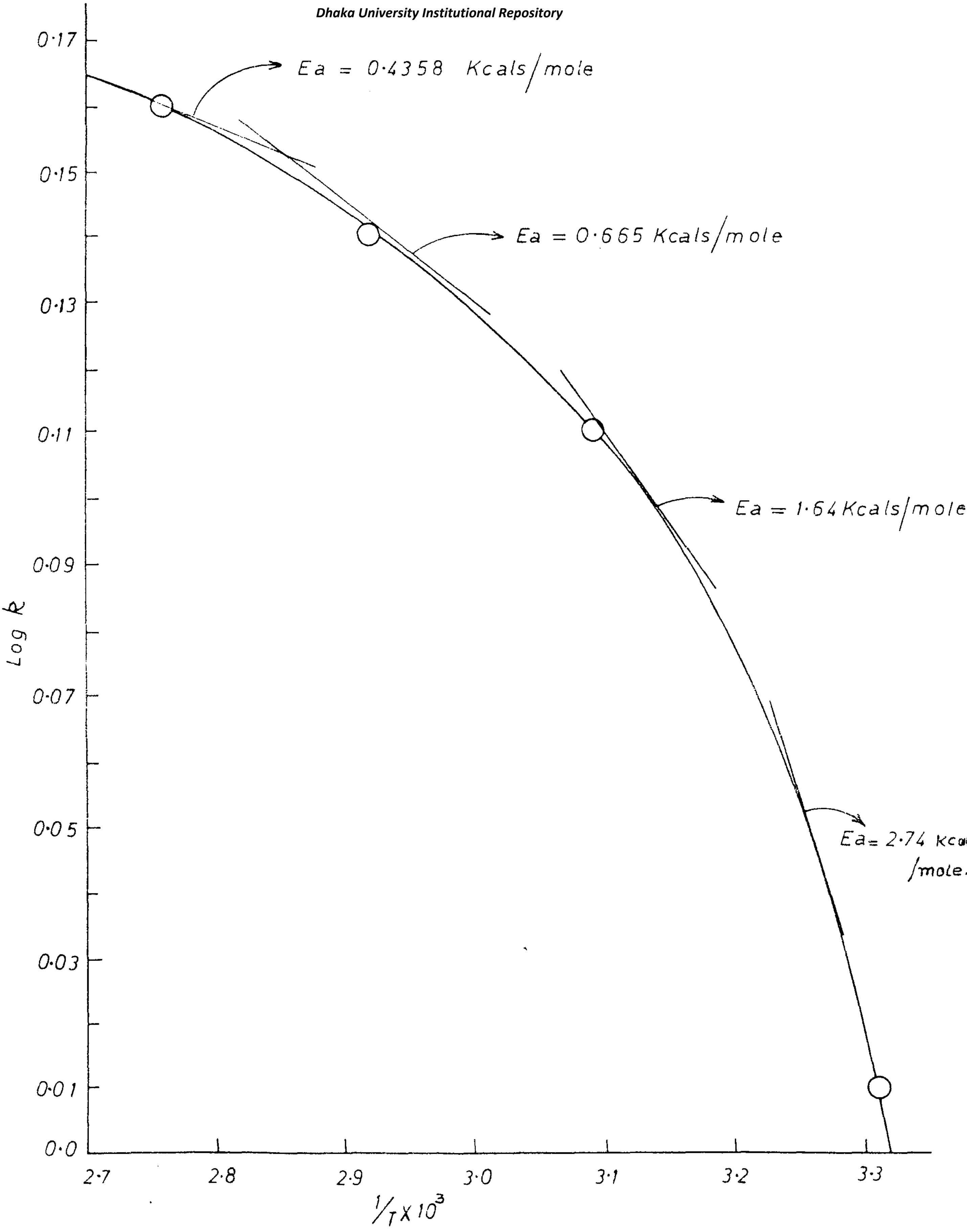


FIGURE:- 3.2.4.14. ARRHENIUS PLOT(Log k vs 1/T) FOR I_2 ADSORPTION ON STEAM ACTIVATED CARBON.

acid. The value of the rate constants as obtained from the intercepts of the $\log \frac{1}{\gamma}$ $\log c$ plots varied from 1.0232 min^{-1} to 1.4454 min^{-1} at the temperature range $303^{o}K$ - $363^{o}K$ (Table 3.2.4.7 Appendix II).

From the shape and nature of the kinetic curves, it is clear that the adsorption of iodine on activated carbon obeys the Liszi equation. The value of ' γ ' and ' δ ' obtained from the plots of 1/v vs 1/t are similar to the corresponding values obtained from the plots of t/v vs t, thus showing the justification of the application of Liszi equation in case of adsorption from solution.

From the values of the order of adsorption at different temperatures, it is apparent that the adsorption of iodine on carbon surface does not follow a single mechanism in the temperature ranges $303^{o}K$ - $363^{o}K$. The same is also reflected in the adsorption isobars (section 3.1.2.2). It may be suggested that at lower temperature ($303^{o}K$) the adsorption of I_2 on active carbon has followed a first order mechanism and with increase of temperature ($323^{o}K$ - $363^{o}K$) there is a departure from the first order mechanism to some fractional order (less than one). It can be explained by suggesting that at higher temperature the process of adsorption of iodine on activated carbon is accompanied by the dissociation of the molecule, the adsorbed species therefore being the atoms. The reason that at higher temperature dissociation is favoured is that the resulting atoms are capable of forming very much stronger bonds with the surface atoms than the case if molecules are present. At the expense of breaking one bond, therefore, two adsorption bonds can be formed.

The concentration of the adsorbed iodine is proportional to the fractional power (0.66 to 0.87) of the rate of iodine, rather than to its first power. This kinetic aspects have been justified in the mechanism we proposed for iodine adsorption on active carbon (section 3.3.1).

3.3. MECHANISM OF ADSORPTION AND ACTIVATION.

3.3.1 Mechanism of adsorption of iodine on activated carbon:

As stated by Gerasimov et al.[240] adsorption from solutions differs from the adsorption from gases or pure liquids in that the surface layer contains both the solvent and the solute. According to them the surface has no free sites, therefore adsorption of one component takes place through the displacement of the other. Such a view finds support in the fact that with the increase of adsorption of iodine, adsorption of water (solvent) falls (Fig. 3.1.1.6)

From Table 3.3.1 (Appendix III) it may also be seen that the equilibrium is established quickly (10 mins.) indicating that the adsorption is a surface action. However, it is further observed that carbon continued to adsorb iodine for weeks and even months. This phenomena lent support to the fact that, in addition to surface action, diffusion into the interior of the carbon has taken place. Since adsorption through diffusion is a slow process, such a course is likely to take weeks or months. In consideration of these facts the entire adsorption phenomena in solution is divided into the following five steps:

(i) Diffusion of adsorbate through the solution to the adsorbent particles.

(ii) Diffusion of adsorbate through the adsorbent particles accompanied by two dimensional movement along the capillary walls.

(iii) Adsorption or exchange on the adsorbent.

(iv) Diffusion of displaced species out of the adsorbent.

(v) Diffusion of displaced species through the solution away from the adsorbent.

Steps (iv) and (v) are the reverse processes of steps (i) and (ii) respectively. The kinetics of adsorption are controlled by the slowest of the above five steps. Steps (i) and (v) have been eliminated from our consideration in view of the fact that the experiments have been conducted under conditions of vigorous shaking so as to maintain a constant concentration of adsorbate at the adsorbent-solution interface. The kinetics are therefore controlled by one of the steps (ii) to (iv) i.e. either by a diffusion or by a mass action mechanism.

Whether the adsorption is controlled by diffusion or by mass action has been verified by using equations (1.26), (1.27) and (1.28) (section 1.8). Data obtained according to the equations are recorded in Table 3.3.1.2. To test the conformity of the experimental results with the equation (1.26), the value of Bt for each experimental value of F is obtained from the data of Reichenberg[131]. It is observed (Table 3.3.1.2 Appendix III) that the value of B varied by a factor of 2 and as such it can be concluded that the adsorption is not fully controlled by particle diffusion. log(1-F) vs t according to the equations (1.27) and (1.28) is plotted (Fig. 3.3.1) to find out the contribution by film diffusion and mass action mechanism. From the nature of the curves (Fig. 3.3.1) it has been found that the value of S in equation (1.28) decreases with time supporting that the adsorption of iodine on active carbon is controlled by mass action mechanism. Since the value of R (equation 1.27) does not increase with progress of exchange (Fig. 3.3.1), it proved that film diffusion mechanism is not operative. Adsorption is therefore governed in the case of iodine mainly by mass action. The fact that after initial rapid adsorption, slow adsorption continued for weeks indicates that some contribution from particle diffusion is also operative.

That the adsorption is completely reversible is exemplified by the results in Table 3.3.1.3 (Appendix III). The extent of adsorption is the same when the concentration of the bulk solution remained constant. It is independent of whether this concentration is achieved by adsorption or desorption.

To find out the mechanism of adsorption, orders of adsorption with respect to iodine have been determined (Table 3.2.1 Appendix II). The order varied from 1.2 at 303°K to 0.66 at 363°K. A mechanism consistent with the above findings is suggested as under.

Mechanism:- The molecule of iodine undergoing adsorption forms a loose surface complex I_2S which is free to move on the surface of the adsorbent (carbon). This mobile complex finally runs into the deepest potential well available and forms the stable adsorption compounds IS. The reaction scheme can be represented as follows:

$$I_2 + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_2S \qquad \ldots\ldots\ldots \qquad (1)$$

$$I_2S \xrightarrow[\text{Slow}]{k_2} IS + I \qquad \ldots\ldots\ldots\ldots \qquad (2)$$

Let the total initial concentration of adsorbent site is $[S_o]$ which is equal to $[S_o] = [S] + [I_2S] + [IS]$. We assume that $[I_2S]$ reaches a steady state, ... (3)

so that,

$$\frac{d[I_2S]}{dt} = k_1[I_2][S] - k_{-1}[I_2S] - k_2[I_2S] = 0$$

$$\text{or } k_1[I_2][S] = k_{-1}[I_2S] + k_2[I_2S]$$

$$= [I_2S](k_{-1} + k_2)$$

$$\text{or } k_1[I_2]\left([S_o] - [I_2S] - [IS]\right) = [I_2S](k_{-1} + k_2)\cdot\left\{\text{from}(3)\right\}$$

$$\text{or, } k_1[I_2]\left([S_o] - [IS]\right) = [I_2S]\left(k_{-1} + k_2 + k_1[I_2]\right)$$

$$\text{or } [I_2S] = \frac{k_1[I_2]\left([S_o] - [IS]\right)}{k_{-1} + k_2 + k_1[I_2]} \quad .... \quad (4)$$

The decomposition of I_2S into products i.e. the formation of IS is the rate determining step.

$\therefore$ The rate of iodine removal by adsorption,

$$r = \frac{d[I]}{dt} = k_2[I_2S]$$

$$= k_2 \cdot \frac{k_1[I_2]\left([S_o] - [IS]\right)}{k_{-1} + k_2 + k_1 \ I_2} \cdot \left\{\text{from (4)}\right\}$$

$$= \frac{k_1k_2[I_2][S_o]}{k_{-1} + k_2 + k_1[I_2]} - \frac{k_1k_2[I_2][IS]}{k_{-1} + k_2 + k_1[I_2]}.$$

$$= \frac{k_2k''[I_2][S_o]}{1 + k''[I_2]} - \frac{k_2k''[I_2][IS]}{1 + k''[I_2]} \quad ... \quad (5)$$

$$\left\{\begin{array}{l}\text{Dividing numerator and denominator of both} \\ \text{the terms by}(k_{-1} + k_2)\text{ i.e. } \dfrac{k_1}{k_{-1} + k_2} = k''\end{array}\right\}$$

As we are considering the initial rate for determining the order of adsorption, at the initial stage the formation of IS is negligible in comparison with S_0 , so the second term in equation (5) can be neglected. Therefore the rate of adsorption becomes,

$$r = \frac{k_2 k'' \left[I_2\right] \left[S_o\right]}{1 + k'' \left[I_2\right]}$$

when $k'' \left[I_2\right] << 1$, the order of the adsorption becomes

$$\begin{aligned} r &= k_2 k'' \left[I_2\right]\left[S_o\right] \\ &= K \left[I_2\right] \qquad \left\{ \left[S_o\right] \text{ is constant} \right\} \end{aligned}$$

which is first order i.e. the rate of adsorption is proportional to the first power of the iodine concentration. When $K'' \left[I_2\right]$ is not negligible in comparison with 1 , the order of the reaction falls below unity and this is consistent with the results we obtained for order of adsorption.

3.3.2 Mechanism of adsorption of Acetic acid:

As in the case of iodine, tests for particle diffusion, film diffusion and mass action controlled adsorptions have been applied to acetic acid also by using equations (1.26), (1.27) and (1.28) [section 1.8] respectively. It has been found that in the case of acetic acid also adsorption is governed mainly by mass action (Fig. 3.3.2.1) (Table - 3.3.2 Appendix III).

To find out the mechanism of adsorption, orders of adsorption with respect to acetic acid have been determined in the

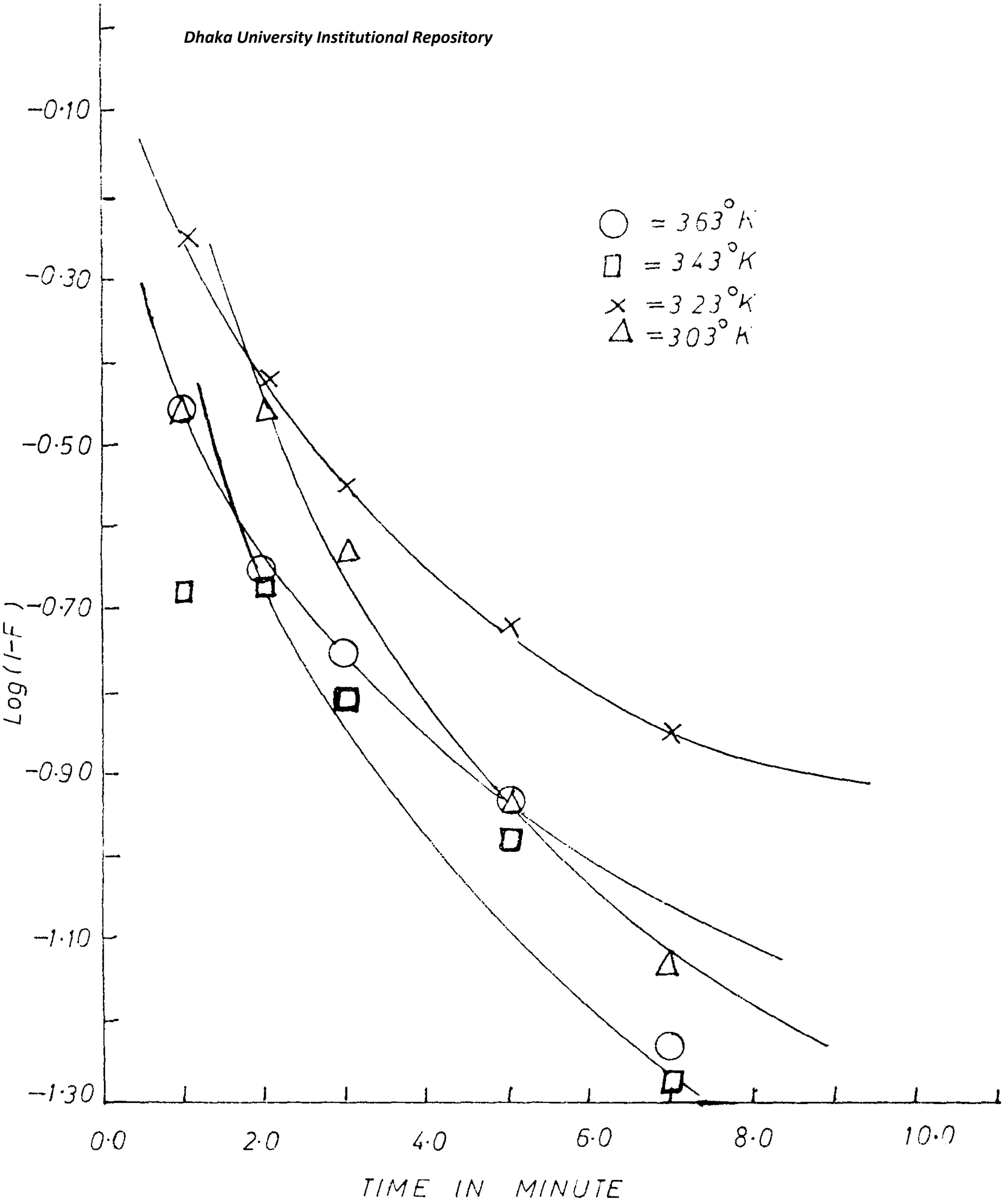


FIGURE:-3.3.21 PLOT OF Log (1-F) vs t FOR 0·575 N CH_3COOH ADSORPTION ON STEAM ACTIVATED CARBON.

temperature range $303^{o}K$ to $363^{o}K$ and concentration range from 0.243N to 0.575N. The order of adsorption is found to vary from 1.48 to 2.00. The order at $323^{o}K$ has been found to be rather unexpectedly low (i.e. 1.07). A mechanism consistent with these results is suggested as given below.

Mechanism :- The mechanism of adsorption of acetic acid on carbon can be represented by the reaction of the type,

$$S + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AS$$

$$AS + A \xrightarrow[\text{Slow}]{k_2} A_2S$$

where 'A' represents acetic acid and 'S' , the surface of carbon. The kinetics of adsorption can be approached in the line similar to the kinetics of heterogeneous solid/liquid reaction. The following mathematical derivation deals with the adsorption process studied in this investigation.

Rate of primary adsorption $= k_1 [A][S]$

Rate of desorption $= k_{-1} [AS]$

Rate of secondary adsorption $= k_2 [AS][A]$

At the steady state,

$$\frac{d[AS]}{dt} = k_1[A][S] - k_{-1}[AS] - k_2[AS][A] = 0$$

$$\text{or} \quad k_1[A][S] = [AS]\left(k_{-1} + k_2[A]\right)$$

$$\text{or} \quad [AS] = \frac{k_1[A][S]}{k_{-1} + k_2[A]} \quad \ldots\ldots\ldots \quad (4)$$

$$r = \text{rate of adsorption} = k_2[A][AS]$$

$$= k_2[A] \cdot \frac{k_1[A][S]}{k_{-1} + k_2[A]}$$

$$= \frac{k_1 k_2 [A]^2 [S]}{k_{-1} + k_2[A]} \quad \ldots\ldots \quad (5)$$

Now, if $k_2[A] \gg k_{-1}$, then equation (5) can be written as,

$$r = \text{rate} = \frac{k_1 k_2 [A]^2 [S]}{k_2[A]} = k_1[A][S] \quad \ldots\ldots\ldots \quad (6)$$

For the initial rates $[S]$ is very close to $[S_o]$ and therefore can be regarded as constant. Equation (6) can then be written as

$$r = k[A]$$

i.e. the rate of adsorption of acetic acid is proportional to the first power of concentration of acetic acid.

On the other hand, if $k_{-1} \gg k_2[A]$, then equation (5) becomes

$$r = \frac{k_1 k_2 [A]^2 [S]}{k_{-1}} = k[A]^2 \quad \text{i.e. the}$$

reaction becomes kinetically second order. It is therefore, the relative values of k_2 and k_{-1} that really govern the order of the reaction. Thus the mechanism suggested and the kinetic formula derived are in agreement with the experimental results.

3.3.3 Mechanism of activation:

As stated earlier that "Carbon has a memory" which means preparatory stages leave an imprint that affects the succeeding stages of processing. Activated carbon prepared from the same raw material by using different methods show different adsorption characteristics. A carbon prepared with calcium chloride is more adsorptive for caramel[3], whereas a carbon prepared with zinc chloride is more effective for iodine[3]. This is reflected in the work of Khan et al.[241] In the present investigation an attempt is made to understand such behaviour (i.e. specificity) of carbon by using zinc chloride in the preparation of activated carbon from cocoanut shell (section 2.2.2).

Mineral salts are found to have a significant influence on the adsorptive properties of activated carbon. One view of the action of these salts is that during carbonization they provide a skeleton on which the carbon is deposited[137]. The freshly formed carbon becomes bonded by adsorptive forces to the mineral elements. For example, in the case of activation in the presence of potassium carbonate, it has been observed by Berl[137] that appreciable decomposition of potassium carbonate begins between 600°C and 700°C with simultaneous formation of the graphite lattice. The potassium formed at this temperature is interstratified between the carbon layers, thus spreading the planes further apart. This is followed by a decrease in particle size. Thus, the larger particles which have been formed during the activation process are disintegrated and a larger surface becomes exposed to the activating gas. Hence, vaporized potassium splits the carbon primary particles, forming active centres. The internal surface is therefore increased.

Another view of the action of mineral salts is that they increase the yield of char[171,237]. This suggests that the salts remain with the carbon and perhaps alter the course of the reaction during activation so that less of the objectionable tarry products are formed. This appears to be the case when dehydrating salts are used[4]. For example, through the presence of zinc chloride at about 500°C, hydrogen and oxygen atoms in the source materials are stripped away as water rather than as a hydrocarbon or as oxygenated organic compound. The zinc chloride inhibits the reunion of carbon particles to form large particles[238]. At elevated temperature, zinc chloride also acts as an excellent solvent for tar which otherwise are adsorbed by the carbon.

It has been found using electrographic method (section 2.4) that small amount of zinc remained in the active carbon. It is very difficult to remove and cannot be washed out with aq.HCl and distilled water. The minute quantities of zinc which have been detected perhaps are held strongly on certain areas of the carbon surface or in the internal pores. These areas may provide adsorptive bonds and impart specific adsorptive properties. It may also alter the size of pores formed during activation and thus increases the internal surface which have been reflected in the work of Homes et al.[239].

That the specific property was due to the presence of zinc in the molecular architecture of carbon was evident from the fact that on removal of zinc from the activated carbon, the activity of the carbon decreased to a considerable extent (i.e. by 57-75%) (Table - 3.3.3).

TABLE - 3.3.3

a = original quantity of iodine in solution (in g.).

x = amount of iodine adsorbed (in g.).

m = Weight of adsorbent = 1 g.

Time = 30 minutes.

Volume of iodine solution taken = 50 ml.

SAMPLE	Initial concentration of iodine solution.	a	Amount adsorbed per g. x/m	Amount unadsorbed (a-x)
$ZnCl_2$ treated carbon.	0.2140M	2.7178	0.7500	1.9678
	0.1925M	2.4447	0.6830	1.7617
(Before removal of zinc)	0.1615M	2.0510	0.6210	1.4300
	0.1020M	1.2954	0.5650	0.7304
$ZnCl_2$ treated carbon.	0.2140M	2.7178	0.3256	2.3922
	0.1925M	2.4447	0.1923	2.2524
(After removal of Zinc)	0.1615M	2.0510	0.1850	1.8660
	0.1020M	1.2954	0.1430	1.1524

3.4 SURFACE AREA OF DIFFERENT CARBON:

As mentioned in section 1.9 and 2.3 , determination of surface area by the gas adsorption method involved complicated and time consuming procedure. An attempt has been made in the present investigation to simplify the procedure. The simplified BET equation is applied to the adsorption of iodine from solution to measure the surface areas of different carbons. The attractiveness of the method lies , of course , in its comparatively simple technique (section 2.2.3). In the present study, surface areas of activated carbon obtained by the nitrogen adsorption method have been compared with those obtained by the iodine adsorption from solution method.

The data for isotherms are presented in Table 3.4.1 (Appendix IV) for different carbons. The plots of $c/\frac{x}{m}$ vs c are shown in Figs. 3.4.2. Three different carbons have been used to compare and show whether the method which have been used by us were applicable to other cases. The data for $c/\frac{x}{m}$ vs c plots have been derived from the experimental isotherms (Fig. 3.4.1) for different carbon and recorded in Table - 3.4.2 (Appendix IV).

The plots of $c/\frac{x}{m}$ vs c for different carbons clearly indicate that they obey the simplified BET equation. The slope of the isotherms gives the value of 'Vm', the quantity of the adsorbate (iodine) which is required for the monolayer. It has been found that the results obtained by the BET method (described in section 2.3) are comparable with those obtained in the present investigation, by the iodine adsorption from solution. Data for the BET surface areas

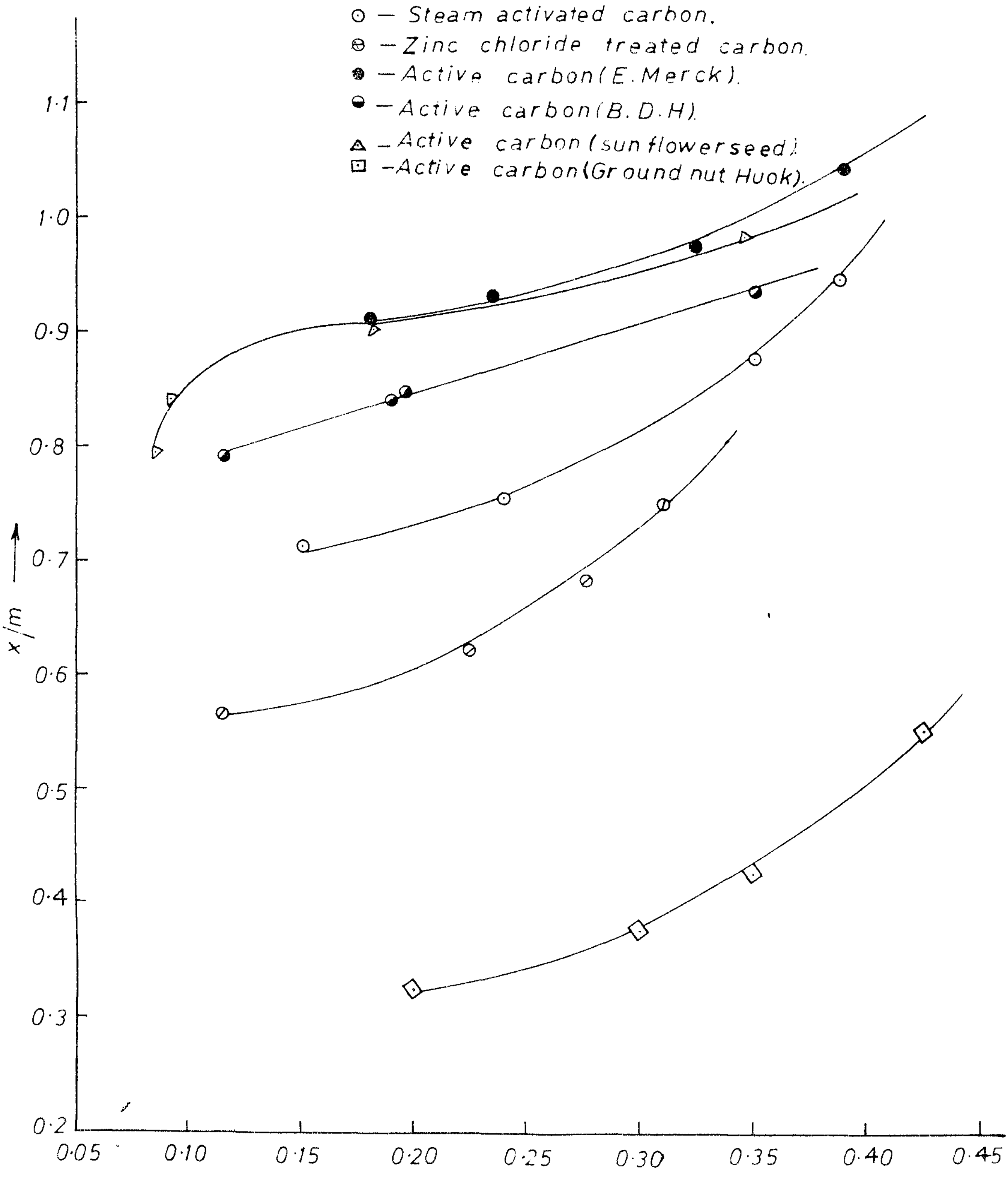


FIGURE: 3·4·1 I_2 ADSORPTION ISOTHERM($\frac{x}{m}$ vs C).

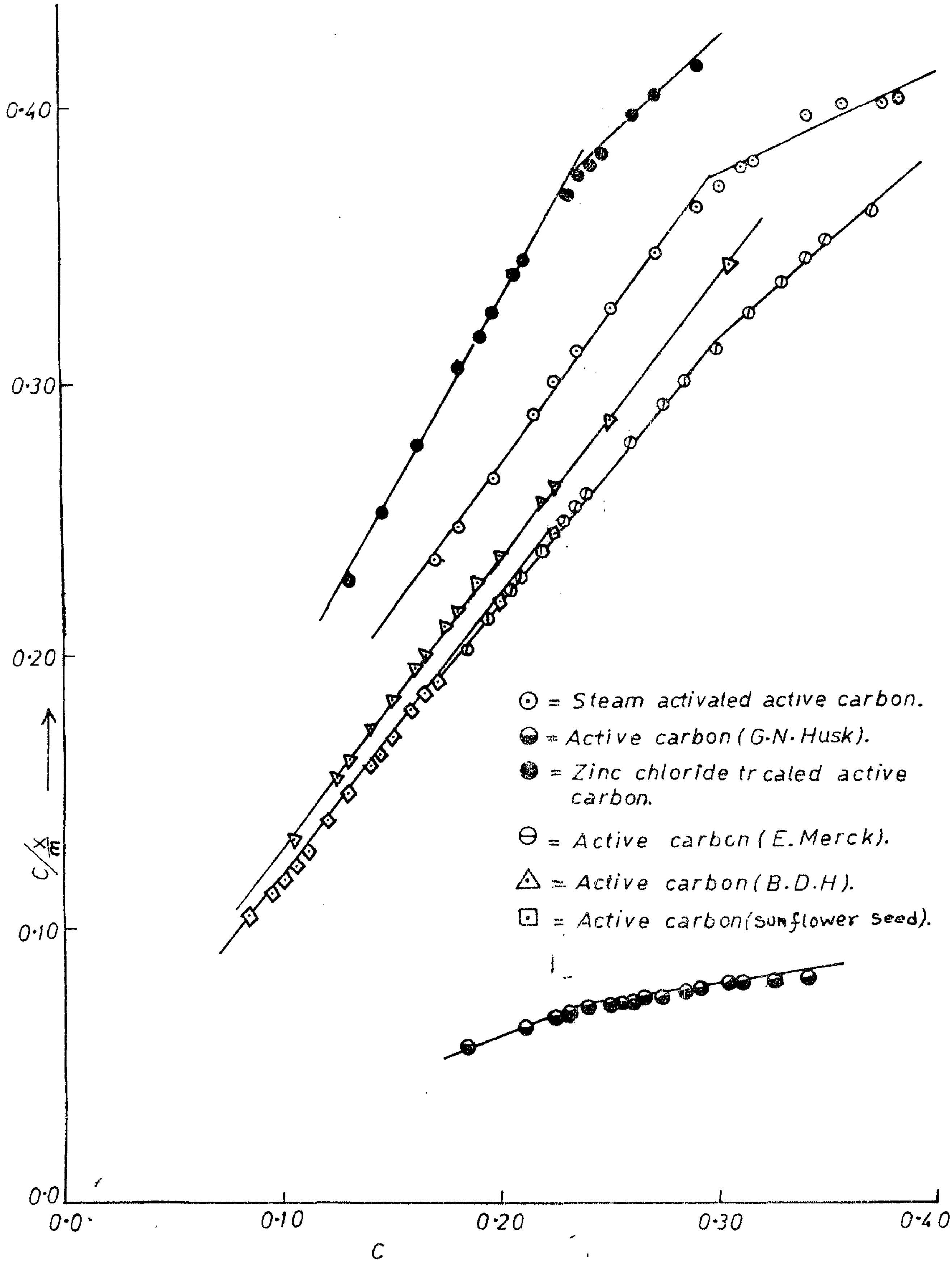


FIGURE:- 3.4.2. $C/\frac{x}{m}$ vs C I_2 ADSORPTION.

are recorded in Table 3.4.3 (Appendix IV). We have assigned a new value for 'σm' for iodine molecule area and this value (41.14 A^{o2}) is acceptable as nearly the same values (obtained by the BET method) for surface areas of different carbons have been obtained by using the iodine adsorption method. The values for surface areas of different carbons determined by the iodine adsorption method are shown in Table 3.4.4 (Appendix IV). The values obtained by both iodine adsorption and BET method are recorded in Table 3.4.5 for comparison.

The same procedure (iodine adsorption method) have been followed by Walker and Zettlemoyer[190] with active magnesia. They compared the BET areas with the value obtained by the iodine adsorption from CCl_4. They have used for iodine the value 21.2 A^{o2} for 'σm', the molecular area. The different values they obtained for surface area are shown in Table 3.4

TABLE - 3.4 Comparison of N_2 and I_2 areas of active magnesia.

Grade	N_2 area in m^2/g $m = 16.2^oA^2$	I_2 area m^2/g. $m = 21.2$ A^{o2}
XP	210	134
2624	151	96
2652-S	149	93
2652	131	83
2641	79	48.5
2661½	35	19.8
2665	35	15.9

It is clear from the above table that the iodine areas are only about two thirds of nitrogen areas. Thus the value used by Zettlemoyer and Walker[190] for 'σm' is untenable.

CHAPTER 4. APPENDIX

APPENDIX I

TABLE - 3.1.1.1

DATA FOR ADSORPTION ISOTHERMS(CH_3COOH)

TEMPERATURE °K	Initial concentration of the adsorbate solution (In normality)	Equilibrium concentration C(in normality)	x/m = amount of CH_3COOH adsorbed by carbon(in g.)
363	0.755	0.700	0.165
	0.694	0.640	0.163
	0.575	0.521	0.160
	0.512	0.460	0.157
	0.446	0.396	0.149
	0.397	0.350	0.140
	0.358	0.315	0.127
	0.243	0.206	0.109
353	0.755	0.6990	0.168
	0.694	0.6390	0.164
	0.575	0.5216	0.160
	0.512	0.4603	0.155
	0.446	0.3960	0.150
	0.397	0.3476	0.148
	0.358	0.3156	0.127
	0.243	0.2063	0.110
343	0.755	0.693	0.185
	0.694	0.633	0.183
	0.575	0.515	0.179
	0.512	0.454	0.175
	0.446	0.392	0.162
	0.397	0.348	0.146
	0.358	0.315	0.127
	0.243	0.212	0.091

TABLE - 3.1.1.1 (Contd.)

DATA FOR ADSORPTION ISOTHERMS(CH_3COOH)

TEMPERATURE °K	Initial concentration of the adsorbate solution(in normality)	Equilibrium concentration C(in normality)	x/m =amount of CH_3COOH adsorbed by carbon(in g.)
333	.755	.6926	.187
	.694	.6320	.185
	.575	.5143	.182
	.512	.4521	.180
	.446	.3920	.162
	.397	.3470	.150
	.358	.3156	.127
	.243	.2126	.0912
323	.755	.688	.200
	.694	.627	.199
	.575	.509	.197
	.512	.447	.194
	.446	.382	.189
	.397	.337	.180
	.358	.315	.127
	.243	.206	.109
313	.755	.698	.170
	.694	.639	.165
	.575	.521	.162
	.512	.460	.155
	.446	.396	.150
	.397	.3496	.142
	.358	.3156	.127
	.243	.2066	.109
303	.755	.699	.167
	.694	.639	.165
	.575	.521	.160
	.512	.460	.156
	.446	.396	.149
	.397	.350	.140
	.358	.315	.127
	.243	.212	.0912

TABLE - 3.1.1.2

DATA FOR LANGMUIR ISOTHERMS (CH_3COOH)

Temperature ^oK	Equilibrium concentration C (in normality)	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
363	0.230	0.112	2.053	0.4795	4.2819
	0.250	0.115	2.1739	0.5000	4.3478
	0.280	0.120	2.3333	0.5291	4.4095
	0.300	0.125	2.4000	0.5477	4.3817
	0.310	0.128	2.4218	0.5567	4.3498
	0.330	0.133	2.4812	0.5744	4.3192
	0.350	0.139	2.5179	0.5916	4.2561
	0.360	0.141	2.5531	0.6000	4.2553
	0.370	0.143	2.5874	0.6082	4.2536
	0.390	0.147	2.6530	0.6244	4.2482
	0.420	0.152	2.7631	0.6480	4.2636
	0.430	0.153	2.8104	0.6557	4.2859
	0.450	0.155	2.9032	0.6708	4.3278
	0.460	0.156	2.9487	0.6782	4.3476
	0.490	0.158	3.1012	0.7000	4.4303
	0.510	0.159	3.2075	0.7141	4.4914
	0.550	0.161	3.4161	0.7416	4.6063
	0.600	0.163	3.6809	0.7745	4.7521

TABLE - 3.1.1.2 (Contd.)

DATA FOR LANGMUIR ISOTHERMS (CH_3COOH)

Temperature °K	Equilibrium concentration C (in normality)	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
343	0.220	0.094	2.3404	0.4690	4.9898
	0.240	0.097	2.4742	0.4898	5.0504
	0.250	0.099	2.5252	0.5000	5.0505
	0.270	0.104	2.5961	0.5196	4.9963
	0.280	0.107	2.6168	0.5291	4.9453
	0.290	0.110	2.6363	0.5385	4.8956
	0.300	0.115	2.6086	0.5477	3.6514
	0.310	0.121	2.5619	0.5567	4.6014
	0.320	0.126	2.5396	0.5656	4.4895
	0.330	0.132	2.5000	0.5744	4.3519
	0.350	0.145	2.4137	0.5916	4.0800
	0.360	0.152	2.3684	0.6000	3.9473
	0.370	0.157	2.3566	0.6082	3.8743
	0.380	0.160	2.3750	0.6164	3.8527
	0.390	0.163	2.3926	0.6244	3.8312
	0.400	0.166	2.4096	0.6324	3.8099
	0.410	0.168	2.4404	0.6403	3.8113
	0.440	0.172	2.5581	0.6633	3.8565
	0.470	0.176	2.6704	0.6855	3.8952

TABLE - 3.1.1.2 (Contd.)

DATA FOR LANGMUIR ISOTHERMS (CH_3COOH)

Temperature ^oK	Equilibrium concentration C	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
	0.240	0.113	2.1238	0.4898	4.3353
	0.250	0.115	2.1739	0.5000	4.3478
	0.270	0.118	2.2881	0.5196	4.4035
	0.280	0.120	2.3333	0.5291	4.4095
	0.300	0.124	2.4193	0.5477	4.4171
	0.320	0.130	2.4615	0.5656	4.3514
323	0.330	0.136	2.4264	0.5744	4.2239
	0.340	0.147	2.3129	0.5830	3.9666
	0.350	0.180	1.9444	0.5916	3.2867
	0.365	0.185	1.9729	0.6041	3.2656
	0.370	0.186	1.9892	0.6082	3.2703
	0.380	0.187	2.0320	0.6164	3.2964
	0.400	0.190	2.1052	0.6324	3.3287
	0.420	0.192	2.1875	0.6480	3.3753
	0.430	0.193	2.2279	0.6557	3.3976
	0.440	0.194	2.2680	0.6633	3.4192
	0.460	0.195	2.3589	0.6782	3.4781
	0.500	0.197	2.5380	0.7071	3.5893

TABLE - 3.1.1.2 (Contd.)

DATA FOR LANGMUIR ISOTHERMS(CH_3COOH)

Temperature °K	Equilibrium concentration C	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
303	0.510	0.160	3.1875	0.7141	4.4633
	0.230	0.096	2.3958	0.4795	4.9956
	0.240	0.098	2.4489	0.4898	4.9989
	0.251	0.101	2.4851	0.5009	4.9603
	0.260	0.104	2.5000	0.5099	4.9029
	0.270	0.107	2.5233	0.5196	4.8562
	0.280	0.110	2.5454	0.5291	4.8104
	0.290	0.113	2.5663	0.5385	4.7656
	0.300	0.118	2.5423	0.5477	4.6417
	0.310	0.123	2.5203	0.5567	4.5266
	0.320	0.128	2.5000	0.5656	4.4194
	0.330	0.132	2.5000	0.5744	4.3519
	0.340	0.135	2.5185	0.5830	4.3192
	0.350	0.139	2.5179	0.5916	4.2561
	0.360	0.142	2.5352	0.6000	4.2253
	0.370	0.144	2.5694	0.6082	4.2241
	0.380	0.146	2.6027	0.6164	4.2222
	0.390	0.148	2.6351	0.6244	4.2195
	0.420	0.152	2.7631	0.6480	4.2636
	0.450	0.155	2.9032	0.6708	4.3278
	0.470	0.157	2.9936	0.6855	4.3666

TABLE - 3.1. ·3

DATA FOR FREUNDLICH ISOTHERM.(CH_3COOH)

Temperature °K	Equilibrium concentration C (in normality).	Amount adsorbed x/m (in g.)	log C	log x/m
363	0.230	0.112	-0.6382	-0.9507
	0.250	0.115	-0.6020	-0.9393
	0.280	0.120	-0.5528	-0.9208
	0.300	0.125	-0.5228	-0.9030
	0.310	0.128	-0.5086	-0.8927
	0.330	0.133	-0.4814	-0.8761
	0.350	0.139	-0.4559	-0.8569
	0.360	0.141	-0.4436	-0.8507
	0.370	0.143	-0.4317	-0.8446
	0.390	0.147	-0.4089	-0.8326
	0.420	0.152	-0.3767	-0.8181
	0.430	0.153	-0.3665	-0.8153
	0.450	0.155	-0.3467	-0.8096
	0.460	0.156	-0.3372	-0.8068
	0.490	0.158	-0.3098	-0.8013
	0.510	0.159	-0.2924	-0.7986
	0.550	0.161	-0.2596	-0.7931
	0.600	0.163	-0.2218	-0.7878

TABLE - 3.1.3(contd.)

DATA FOR FREUNDLICH ISOTHERM (CH$_3$COOH)

Temperature ^oK	Equilibrium concentration C (in normality)	Amount adsorbed adsorbed x/m(in g.)	log C	log x/m
343	0.220	0.094	-0.6575	-1.0268
	0.240	0.097	-0.6197	-1.0132
	0.250	0.099	-0.6020	-1.0043
	0.270	0.104	-0.5686	-0.9829
	0.280	0.107	-0.5528	-0.9706
	0.290	0.110	-0.5376	-0.9586
	0.300	0.115	-0.5228	-0.9393
	0.310	0.121	-0.5086	-0.9172
	0.320	0.126	-0.4948	-0.8996
	0.330	0.132	-0.4814	-0.8794
	0.350	0.145	-0.4559	-0.8386
	0.360	0.152	-0.4436	-0.8181
	0.370	0.157	-0.4317	-0.8041
	0.380	0.160	-0.4202	-0.7958
	0.390	0.163	-0.4089	-0.7878
	0.400	0.166	-0.3979	-0.7798
	0.410	0.168	-0.3872	-0.7746
	0.440	0.172	-0.3565	-0.7644
	0.470	0.176	-0.3279	-0.7544

TABLE - 3.1.1.3 (Contd.)

Temperature °K	Equilibrium concentration C (in normality)	Amount adsorbed x/m (g)	log x/m	log C
323	0.240	0.113	-0.9469	-0.6197
	0.250	0.115	-0.9393	-0.6020
	0.270	0.118	-0.9281	-0.5686
	0.280	0.120	-0.9208	-0.5528
	0.300	0.124	-0.9065	-0.5228
	0.320	0.130	-0.8860	-0.4948
	0.330	0.136	-0.8664	-0.4814
	0.340	0.147	-0.8326	-0.4685
	0.350	0.180	-0.7447	-0.4559
	0.365	0.185	-0.7328	-0.4377
	0.370	0.186	-0.7304	-0.4317
	0.380	0.187	-0.7281	-0.4202
	0.400	0.190	-0.7212	-0.3979
	0.420	0.192	-0.7166	-0.3767
	0.430	0.193	-0.7144	-0.3665
	0.440	0.194	-0.7121	-0.3565
	0.460	0.195	-0.7099	-0.3372
	0.500	0.197	-0.7055	-0.3010

TABLE - 3.1.1.3 (Contd.)

Temperature ^{o}K	Equilibrium concentration C	Amount adsorbed x/m(g).	log x/m	log C
303	0.230	0.096	-1.0177	-0.6382
	0.240	0.098	-1.0087	-0.6197
	0.251	0.101	-0.9956	-0.6003
	0.260	0.104	-0.9829	-0.5850
	0.270	0.107	-0.9706	-0.5686
	0.280	0.110	-0.9586	-0.5528
	0.290	0.113	-0.9469	-0.5376
	0.300	0.118	-0.9281	-0.5228
	0.310	0.123	-0.9100	-0.5086
	0.320	0.128	-0.8927	-0.4984
	0.330	0.132	-0.8794	-0.4814
	0.340	0.135	-0.8696	-0.4685
	0.350	0.139	-0.8569	-0.4559
	0.360	0.142	-0.8477	-0.4436
	0.370	0.144	-0.8416	-0.4317
	0.380	0.146	-0.8356	-0.4202
	0.390	0.148	-0.8297	-0.4089
	0.420	0.152	-0.8181	-0.3767
	0.450	0.155	-0.8096	-0.3467
	0.470	0.157	-0.8041	-0.3279
	0.510	0.160	-0.7958	-0.2924

TABLE - 3.1.4

DATA FOR ADSORPTION ISOTHERMS. (I_2)

TEMPERATURE °K	Initial concentration of the adsorbate solution. (in normality)	Equilibrium concentration C (in normality)	x/m = amount of I_2 adsorbed (in g.)
363	0.600	0.3937	1.0500
	0.538	0.3886	0.9486
	0.490	0.3554	0.8542
	0.446	0.3160	0.8250
	0.360	0.2340	0.8000
	0.346	0.2215	0.7900
	0.264	0.1400	0.7860
	0.200	0.0787	0.7700
353	0.600	0.4031	1.025
	0.538	0.3886	0.9486
	0.490	0.3569	0.8450
	0.446	0.3176	0.8150
	0.360	0.2418	0.7500
	0.346	0.2302	0.7350
	0.264	0.1537	0.7000
	0.200	0.0921	0.6850
343	0.600	0.4425	1.00
	0.538	0.3974	0.8924
	0.490	0.3569	0.8450
	0.446	0.3184	0.8100
	0.360	0.2344	0.7969
	0.346	0.2230	0.7805
	0.264	0.1422	0.7734
	0.200	0.0806	0.7580

TABLE - 3.1.1.4(Contd.)

DATA FOR ADSORPTION ISOTHERMS.(I_2)

TEMPERATURE ^{o}K	Initial concentration of the adsorbate solution. (in normality)	Equilibrium concentration C (in normality)	x/m = amount of I_2 adsorbed (in g.)
333	0.600	0.3937	1.05
	0.538	0.3886	0.9486
	0.490	0.3554	0.8542
	0.446	0.3184	0.8100
	0.360	0.2418	0.7500
	0.346	0.2302	0.7350
	0.264	0.1503	0.7218
	0.200	0.0881	0.7100
323	0.600	0.4031	1.02500
	0.538	0.3886	0.9486
	0.490	0.3554	0.8542
	0.446	0.3176	0.8150
	0.360	0.2410	0.7555
	0.346	0.2302	0.7350
	0.264	0.1503	0.7218
	0.200	0.0881	0.7100
313	0.600	0.4425	1.00
	0.538	0.3974	0.8924
	0.490	0.3569	0.8450
	0.446	0.3160	0.8250
	0.360	0.2344	0.7965
	0.346	0.2230	0.7805
	0.264	0.1422	0.7734
	0.200	0.0806	0.7580

TABLE - 3.1.4(Contd.)

DATA FOR ADSORPTION ISOTHERMS.(I_2).

TEMPERATURE °K	Initial concentration of the adsorbate solution. (in normality)	Equilibrium concentration C (in normality)	x/m = amount of I_2 adsorbed (in g.)
303	0.600	0.4464	0.9750
	0.538	0.3956	0.9036
	0.490	0.3554	0.8542
	0.446	0.3176	0.8150
	0.360	0.2447	0.7320
	0.346	0.2318	0.7250
	0.264	0.1537	0.7000
	0.200	0.0921	0.6850

TABLE - 3.1.1.5

DATA FOR LANGMUIR ISOTHERM.(I_2)

Temp. ^{o}K.	Equilibrium concentration. C. (in normality.	Amount adsorbed. x/m. (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
363	0.130	0.780	0.1666	0.3605	0.4622
	0.180	0.785	0.2292	0.4242	0.5404
	0.200	0.787	0.2541	0.4472	0.5682
	0.215	0.790	0.2721	0.4636	0.5869
	0.220	0.792	0.2777	0.4690	0.5922
	0.245	0.795	0.3081	0.4949	0.6226
	0.260	0.800	0.3250	0.5099	0.6373
	0.275	0.805	0.3416	0.5244	0.6514
	0.290	0.810	0.3580	0.5385	0.6648
	0.300	0.815	0.3680	0.5477	0.6720
	0.310	0.820	0.3780	0.5567	0.6789
	0.317	0.825	0.3842	0.5630	0.6824
	0.325	0.830	0.3915	0.5700	0.6868
	0.335	0.837	0.4002	0.5787	0.6915
	0.343	0.840	0.4083	0.5856	0.6972
	0.350	0.854	0.4098	0.5916	0.6927
	0.355	0.860	0.4127	0.5958	0.6928
	0.360	0.865	0.4161	0.6000	0.6936
	0.370	0.880	0.4204	0.6082	0.6912
	0.375	0.890	0.4213	0.6123	0.6880

TABLE - 3.1.1.5 (Contd)

DATA FOR LANGMUIR ISOTHERM.(I_2)

Temp. ^oK.	Equilibrium concentration. C. (in normality.	Amount adsorbed x/m. (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
	0.090	0.685	0.1313	0.3000	0.4379
	0.110	0.690	0.1594	0.3316	0.4806
	0.125	0.695	0.1798	0.3535	0.5087
	0.135	0.700	0.1928	0.3674	0.5248
	0.150	0.705	0.2127	0.3872	0.5493
	0.165	0.710	0.2323	0.4062	0.5721
	0.175	0.715	0.2447	0.4183	0.5850
353	0.190	0.720	0.2638	0.4358	0.6054
	0.200	0.725	0.2758	0.4472	0.6168
	0.210	0.730	0.2876	0.4582	0.6277
	0.225	0.735	0.3061	0.4743	0.6453
	0.245	0.745	0.3288	0.4949	0.6643
	0.260	0.755	0.3443	0.5099	0.6753
	0.270	0.760	0.3552	0.5196	0.6837
	0.275	0.765	0.3594	0.5244	0.6854
	0.290	0.775	0.3741	0.5385	0.6948
	0.305	0.787	0.3875	0.5522	0.7017
	0.320	0.805	0.3975	0.5656	0.7027
	0.325	0.810	0.4012	0.5700	0.7038
	0.330	0.815	0.4049	0.5744	0.7048
	0.345	0.835	0.4131	0.5873	0.7034
	0.350	0.845	0.4142	0.5916	0.7001

TABLE - 3.1.1.5 (Contd.)

DATA FOR LANGMUIR ISOTHERMS.(I_2).

Temp. °K.	Equilibrium concentration. C (in normality)	Amount adsorbed x/m. (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
343	0.080	0.760	0.1052	0.2828	0.3721
	0.120	0.765	0.1568	0.3464	0.4528
	0.140	0.767	0.1825	0.3741	0.4878
	0.155	0.770	0.2012	0.3937	0.5112
	0.190	0.775	0.2451	0.4358	0.5624
	0.215	0.780	0.2756	0.4636	0.5944
	0.240	0.785	0.3057	0.4898	0.6240
	0.255	0.790	0.3227	0.5049	0.6392
	0.275	0.795	0.3459	0.5244	0.6596
	0.285	0.800	0.3562	0.5338	0.6673
	0.300	0.805	0.3726	0.5477	0.6804
	0.310	0.810	0.3827	0.5567	0.6873
	0.320	0.815	0.3926	0.5656	0.6940
	0.325	0.820	0.3963	0.5700	0.6952
	0.340	0.830	0.4096	0.5830	0.7025
	0.345	0.835	0.4131	0.5873	0.7034
	0.370	0.860	0.4302	0.6082	0.7072
	0.375	0.865	0.4335	0.6123	0.7079
	0.380	0.875	0.4342	0.6164	0.7045
	0.390	0.890	0.4382	0.6244	0.7016
	0.400	0.905	0.4419	0.6324	0.6988
	0.410	0.925	0.4432	0.6403	0.6922

TABLE - 3.1.1.5 (Contd.)

DATA FOR LANGMUIR ISOTHERMS.(I_2).

Temp. °K.	Equilibrium concentration C (in normality)	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
333	0.080	0.710	0.1126	0.2828	0.3983
	0.100	0.713	0.1402	0.3162	0.4435
	0.125	0.715	0.1748	0.3535	0.4944
	0.150	0.720	0.2083	0.3872	0.5379
	0.175	0.725	0.2413	0.4183	0.5770
	0.190	0.730	0.2602	0.4358	0.5969
	0.210	0.735	0.2857	0.4582	0.6234
	0.225	0.740	0.3040	0.4743	0.6410
	0.235	0.745	0.3154	0.4847	0.6506
	0.240	0.750	0.3200	0.4898	0.6531
	0.255	0.755	0.3377	0.5049	0.6688
	0.265	0.760	0.3486	0.5147	0.6773
	0.275	0.768	0.3580	0.5244	0.6828
	0.285	0.775	0.3677	0.5338	0.6888
	0.290	0.780	0.3717	0.5385	0.6904
	0.300	0.787	0.3811	0.5477	0.6959
	0.315	0.800	0.3937	0.5612	0.7015
	0.325	0.813	0.3997	0.5700	0.7012
	0.340	0.830	0.4096	0.5830	0.7025
	0.350	0.845	0.4142	0.5916	0.7001
	0.370	0.885	0.4180	0.6082	0.6873

TABLE - 3.1.1.5 (Contd.)

DATA FOR LANGMUIR ISOTHERMS.(I_2).

Temp. °K.	Equilibrium concentration C (in normality)	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
323	0.100	0.710	0.1408	0.3162	0.4453
	0.125	0.713	0.1753	0.3535	0.4958
	0.140	0.715	0.1958	0.3741	0.5233
	0.165	0.720	0.2291	0.4062	0.5641
	0.180	0.725	0.2482	0.4242	0.5851
	0.200	0.730	0.2739	0.4472	0.6126
	0.210	0.735	0.2857	0.4582	0.6234
	0.225	0.740	0.3040	0.4743	0.6410
	0.235	0.745	0.3154	0.4847	0.6506
	0.250	0.755	0.3311	0.5000	0.6622
	0.260	0.760	0.3421	0.5099	0.6709
	0.275	0.770	0.3571	0.5244	0.6810
	0.300	0.790	0.3797	0.5477	0.6933
	0.310	0.800	0.3875	0.5567	0.6959
	0.320	0.810	0.3950	0.5656	0.6983

TABLE - 3.1.1.5 (Contd.)

DATA FOR LANGMUIR ISOTHERMS.(I_2).

Temp. ^{o}K	Equilibrium concentration C (in normality)	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
313	0.080	0.760	0.1052	0.2828	0.3721
	0.100	0.763	0.1310	0.3162	0.4144
	0.115	0.765	0.1503	0.3391	0.4432
	0.145	0.770	0.1883	0.3807	0.4945
	0.165	0.775	0.2129	0.4062	0.5241
	0.195	0.780	0.2500	0.4415	0.5661
	0.220	0.785	0.2802	0.4690	0.5975
	0.235	0.790	0.2974	0.4847	0.6136
	0.255	0.795	0.3207	0.5049	0.6351
	0.270	0.800	0.3375	0.5196	0.6495
	0.285	0.805	0.3540	0.5338	0.6631
	0.300	0.812	0.3694	0.5477	0.6745
	0.310	0.815	0.3803	0.5567	0.6831
	0.320	0.820	0.3902	0.5656	0.6898
	0.335	0.830	0.4036	0.5787	0.6973
	0.350	0.840	0.4166	0.5916	0.7042
	0.360	0.850	0.4235	0.6000	0.7058

TABLE - 3.1.1.5 (Contd.)

DATA FOR LANGMUIR ISOTHERMS.(I_2).

Temp. ^{o}K	Equilibrium concentration C (in normality).	Amount adsorbed x/m (in g.)	$C/\frac{x}{m}$	$\sqrt{C}$	$\sqrt{C}/\frac{x}{m}$
303	0.090	0.685	0.1313	0.3000	0.4379
	0.100	0.690	0.1449	0.3162	0.4583
	0.140	0.695	0.2014	0.3741	0.5383
	0.160	0.700	0.2285	0.4000	0.5714
	0.180	0.705	0.2553	0.4242	0.6017
	0.190	0.709	0.2679	0.4358	0.6147
	0.205	0.715	0.2867	0.4527	0.6332
	0.215	0.720	0.2986	0.4636	0.6440
	0.225	0.725	0.3103	0.4743	0.6542
	0.235	0.730	0.3219	0.4847	0.6640
	0.245	0.735	0.3333	0.4949	0.6734
	0.250	0.740	0.3378	0.5000	0.6756
	0.265	0.750	0.3533	0.5147	0.6863
	0.270	0.755	0.3576	0.5196	0.6882
	0.275	0.760	0.3618	0.5244	0.6900
	0.290	0.775	0.3741	0.5385	0.6948
	0.300	0.785	0.3821	0.5477	0.6977
	0.314	0.800	0.3925	0.5603	0.7004
	0.330	0.820	0.4024	0.5744	0.7005

TABLE - 3.1.1.6

DATA FOR FREUNDLICH ISOTHERMS(I_2)

Temperature ^{o}K	Equilibrium concentration C (in normality.	log C	Amount adsorbed x/m (g).	log x/m.
363	0.130	-0.8860	0.780	-0.1079
	0.200	-0.6989	0.782	-0.1067
	0.220	-0.6575	0.785	-0.1051
	0.245	-0.6108	0.790	-0.1023
	0.265	-0.5767	0.795	-0.0996
	0.280	-0.5528	0.800	-0.0969
	0.290	-0.5376	0.805	-0.0942
	0.300	-0.5228	0.809	-0.0920
	0.310	-0.5086	0.815	-0.0888
	0.325	-0.4881	0.825	-0.0835
	0.335	-0.4749	0.835	-0.0783
	0.340	-0.4685	0.840	-0.0757
	0.350	-0.4559	0.850	-0.0705
	0.365	-0.4377	0.870	-0.0604
	0.385	-0.4145	0.925	-0.0338

TABLE - 3.1.1.6 (Contd.)

DATA FOR FREUNDLICH ISOTHERMS(I_2).

Temperature °K	Equilibrium concentration C (in normality.)	log C	Amount adsorbed x/m (g).	log x/m.
	0.165	-0.7825	0.775	-0.1106
	0.195	-0.7099	0.780	-0.1079
	0.215	-0.6675	0.785	-0.1051
	0.225	-0.6478	0.789	-0.1029
	0.240	-0.6197	0.795	-0.0996
343	0.250	-0.6020	0.800	-0.0969
	0.260	-0.5850	0.806	-0.0936
	0.275	-0.5606	0.815	-0.0888
	0.290	-0.5376	0.824	-0.0840
	0.300	-0.5228	0.830	-0.0809
	0.320	-0.4948	0.845	-0.0731
	0.325	-0.4881	0.850	-0.0705
	0.335	-0.4749	0.860	-0.0655
	0.345	-0.4621	0.870	-0.0604
	0.350	-0.4559	0.875	-0.0579

TABLE - 3.1.1.6 (Contd.)

DATA FOR FREUNDLICH ISOTHERMS (I_2).

Temperature °K	Equilibrium concentration C (in normality.)	log C	Amount adsorbed x/m (in g.)	log x/m.
323	0.170	-0.7695	0.725	-0.1396
	0.180	-0.7447	0.730	-0.1366
	0.195	-0.7099	0.735	-0.1337
	0.215	-0.6675	0.745	-0.1278
	0.225	-0.6478	0.750	-0.1249
	0.235	-0.6289	0.755	-0.1220
	0.250	-0.6020	0.765	-0.1163
	0.270	-0.5686	0.780	-0.1079
	0.290	-0.5376	0.800	-0.0969
	0.300	-0.5228	0.810	-0.0915
	0.310	-0.5086	0.820	-0.0861
	0.315	-0.5016	0.825	-0.0835
	0.340	-0.4685	0.855	-0.0680
	0.355	-0.4497	0.875	-0.0579
	0.375	-0.4259	0.900	-0.0457
	0.380	-0.4202	0.910	-0.0409

TABLE - 3.1.1.6 (Contd.)

DATA FOR FREUNDLICH ISOTHERMS (I_2)

Temperature ^{o}K	Equilibrium concentration C (in normality.)	log C	Amount adsorbed x/m (in g.)	log x/m.
303	0.170	-0.7695	0.650	-0.1870
	0.190	-0.7212	0.675	-0.1706
	0.200	-0.6989	0.683	-0.1655
	0.210	-0.6777	0.695	-0.1580
	0.220	-0.6575	0.705	-0.1518
	0.225	-0.6478	0.710	-0.1487
	0.240	-0.6197	0.725	-0.1396
	0.250	-0.6020	0.739	-0.1313
	0.265	-0.5767	0.755	-0.1220
	0.270	-0.5686	0.760	-0.1191
	0.295	-0.5301	0.790	-0.1023
	0.305	-0.5157	0.800	-0.0969
	0.325	-0.4881	0.825	-0.0835
	0.335	-0.4749	0.837	-0.0772
	0.360	-0.4436	0.865	-0.0629
	0.370	-0.4317	0.875	-0.0579
	0.380	-0.4202	0.885	-0.0530

TABLE - 3.1.1.7

DATA FOR THE DETERMINATION OF IODINE IN KI.

Strength of thiosulphate solution.	Volume of thiosulphate solution required.		Amount of I_2 in KI solution (g.)	
	Before adsorption (ml)	After adsorption (ml)	Before adsorption	After adsorption
0.185N	10.8	10.6	2.2937	2.2500
0.100N	20.00	19.0	2.2937	2.1790

DATA FOR MODIFIED LANGMUIR ISOTHERM

TABLE - 3.1.1.8

I_2 ADSORPTION.

Temp. °K	log C	log x	log x + 1
	-1.75945	-0.0166	0.98388
	-1.61978	-9.0665×10^{-3}	0.9909
303	-1.4202	2.7447×10^{-3}	1.0027
	-1.3383	0.0050	1.0050
	-1.7569	-0.01556	0.9844
	-1.60941	-6.8637×10^{-3}	0.99313
323	-1.4144	7.4362×10^{-3}	1.00743
	-1.3492	0.01206	1.01206

DATA FOR MODIFIED LANGMUIR ISOTHERM

TABLE - 3.1.1.9

I_2 ADSORPTION.

Temp.°C	$\log\left\|\frac{\Delta}{C}\right\|$	log (1-C)	log(1 - C) + 1
303	1.0515	-7.6232×10^{-3}	0.9924
	0.9145	-0.01055	0.9894
	0.7227	-0.01682	0.9831
	0.6309	-0.0204	0.9795
323	1.1143	-7.6674×10^{-3}	0.9923
	0.9692	-0.01073	0.9892
	0.7884	-0.01705	0.9829
	0.6816	-0.0199	0.9800

TABLE - 3.1.1.10

I_2 ADSORPTION

DATA FOR MODIFIED LANGMUIR ISOTHERM

Temp. °C	Initial concentration C_o	Concentration at Equilibrium C	Amount of solute adsorbed x	Amount of solvent adsorbed y
303°K	0.03500	0.0174	0.7642	1.3694
	0.04162	0.0240	0.7778	1.1241
	0.05550	0.0380	0.7978	0.7362
	0.06153	0.0460	0.8602	0.5766
323°K	0.03530	0.01753	0.7333	1.3476
	0.04228	0.02437	0.7494	1.0836
	0.05652	0.03851	0.77239	0.6872
	0.06423	0.04475	0.7800	0.5608

TABLE - 3.1.1.11

DATA FOR THE DETERMINATION OF DENSITY OF IODINE SOLUTION.

Temp. ^oK	Strength of I_2 solution.	Weight of water (in g.)	Weight of I_2 solution. (in g.)	Density of I_2 solution.
303	0.296N	50.5355	54.6100	1.0759
	0.356N	50.5355	55.1301	1.0861
	0.484N	50.5355	56.2005	1.1064
	0.542N	50.5355	56.7755	1.1186
323	0.296N	50.1200	54.0255	1.0650
	0.356N	50.1200	54.2325	1.0691
	0.484N	50.1200	55.1565	1.0873
	0.542N	50.1200	55.7495	1.0990
343	0.296N	49.7615	53.6415	1.0540
	0.356N	49.7615	53.8435	1.0580
	0.484N	49.7615	54.8245	1.0772
	0.542N	49.7615	55.7155	1.0947
363	0.296N	49.1307	52.9290	1.0409
	0.356N	49.1307	53.1035	1.0444
	0.484N	49.1307	54.0895	1.0638
	0.542N	49.1307	55.0880	1.0834

TABLE - 3.1.2.1

DATA FOR ADSORPTION ISOBARS.(CH_3COOH).

Concentration (in normality)	Temperature °K	Coverage θ (amount adsorbed) in g.
	363	0.1595
	353	0.1580
.50	343	0.1775
	333	0.1820
	323	0.1960
	313	0.1595
	303	0.1590
	363	0.1500
	353	0.1500
	343	0.1665
.40	333	0.1705
	323	0.1892
	313	0.1500
	303	0.1499

TABLE - 3.1.2.1 (Contd.)

DATA FOR ADSORPTION ISOBARS. (CH_3COOH).

Concentration (in normality)	Temperature °K	Coverage θ (amount adsorbed) in g.
.30	363	0.1250
	353	0.1250
	343	0.1230
	333	0.1210
	323	0.1205
	313	0.1250
	303	0.1240
20	363	0.1080
	353	0.1090
	343	0.0900
	333	0.0905
	323	0.1090
	313	0.1082
	303	0.0900
105	363	0.1030
	353	0.1050
	343	0.0850
	333	0.1055
	323	0.1040
	313	
	303	0.0820

TABLE - 3.1.2.2

DATA FOR ADSORPTION ISOBARS. (I_2).

Equilibrium concentration (in normality)	TEMPERATURE °K.	Amount adsorbed x/m (in g.) or θ = Coverage
.375	363	0.8900
	353	0.9030
	343	0.8650
	333	0.8980
	323	0.9230
	313	0.8650
	303	0.8800
.350	363	0.8540
	353	0.8450
	343	0.8390
	333	0.8450
	323	0.8580
	313	0.8400
	303	0.8450
.30	363	0.8150
	353	0.7830
	343	0.8060
	333	0.7870
	323	0.7900
	313	0.8100
	303	0.7860

TABLE - 3.1.2.2 (Contd.)

DATA FOR ADSORPTION ISOBARS. (I_2)

Equilibrium concentration (in normality)	TEMPERATURE °K.	Amount adsorbed x/m (in g.) or θ = Coverage
.25	363	0.7970
	353	0.7490
	343	0.7880
	333	0.7520
	323	0·7550
	313	0·7940
	303	0·7400
.15	363	0.7830
	353	0.7050
	343	0.7690
	333	0.7200
	323	0.7180
	313	0.7720
	303	0.6980

TABLE - 3.1.3.1

DATA FOR ADSORPTION ISOSTERES.(CH_3COOH).

Coverage = θ (or x/m)	Temperature °K	Concentration C
0.145 g.	363	0.375
	353	0.365
	343	0.340
	333	0.342
	323	0.340
	313	0.365
	303	0.370
0.135 g.	363	0.334
	353	0.326
	343	0.322
	333	0.325
	323	0.340
	313	0.331
	303	0.325
0.125 g.	363	0.300
	353	0.301
	343	0.305
	333	0.305
	323	0.320
	313	0.300
	303	0.301
0.115 g.	363	0.251
	353	0.251
	343	0.285
	333	0.290
	323	0.261
	313	0.250
	303	0.285

TABLE - 3.1.3.1 (Contd.)

DATA FOR ADSORPTION ISOSTERES.(CH_3COOH).

Coverage = θ (or x/m)	Temperature °K	Concentration C
0.105 g.	363	0.175
	353	0.155
	343	0.265
	333	0.270
	323	0.140
	313	0.160
	303	0.260

TABLE - 3.1.3.2

DATA FOR ADSORPTION ISOSTERES.(I_2))

Coverage = θ (or x/m)	Temperature °K	Equilibrium concentration
	363	
	353	
0.875 g.	343	0.382
	333	0.367
	323	0.358
	313	0.383
	303	0.373
	363	0.3490
	353	0.3540
0.850 g.	343	0.3620
	333	0.354
	323	0.347
	313	0.360
	303	0.353
	363	0.315
	353	0.338
	343	0.334
0.825 g.	333	0.337
	323	0.332
	313	0.330
	303	0.334

TABLE - 3.1.3.2 (Contd.)

DATA FOR ADSORPTION ISOSTERES.(I_2)

Coverage = θ (or x/m)	Temperature ^{o}K	Equilibrium concentration
0.800 g.	363	0.262
	353	0.318
	343	0.285
	333	0.314
	323	0.310
	313	0.271
	303	0.313
0.7900 g.	363	0.225
	353	0.309
	343	0.260
	333	0.305
	323	0.300
	313	0.235
	303	0.304

TABLE - 3.1.4.1

DATA FOR ISOSTERIC HEAT OF ADSORPTION.(CH_3COOH).

θ or (x/m) Coverage.	Data derived from the region of isosteres	Concentration C (In normality).	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{st} KCals/mole
0.145g.	Full line (Right)	0.342	-0.4659	343.0	2.9154	1.68 KCals/mole
		0.344	-0.4634	343.5	2.9112	
		0.346	-0.4609	344.0	2.9069	
		0.350	-0.4559	345.0	2.8985	
		0.353	-0.4522	346.0	2.8901	
		0.356	-0.4485	347.0	2.8818	
		0.358	-0.4461	348.0	2.8735	
		0.360	-0.4436	349.0	2.8653	
		0.3615	-0.4418	350.0	2.8571	
		0.363	-0.4400	351.0	2.8490	
		0.3645	-0.4383	352.0	2.8409	
		0.367	-0.4353	354.0	2.8248	
		0.368	-0.4341	355.0	2.8169	
		0.370	-0.4317	357.0	2.8011	

TABLE - 3.1.4.1 (Contd)

DATA FOR ISOSTERIC HEAT OF ADSORPTION.(CH_3COOH).

θ or (x/m) Coverage.	Data derived from the region of isosteres	Concentration C (In normality).	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{st} KCals/mole
0.135 g.	Full line (Left)	0.3255	-0.4874	304	3.2894	0.44 KCals per mole
		0.3259	-0.4869	305	3.2786	
		0.3265	-0.4861	306	3.2679	
		0.3270	-0.4864	307	3.2573	
		0.3275	-0.4847	308	3.2467	
		0.3280	-0.4841	309	3.2362	
		0.3285	-0.4834	310	3.2258	
		0.3295	-0.4821	311	3.2154	
		0.3305	-0.4808	313	3.1948	
		0.3325	-0.4782	315	3.1746	
		0.3330	-0.4775	316	3.1645	
		0.3339	-0.4763	317	3.1545	
		0.3349	-0.4750	318	3.1446	
		0.3355	-0.4743	319	3.1347	
		0.3365	-0.4730	320	3.1250	
		0.3375	-0.4717	321	3.1152	
		0.3385	-0.4704	322	3.1055	
		0.3400	-0.4685	323	3.0959	

TABLE - 3.1.4.1 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION.(CH_3COOH).

θ or (x/m) Coverage.	Data derived from the region of isosteres.	Concentration C (in normality).	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{st} KCals/mole
0.135 g.	Full line (Right)	0.3220	-0.4921	343	2.9154	0.4395 KCals/mole
		0.3230	-0.4907	345	2.8985	
		0.3235	-0.4901	346	2.8901	
		0.3239	-0.4895	347	2.8818	
		0.3242	-0.4891	348	2.8735	
		0.3250	-0.4881	350	2.8571	
		0.3255	-0.4874	351	2.8490	
		0.3270	-0.4854	354	2.8248	
		0.3280	-0.4841	355	2.8169	
		0.3297	-0.4818	357	2.8011	
		0.3305	-0.4808	358	2.7932	
		0.3313	-0.4797	359	2.7855	
		0.3320	-0.4788	360	2.7777	
		0.3328	-0.4778	361	2.7700	
		0.3334	-0.4770	362	2.7624	
0.125 g.	Full line (Middle)	0.3030	-0.5185	314	3.1847	0.9914 KCals/mole
		0.3055	-0.5149	315	3.1746	
		0.3080	-0.5114	316	3.1645	
		0.3100	-0.5086	317	3.1545	
		0.3120	-0.5058	318	3.1446	
		0.3140	-0.5030	319	3.1347	
		0.3152	-0.5014	320	3.1250	
		0.3170	-0.4989	321	3.1152	
		0.3180	-0.4975	322	3.1055	
		0.320	-0.4948	323	3.0959	

TABLE - 3.1.4.1 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION.(CH_3COOH).

θ or (x/m) Coverage.	Data derived from the region of isosteres.	Concentration C (in normality).	log C	T°K	$\frac{1}{T}$ x 10^3	q_{st} KCals/mole
0.115 g.	Full line (Middle)	0.2520	-0.5985	314	3.1847	1.4259 KCals/mole
		0.2532	-0.5965	315	3.1746	
		0.2555	-0.5926	317	3.1545	
		0.2565	-0.5909	318	3.1446	
		0.2579	-0.5885	319	3.1347	
		0.2589	-0.5868	320	3.1250	
		0.2600	-0.5850	321	3.1152	
		0.2610	-0.5833	322	3.1055	
		0.2670	-0.5734	324	3.0864	
		0.2715	-0.5662	325	3.0769	
		0.2750	-0.5606	326	3.0674	
		0.2780	-0.5559	327	3.0581	
		0.2800	-0.5528	328	3.0487	
		0.2825	-0.5489	329	3.0395	
		0.2850	-0.5451	330	3.0303	
		0.2870	-0.5421	331	3.0211	
		0.2885	-0.5398	332	3.0120	
		0.2900	-0.5376	333	3.0030	
0.105 g.		0.1740	-0.7594	323	3.0959	7.4469 KCals/mole
		0.1940	-0.7121	324	3.0864	
		0.2080	-0.6819	325	3.0769	
		0.2200	-0.6575	326	3.0674	
		0.2280	-0.6420	327	3.0581	
		0.2365	-0.6261	328	3.0487	
		0.2460	-0.6090	329	3.0395	
		0.2525	-0.5977	330	3.0303	
		0.2600	-0.5850	331	3.0211	
		0.2658	-0.5754	332	3.0120	
		0.2700	-0.5686	333	3.0030	

TABLE - 3.1.4.2

DATA FOR ISOSTERIC HEAT OF ADSORPTION. (I_2).

Coverage (amount of I_2 adsorbed/g. (x/m.)	Data derived from the region of isosteres.	Concentration C (in normality)	log C	T^0K	$\frac{1}{T} \times 10^3$	q_{iso} KCals per mole
0.875 g.	Full line (Middle)	0.355	-0.4497	324.0	3.0864	0.7080 KCals/mole
		0.360	-0.4436	325.2	3.0750	
		0.361	-0.4424	326.5	3.0627	
		0.362	-0.4412	327.5	3.0534	
		0.363	-0.4400	329.0	3.0395	
		0.364	-0.4388	330.0	3.0303	
		0.365	-0.4377	331.0	3.0211	
		0.366	-0.4365	332.0	3.0120	
		0.367	-0.4353	333.0	3.0030	
		0.369	-0.4329	334.5	2.9895	
		0.371	-0.4306	336.0	2.9761	
		0.372	-0.4294	336.9	2.9682	
		0.374	-0.4271	338.0	2.9585	
		0.375	-0.4259	339.0	2.9498	
		0.377	-0.4236	340.0	2.9411	
		0.3785	-0.4219	341.0	2.9315	
		0.380	-0.4202	342.0	2.9239	
		0.382	-0.4179	343.0	2.9154	

TABLE - 3.1.4.2 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION. (I_2)

Coverage (amount of I_2 adsorbed/g. x/m.	Data derived from the region of isosteres.	Concentration C (in normality)	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{iso} KCals per mole
		0.347	-0.4596	323.0	3.0959	
		0.348	-0.4584	325.1	3.0759	
		0.349	-0.4571	326.8	3.0599	
		0.350	-0.4559	328.0	3.0487	
		0.351	-0.4546	329.8	3.0321	
		0.352	-0.4534	331.0	3.0211	
		0.353	-0.4522	332.4	3.0084	
0.850 g.	Full line	0.354	-0.4509	333.0	3.0030	0.49195
	(Middle)	0.355	-0.4497	334.8	2.9868	KCals/mole
		0.356	-0.4485	335.8	2.9779	
		0.357	-0.4473	337.0	2.9673	
		0.358	-0.4461	338.0	2.9585	
		0.359	-0.4449	339.2	2.9481	
		0.360	-0.4436	340.2	2.9394	
		0.362	-0.4412	342.0	2.9239	

TABLE - 3.1.4.2 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION. (I_2).

Coverage (amount of I_2 adsorbed/g. x/m.	Data derived from the region of isosteres.	Concentration C (in normality)	log C	T°K	$\frac{1}{T} \times 10^3$	q_{iso} KCals per mole
		0.271	-0.5670	313.0	3.1948	
		0.276	-0.5590	314.0	3.1847	
		0.279	-0.5543	314.5	3.1796	
		0.282	-0.5497	315.0	3.1746	
		0.285	-0.5451	315.5	3.1695	
		0.287	-0.5421	316.0	3.1645	
		0.289	-0.5391	316.5	3.1595	
		0.291	-0.5361	317.0	3.1545	
		0.293	-0.5331	317.5	3.1496	
0.80 g.	Full line (Left)	0.2945	-0.5309	318.0	3.1446	2.2142 KCals/mole
		0.296	-0.5287	318.5	3.1397	
		0.2975	-0.5265	319.0	3.1347	
		0.300	-0.5228	320.0	3.1250	
		0.303	-0.5185	321.0	3.1152	
		0.306	-0.5142	322.0	3.1055	
		0.308	-0.5114	323.0	3.0959	
		0.311	-0.5072	325.0	3.0769	
		0.312	-0.5058	328.0	3.0487	
		0.313	-0.5044	330.0	3.0393	
		0.314	-0.5030	333.0	3.0030	

TABLE - 3.1.4.2 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION. (I_2)

Coverage (amount of I_2 adsorbed/g. x/m.	Data derived from the region of isosteres.	Concentration C (in normality)	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{iso} KCals per mole
		0.285	-0.5451	343.0	2.9154	
		0.286	-0.5436	344.0	2.9069	
		0.290	-0.5376	344.5	2.9027	
		0.294	-0.5316	345.0	2.8985	
		0.296	-0.5287	345.5	2.8943	
		0.298	-0.5257	346.0	2.8901	
		0.300	-0.5228	346.5	2.8860	
0.80 g.	Full line (Right)	0.301	-0.5214	347.0	2.8818	2.7065 KCals/mole
		0.303	-0.5185	347.5	2.8776	
		0.305	-0.5157	348.0	2.8735	
		0.306	-0.5142	348.5	2.8694	
		0.308	-0.5114	349.0	2.8653	
		0.310	-0.5086	350.0	2.8571	
		0.3125	-0.5051	351.0	2.8490	
		0.315	-0.5016	352.0	2.8409	
		0.316	-0.5003	354.0	2.8248	

TABLE - 3.1.4.2 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION. (I_2)

Coverage (amount of I_2 adsorbed/g. x/m.	Data derived from the region of isosteres.	Concentration C (in normality)	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{iso} KCals per mole
	0.260	-0.5850	343.0			
		0.260	-0.5850	343.0	2.9154	
		0.271	-0.5670	344.0	2.9069	
		0.276	-0.5590	344.5	2.9027	
		0.279	-0.5543	345.0	2.8985	
		0.282	-0.5497	345.5	2.8943	
		0.284	-0.5466	346.0	2.8901	
0.79	Full line	0.286	-0.5436	346.5	2.8860	3.0926
	(Right)	0.288	-0.5406	347.0	2.8818	KCals/mole
		0.293	-0.5331	348.0	2.8735	
		0.295	-0.5301	348.5	2.8694	
		0.297	-0.5272	349.0	2.8653	
		0.301	-0.5214	350.0	2.8571	
		0.305	-0.5157	351.5	2.8449	
		0.306	-0.5142	352.0	2.8409	
		0.309	-0.5100	353.0	2.8328	

TABLE - 3.1.4.2 (Contd.)

DATA FOR ISOSTERIC HEAT OF ADSORPTION.(I_2).

Coverage (amount of I_2 adsorbed/g. x/m.	Data derived from the region of Isosteres.	Concentration C (in normality).	log C	T^oK	$\frac{1}{T} \times 10^3$	q_{iso} KCals per mole
0.79 g.	Full line (Left)	0.241	-0.6179	314	3.1847	2.9417 KCals/mole
		0.255	-0.5934	315	3.1746	
		0.260	-0.5850	315.4	3.1705	
		0.266	-0.5751	316.0	3.1645	
		0.270	-0.5686	316.5	3.1595	
		0.275	-0.5606	317.0	3.1545	
		0.280	-0.5528	318.0	3.1446	
		0.285	-0.5451	319.0	3.1347	
		0.290	-0.5376	320.0	3.1250	
		0.293	-0.5331	321.0	3.1152	
		0.295	-0.5301	321.5	3.1104	
		0.297	-0.5272	322.2	3.1036	
		0.300	-0.5228	324.0	3.0864	
		0.301	-0.5214	327.0	3.0581	
		0.303	-0.5185	329.0	3.0395	
		0.304	-0.5171	331.0	3.0211	
		0.305	-0.5157	333.0	3.0030	

APPENDIX II

TABLE - 3.2.1.1

Weight of the adsorbent = 0.5 g.

Strength of I_2 solution = 0.1828 N.

Volume of I_2 solution = 50 ml.

PH of I_2 solution = 3.1

Temp. = 28°C ± 2°C.

Strength of $Na_2s_2O_3$ solution = 0.2N

Time in minute	Volume of $Na_2S_2O_3$ solution required.	$x \rightarrow$ amount of I_2 adsorbed by carbon g.	V or x/m	$\frac{1}{V}$	$\frac{1}{t}$	$\frac{t}{V}$
0.0	45.7	-	-	-	-	-
2.0	23.6	0.5619	1.1226	0.8907	0.50	1.7814
3.0	23.3	0.5689	1.1379	0.8787	0.33	2.6363
4.0	23.0	0.5765	1.1531	0.8671	0.25	3.4234
5.0	22.9	0.5791	1.1582	0.8633	0.20	4.3168
6.0	22.8	0.5816	1.1633	0.8596	0.16	5.1576
8.0	22.7	0.5842	1.1684	0.8558	0.12	6.8469
10.0	22.4	0.5918	1.1836	0.8448	0.10	8.4485
15.0	22.3	0.5943	1.1887	0.8412	0.06	12.6186
20.0	22.3	0.5943	1.1887	0.8412	0.05	16.8248
25.0	22.3	0.5943	1.1887	0.8412	0.04	21.0310
30.0	22.3	0.5943	1.1887	0.8412	0.03	25.2372

Value of γ = 0.094

and δ = 0.85

TABLE - 3.2.1.2

Wt of adsorbent = 0.5 g.
Volume of adsorbate (CH_3COOH) = 25 ml
Strength of CH_3 COOH = 0.5191N
Strength of alkali(NaOH) = .2027N
PH of CH_3COOH solution = 2.3
temp of the experiment = $28^oC \pm 2^oC$.

t time in min.	Volume of NaoH solution required.	X ⟶ amount CH_3COOH adsorbed g.	V or x/m	$\frac{I}{V}$	$\frac{I}{t}$	$\frac{t}{V}$
0.0	64.0	-	-	-	-	-
2.0	45.8	0.2213	0.4426	2.2588	.50	4.5177
2.5	45.7	0.2225	0.4451	2.2465	.40	5.6163
3.0	45.6	0.2237	0.4475	2.2343	.33	6.7029
3.5	45.3	0.2274	0.4548	2.1984	.28	7.6946
4.0	45.0	0.2310	0.4621	2.1637	.25	8.6550
4.5	44.6	0.2359	0.4718	2.1091	.22	9.5362
5.0	44.6	0.2357	0.4718	2.1091	.20	10.5957
6.0	44.2	0.2408	0.4816	2.0763	.16	12.4580
8.0	44.1	0.2420	0.4840	2.0659	.12	16.5273
10.0	44.0	0.2432	0.4864	2.0555	.10	20.5550
15.0	44.0	0.2432	0.4864	2.0555	.06	30.8325
20.0	44.0	0.2432	0.4864	2.0555	.05	41.4100

Value of γ = 0.52
and δ = 2.00

TABLE - 3.2.1.3

Wt of the adsorbent = 0.5 g.

Strength of $KMno_4$ solution = 0.6055N

Strength of this sulphate solution = 0.254N

Volume of $KMnO_4$ taken = 25 ml

PH of the $KMnO_4$ solution = 7.2

temp = 28°C ± 2°C

Time in minute	Volume of $Na_2S_2O_3$ solution	X ⟶ amount of $KMno_4$ adsorbed(g)	V or x/m	$\frac{I}{V}$	$\frac{I}{t}$	$\frac{t}{v}$
0	59.6	-	-	-	-	-
2	18.8	0.3275	1.5263	0.6551	.50	3.0526
3	17.2	0.3404	0.6808	1.4687	.33	4.4062
4	17.1	.3412	0.6824	1.465	.25	5.8611
5	16.6	.3452	0.6804	1.4482	.20	7.2412
6	16.3	.3476	0.6953	1.4382	.16	8.6292
7	15.8	.3516	0.7033	1.4217	.14	9.9525
8	15.7	.3524	0.7049	1.4185	.12	11.3484
9	15.0	.3580	0.7161	1.3962	.11	12.5666
10	14.9	.3558	0.7177	1.3931	.10	13.9317
15	11.8	.3837	0.7675	1.3028	.06	19.5422
20	11.8	.3837	0.7675	1.3028	.05	26.0560
25	11.8	.3837	0.7675	1.3028	.04	32.5700

Value of γ = 0.29

and δ = 1.375

TABLE - 3.2.1.4

Strength of phenol solution = 400 mg/litre.
volume of phenol solution taken = 200 ml.
Strength of $Na_2S_2O_3$ solution = 0.01082N
Strength of $KBrO_3$-KBr solution = 0.1N
wt of carbon = 0.5 g.
pH of phenol solution = 6.5
Temp. = 28° ± 2°C.

Time in min.	Volume of (.1N) $KBrO_3$-KBr solution required.	Volume of $Na_2S_2O_3$ solution required.	Difference.	Amount of phenol unadsorbed.	Total amount of phenol unadsorbed.	Amount of phenol adsorbed in mg.	V or x/m.	1/V	1/t	t/V
2	14.3	42.5	10.05	13.40	21.03	58.96	0.1179	8.480	0.50	16.9600
3	12.7	37.0	9.00	12.00	18.84	61.16	0.1223	8.1752	0.33	24.5250
4	10.4	19.2	8.48	11.30	17.75	62.24	0.1244	8.0323	0.25	32.1292
5	10.2	19.1	8.29	11.05	17.35	62.64	0.1252	7.9813	0.20	39.9065
6	9.8	15.6	8.24	10.98	17.24	62.75	0.1255	7.9680	0.16	47.8080
8	9.2	13.4	7.86	10.48	16.45	63.54	0.1270	7.8682	0.12	62.9461
10	9.4	20.7	7.33	9.77	15.34	64.65	0.1293	7.7330	0.10	77.3300
15	9.5	22.0	7.30	9.73	15.28	64.71	0.1294	7.7250	0.06	115.8860
20	10.0	28.0	7.20	9.60	15.07	64.92	0.1298	7.7008	0.05	154.0167
25	10.1	30.0	7.10	9.46	14.86	65.13	0.1302	7.6760	0.04	191.9020
30	10.65	36.5	7.00	9.33	14.65	65.34	0.1306	7.6514	0.03	229.5440

Value of γ = 1.62
and δ = 7.65

TABLE - [illegible].1.[illegible]

Strength of $KClo_4$ solution = 0.5N

Strength of KCNS solution = .097N

Strength of $AgNO_3$ solution = 0.IN

Volume of $KClo_4$ taken = 30 ml.

Wt of the adsorbent = 0.5 g.

Temp. of the experiment = 28°C ± 2°C

Time in min.	Volume of KCNS requir-ed. in ml.	Volume $AgNO_3$ requir-ed. in ml.	Amount of Cl_2 obtai-ned after adsorp-tion.	Amount of Cl_2 adsor-bed.	V or x/m	$\frac{I}{V}$	$\frac{I}{t}$	$\frac{t}{V}$
2	8.730	16.270	0.058	.0079	.0158	63.1672	.50	126.33
2.5	8.827	16.173	0.058	.0082	.0165	60.4982	.40	151.24
3.0	8.924	16.076	0.057	.0086	.0178	58.0457	.33	174.13
4.0	9.118	15.882	0.057	.0093	.0186	53.6924	.25	214.00
5.0	9.215	15.785	0.056	.0096	.0193	51.7517	.20	258.75
6.0	9.312	15.688	0.056	.0100	.0200	49.9465	.16	299.69
8.0	9.409	15.591	0.056	.0103	.0207	48.2630	.12	386.10
10.0	9.506	15.494	0.055	.0107	.0214	46.6892	.10	466.89
12.0	9.797	15.203	0.054	.0117	.0235	42.5289	.08	510.34
15.0	9.894	15.106	0.054	.0121	.0242	41.3021	.06	619.53
20.0	10.088	14.912	0.053	.0128	.0256	39.0493	.05	780.98
25.0	10.088	14.912	0.053	.0128	.0256	39.0493	.04	976.23
30.0	10.088	14.912	0.053	.0128	.0256	39.0493	.03	1171.48

Values of γ = 40.00

and δ = 43.75

TABLE - 3.2.2.1

DATA FOR KINETIC PLOTS OF VARIOUS ORDERS.(CH_3COOH).

Temp. ^oK	Time in min.	Equilibrium concentration C (in normality)	$\frac{1}{C}$	$\frac{1}{\sqrt{C}}$	log C	log C+1
	1	0.5730	1.7449	1.3210	-0.2418	0.7581
	2	0.5333	1.8750	1.3693	-0.2730	0.7269
	3	0.5308	1.8837	1.3725	-0.2750	0.7219
	5	0.5277	1.8948	1.3765	-0.2776	0.7223
	7	0.5246	1.9060	1.3806	-0.2801	0.7198
363	10	0.5215	1.9174	1.3847	-0.2827	0.7172
	15	0.5215	1.9174	1.3847	-0.2827	0.7172
	20	0.5215	1.9174	1.3847	-0.2827	0.7172
	25	0.5215	1.9174	1.3847	-0.2827	0.7172
	30	0.5215	1.9174	1.3847	-0.2827	0.7172
	1	0.5277	1.8948	1.3765	-0.2776	0.7223
	2	0.5277	1.8948	1.3765	-0.2776	0.7223
	3	0.5246	1.9060	1.3806	-0.2801	0.7198
	5	0.5215	1.9174	1.3847	-0.2827	0.7172
	7	0.5184	1.9290	1.3888	-0.2853	0.7146
343	10	0.5153	1.9406	1.3930	-0.2879	0.7120
	15	0.5153	1.9406	1.3930	-0.2879	0.7120
	20	0.5153	1.9406	1.3930	-0.2879	0.7120
	25	0.5153	1.9406	1.3930	-0.2879	0.7120
	30	0.5153	1.9406	1.3930	-0.2879	0.7120

TABLE - 3.2.2.1 (Contd.)

DATA FOR KINETIC PLOTS OF VARIOUS ORDERS.(CH_3COOH).

Temp. °K	Time in min.	Equilibrium concentration C (in normality)	$\frac{1}{C}$	$\frac{1}{\sqrt{C}}$	log C	log C+1
323	1	0.5464	1.8301	1.3528	-0.2624	0.7375
	2	0.5339	1.8727	1.3685	-0.2725	0.7274
	3	0.5277	1.8948	1.3765	-0.2776	0.7223
	5	0.5215	1.9174	1.3847	-0.2827	0.7172
	7	0.5184	1.9290	1.3888	-0.2853	0.7146
	10	0.5091	1.9642	1.4015	-0.2931	0.7068
	15	0.5091	1.9642	1.4015	-0.2931	0.7068
	20	0.5091	1.9642	1.4015	-0.2931	0.7068
	25	0.5091	1.9642	1.4015	-0.2931	0.7068
	30	0.5091	1.9642	1.4015	-0.2931	0.7068
303	1	0.5402	1.8511	1.3605	-0.2674	0.7325
	2	0.5402	1.8511	1.3605	-0.2674	0.7325
	3	0.5339	1.8727	1.3685	-0.2725	0.7274
	5	0.5277	1.8948	1.3765	-0.2776	0.7223
	7	0.5246	1.9060	1.3806	-0.2801	0.7198
	10	0.5215	1.9174	1.3847	-0.2827	0.7172
	15	0.5215	1.9174	1.3847	-0.2827	0.7172
	20	0.5215	1.9174	1.3847	-0.2827	0.7172
	25	0.5215	1.9174	1.3847	-0.2827	0.7172
	30	0.5215	1.9174	1.3847	-0.2827	0.7172

TABLE - 3.2.2.2

DATA FOR THE KINETIC PLOTS OF VARIOUS ORDERS.(I_2 adsorption)

Temp. ^oK	Time in min.	Equilibrium concentration. C (in normality)	$\frac{1}{C}$	$\frac{1}{\sqrt{C}}$	log C	log C + 1
363	1	0.4134N	2.4189	1.5553	-0.3836	0.6164
	2	0.4063N	2.4612	1.5688	-0.3911	0.6089
	3	0.4045N	2.4721	1.5723	-0.3930	0.6070
	5	0.4027N	2.4832	1.5758	-0.3950	0.5993
	7	0.3974N	2.5163	1.5863	-0.4007	0.5993
	10	0.3957N	2.5271	1.5897	-0.4026	0.5974
	15	0.3886N	2.5733	1.6041	-0.4104	0.5896
	20	0.3886N	2.5733	1.6041	-0.4104	0.5896
	25	0.3886N	2.5733	1.6041	-0.4104	0.5896
	30	0.3886N	2.5733	1.6041	-0.4104	0.5896
343	1	0.4204	2.3786	1.5422	-0.3763	0.6237
	2	0.4098	2.4402	1.5621	-0.3874	0.6126
	3	0.4063	2.4612	1.5688	-0.3911	0.6089
	5	0.4045	2.4721	1.5723	-0.3930	0.6070
	7	0.3992	2.5050	1.5827	-0.3988	0.6012
	10	0.3974	2.5163	1.5863	-0.4007	0.5993
	15	0.3970	2.5188	1.5871	-0.4012	0.5988
	20	0.3970	2.5188	1.5871	-0.4012	0.5988
	25	0.3970	2.5188	1.5871	-0.4012	0.5988
	30	0.3970	2.5188	1.5871	-0.4012	0.5988

TABLE - 3.2.2.2 (Contd.)

DATA FOR THE KINETIC PLOTS OF VARIOUS ORDERS.(I_2 adsorption)

Temp. °K	Time in min.	Equilibrium concentration C (in normality)	$\frac{1}{C}$	$\frac{1}{\sqrt{C}}$	log C	log C+1
323	1	0.4204	2.3786	1.5422	-0.3763	0.6237
	2	0.4098	2.4402	1.5621	-0.3874	0.6126
	3	0.4063	2.4612	1.5688	-0.3911	0.6089
	5	0.4027	2.4832	1.5758	-0.3950	0.6050
	7	0.3992	2.5050	1.5827	-0.3988	0.6012
	10	0.3957	2.5271	1.5897	-0.4026	0.5974
	15	0.3886	2.5733	1.6041	-0.4104	0.5896
	20	0.3886	2.5733	1.6041	-0.4104	0.5896
	25	0.3886	2.5733	1.6041	-0.4104	0.5896
	30	0.3886	2.5733	1.6041	-0.4104	0.5896
303	1	0.4204	2.3786	1.5422	-0.3763	0.6237
	2	0.4098	2.4402	1.5621	-0.3874	0.6126
	3	0.4063	2.4612	1.5688	-0.3911	0.6089
	5	0.4027	2.4832	1.5758	-0.3950	0.6050
	7	0.3974	2.5163	1.5863	-0.4007	0.5993
	10	0.3957	2.5271	1.5897	-0.4026	0.5974
	15	0.3925	2.5477	1.5961	-0.4881	0.5858
	20	0.3925	2.5477	1.5961	-0.4881	0.5858
	25	0.3925	2.5477	1.5961	-0.4881	0.5858
	30	0.3925	2.5477	1.5961	-0.4881	0.5858

TABLE - 3.2.3.1(a)

CH_3COOH adsorption

Strength of CH_3COOH solution = 0.575N

Strength of NaoH solution = 0.311N

Volume of CH_3COOH taken = 50 ml

Temp. = 363^{o}k

Weight of carbon = 1 g

pH of CH_3COOH = 1.95

Time in min.	Volume of alkali required after adsorption.	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	I/v	I/t	t/v
1	87.0	.1044	.1044	9.5697	1.00	9.5697
2	85.9	.1250	.1250	7.9985	0.50	15.9971
3	85.5	.1324	.1324	7.5479	0.33	22.6439
5	85.0	.1418	.1418	7.0513	0.20	35.2569
7	84.5	.1511	.1511	6.6161	0.14	46.3128
10	84.0	.1604	.1604	6.2314	0.10	62.3146
15	84.0	.1604	.1604	6.2314	0.06	93.4719
20	84.0	.1604	.1604	6.2314	0.05	124.6292
25	84.0	.1604	.1604	6.2314	0.04	155.7865
30	84.0	.1604	.1604	6.2314	0.03	186.9420

Value of γ and δ from the graph

$$\frac{1}{\gamma} = 0.3125$$

$$\frac{1}{\delta} = 0.1587$$

γ = 3.2

δ = 6.3

TABLE - 3.2.3.1(b)

CH_3COOH

Strength of CH_3COOH solution =0.575N

Strength of NaoH solution =0.311N

Volume of CH_3COOH taken = 50 ml

Temp. = 343^0k

Weight of carbon = 1 g.

pH of CH_3COOH = 1.95

Time in min.	Volume of NaoH required after adsorption.	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	85.0	.1418	0.1418	7.0521	1.0	7.0521
2	85.0	.1418	0.1418	7.0521	0.5	14.1043
3	84.5	.1511	0.1511	6.6181	0.33	19.8544
5	84.0	.1604	0.1604	6.2344	0.20	31.1720
7	83.5	.1698	0.1698	5.8892	0.142	41.2249
10	83.0	.1791	0.1791	5.5834	0.10	55.8347
15	83.0	.1791	0.1791	5.5834	0.06	83.7520
20	83.0	.1791	0.1791	5.5834	0.05	111.6694
25	83.0	.1791	0.1791	5.5834	0.04	139.5850
30	83.0	.1791	0.1791	5.5834	0.03	167.5020

Value of γ, δ from the graph.

γ = 3.3

δ = 5.4

$\frac{1}{\gamma}$ = .303

$\frac{1}{\delta}$ = .1851

TABLE - 3.2.3.1(c)

CH_3COOH

Strength of CH_3COOH = 0.575N

Strength of NaoH = 0.311N

Volume of CH_3COOH = 50 ml

Temp. = 323^{o}k

Weight of carbon = 1 g.

pH of CH_3COOH = 1.95

Time in min.	Volume of alkali required after adsorption(in ml)	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	88.0	.0858	0.0858	11.7150	1.0	11.7150
2	86.0	.1231	0.1231	8.1197	0.5	16.2395
3	85.0	.1418	0.1418	7.0513	0.33	21.1541
5	84.0	.1604	0.1604	6.2314	0.20	31.1573
7	83.5	.1698	0.1698	5.8890	0.142	41.2235
10	82.0	.1977	0.1977	5.0557	0.10	55.8235
15	82.0	.1977	0.1977	5.0557	0.06	79.5899
20	82.0	.1977	0.1977	5.0557	0.05	101.1142
25	82.0	.1977	0.1977	5.0557	0.04	126.3928
30	82.0	.1977	0.1977	5.0557	0.03	151.6713

Value of γ and δ from the graph

γ = 6.6

δ = 4.8

$\frac{1}{\gamma}$ = 0.1515

$\frac{1}{\delta}$ = 0.2083

TABLE - 3.2.3.1(d)

CH_3COOH adsorption

Strength of CH_3COOH solution =0.575N

Strength of NaoH solution =0.311N

Volume of CH_3COOH taken = 50 ml

Temp. = 303°k

Weight of carbon = 1 g.

pH of CH_3COOH = 1.95

Blank titration = .92.6 ml

Time of min.	Volume of alkali required after adsorption.	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	87.0	.1044	0.1044	9.5697	1.0	9.5697
2	87.0	.1044	0.1044	9.5697	0.5	19.1394
3	86.0	.1231	0.1231	8.1197	0.33	24.3593
5	85.0	.1418	0.1418	7.0513	0.20	35.2569
7	84.5	.1511	0.1511	6.6161	0.142	46.3128
10.	84.0	.1604	0.1604	6.2314	0.10	62.3146
15	84.0	.1604	0.1604	6.2314	0.06	93.4719
20	84.0	.1604	0.1604	6.2314	0.05	124.6292
25	84.0	.1604	0.1604	6.2314	0.04	155.7865
30	84.0	.1604	0.1604	6.2314	0.03	186.9420

Value of γ and δ from the graph

$\gamma = 7.8$

$\delta = 5.6$

$\frac{1}{\gamma} = 0.1282$

$\frac{1}{\delta} = 0.1785$

Appendix - II

TABLE - 3.2.3.2(a)

CH_3COOH

Strength of CH_3COOH = 0.446N
Strength of alkali = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the expt. = 90°C
Weight of carbon = 1 g.
pH of CH_3COOH = 2.75
Blank titration = 73.4 ml

Time in min.	Volume of alkali required	X → amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	67.0	0.1167	0.1167	8.5667	1.0	8.5667
2	66.0	0.1349	0.1349	7.4087	0.5	14.8174
3	65.0	0.1532	0.1532	6.5267	0.33	19.5802
5	64.5	0.1623	0.1623	6.1600	0.20	30.8003
7	64.0	0.1714	0.1714	5.8324	0.14	40.8268
10	63.0	0.1896	0.1896	5.27159	0.10	52.7159
15	63.0	0.1896	0.1896	5.2715	0.06	79.0738
20	63.0	0.1896	0.1896	5.2715	0.05	105.4351
25	63.0	0.1896	0.1896	5.2715	0.04	131.7897
30	63.0	0.1896	0.1896	5.2715	0.03	158.1477

Value of γ and δ from the graph.

$$\frac{1}{\gamma} = 0.3030$$

$\gamma = 3.3$
$\delta = 5.4$

$$\frac{1}{\delta} = 0.1851$$

Appendix - II

TABLE - 3.2.3.2(b)

CH_2COOH

Strength of CH_3COOH = 0.446N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the expt. = 70°C
Weight of carbon = 1 g.
pH of CH_3COOH = 2.75
Blank titration = 73.4 ml

Time in min.	Volume of alkali required after adsorption	X → amount of of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	68.0	0.0984	0.0984	10.1626	1.0	10.1616
2	66.0	0.1349	0.1349	7.4128	0.5	14.8257
3	66.0	0.1349	0.1349	7.4128	0.33	22.2386
5	64.0	0.1714	0.1714	5.8343	0.20	29.1715
7	64.0	0.1714	0.1714	5.8343	0.142	40.8401
10	63.5	0.1805	0.1805	5.5401	0.10	55.4016
15	63.5	0.1805	0.1805	5.5401	0.06	83.1024
20	63.5	0.1805	0.1805	5.5401	0.05	110.8033
25	63.55	0.1805	0.1805	5.5401	0.04	138.5041
30	63.5	0.1805	0.1805	5.5401	0.03	166.2049

Value of γ and δ

from the graph $\frac{1}{\gamma} = 0.2000$

$\gamma = 5.0$

$\delta = 5.5$ $\frac{1}{\delta} = 0.1818$

Appendix - II

TABLE - 3.2.3.2(c)

CH_3COOH

Strength of CH_3COOH = 0.446N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the expt. = 50°C
pH of the CH_3COOH = 2.75
Weight of carbon = 1 g.
Blank titration = 73.4 ml

Time in min.	Volume of alkali required after adsorption.	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	69.55	0.0702	0.0702	14.2401	1.0	14.2401
2	68.0	0.9984	0.0984	10.1626	0.5	20.3252
3	67.0	0.1167	0.1167	8.5689	0.33	25.7069
5	66.0	0.1349	0.1349	7.4128	0.20	37.0644
7	64.0	0.1714	0.1714	5.8343	0.14	40.8401
10	63.0	0.1896	0.1896	5.2742	0.10	52.7426
15	63.0	0.1896	0.1896	5.2742	0.06	79.1139
20	63.0	0.1896	0.1896	5.2742	0.05	105.4852
25	63.0	0.1896	0.1896	5.2742	0.04	131.8565
30	63.0	0.1896	0.1896	5.2742	0.03	158.2278

Value of γ and δ

from the graph $\frac{1}{\gamma} = 0.1182$

$\gamma = 8.46$

$\delta = 5.8$ $\frac{1}{\delta} = 0.1724$

Appendix - II

TABLE - 3.2.3.2(d)

CH_3COOH

Strength of CH_3COOH = 0.446N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the experiment = 30°C
pH of the CH_3COOH = 2.75
Weight of carbon = 1 g.
Blank titration = 73.4 ml

Time in min.	Volume of alkali required after adsorption	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	68.0	0.0984	0.0984	10.1626	1.0	10.1626
2	68.0	0.0984	0.0984	10.1626	0.5	20.3252
3	67.0	0.1167	0.1167	8.5689	0.33	25.7069
5	66.0	0.1349	0.1349	7.4128	0.20	37.0644
7	64.0	0.1714	0.1714	5.8343	0.42	40.8401
10	63.0	0.1896	0.1896	5.2742	0.10	52.7426
15	63.0	0.1896	0.1896	5.2742	0.06	79.1139
20	63.0	0.1896	0.1896	5.2742	0.05	105.4852
25	63.0	0.1896	0.1896	5.2742	0.04	131.8565
30	63.0	0.1896	0.1896	5.2742	0.03	158.2278

Value of γ and δ

from the graph $\frac{1}{\gamma}$ = 0.0929

γ = 10.78

δ = 5.0 $\frac{1}{\delta}$ = 0.2000

Appendix - II

TABLE - 3.2.3.3 (a)

CH_3COOH

Strength of CH_3COOH = 0.358N

Strength of NaOH = 0.304N

Volume of CH_3COOH solution = 50 ml

Temp. of the expt. = 90°C

Weight of carbon = 1 g.

pH of CH_3COOH = 2.85

Blank titration = 59 ml

Time in min.	Volume of alkali required after adsorption	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	54.0	0.0912	0.0912	10.9649	1.00	10.9649
2	54.0	0.0912	0.0912	10.9649	0.50	21.9298
3	53.5	0.1003	0.1003	9.9681	0.33	29.9043
5	53.0	0.1094	0.1094	9.1374	0.20	45.6871
7	52.5	0.1185	0.1185	8.4345	0.142	59.0418
10	52.0	0.1276	0.1276	7.8320	0.10	78.3208
15	52/0	0.1276	0.1276	7.8320	0.06	117.4812
20	52.0	0.1276	0.1276	7.8320	0.05	156.6416
25	52.0	0.1276	0.1276	7.8320	0.04	195.8020
30	52.0	0.1276	0.1276	7.8320	0.03	234.9600

Value of γ and δ from the graph.

$\frac{1}{\gamma}$ = 0.1515

γ = 6.6

$\frac{1}{\delta}$ = 0.1315

δ = 7.6

Appendix - II

TABLE - 3.2.3.3(b)

CH_2COOH

Strength of CH_3COOH = 0.358N
Strength of NaOH = 0.304N
Volume of CH_3COOH taken = 50 ml
Temp. of the expt. = 70°C
Weight of carbon = 1 g.
pH of CH_3COOH = 2.85
Blank titration = 59.0 ml

Time in min.	Volume of alkali required after adsorption	X $\rightarrow$ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	54.0	0.0912	0.0912	10.9649	1.00	10.9649
2	54.0	0.0912	0.0912	10.9649	0.50	21.9298
3	53.5	0.1003	0.1003	9.9681	0.33	29.9043
5	53.0	0.1094	0.1094	9.1374	0.20	45.6871
7	52.5	0.1185	0.1185	8.4345	0.14	59.0418
10	52.0	0.1276	0.1276	7.8320	0.10	78.3208
15	52.0	0.1276	0.1276	7.8320	0.06	117.4812
20	52.0	0.1276	0.1276	7.8320	0.05	156.6416
25	52.0	0.1276	0.1276	7.8320	0.04	195.8020
30	52.0	0.1276	0.1276	7.8320	0.03	234.96

Value of γ and δ from the graph.

γ = 7.2

δ = 7.5

$\frac{1}{\gamma}$ = 0.1388

$\frac{1}{\delta}$ = 0.1333

Appendix - II

TABLE - 3.2.3.3(c)

CH_3COOH

Strength of CH_3COOH = 0.358N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the expt. = 50°C
pH of CH_3COOH = 2.85
Weight of carbon = 1 g.
Blank titration = 59.0 ml

Time in min.	Volume of alkali required after adsorption	X ⟶ amount of CH_3COOH adsorbed.	x/m	1/v	1/t	t/v
1	56.0	0.05472	0.05472	18.2748	1.00	18.2748
2	54.0	0.0912	0.0912	10.9649	0.50	21.9298
3	54.0	0.0912	0.0912	10.9649	0.33	32.8947
5	53.5	0.1003	0.1003	9.9681	0.20	49.8405
7	53.0	0.1094	0.1094	9.1374	0.14	63.9661
10	52.0	0.1276	0.1276	7.8320	0.10	78.3200
15	52.0	0.1276	0.1276	7.8320	0.06	117.4812
20	52.0	0.1276	0.1276	7.8320	0.05	156.6416
25	52.0	0.1276	0.1276	7.8320	0.04	195.8000
30	52.0	0.1276	0.1276	7.8320	0.03	234.9600

Value of γ and δ from the graph

γ = 10.4
δ = 7.4

$\frac{1}{\gamma}$ = 0.0961
$\frac{1}{\delta}$ = 0.1351

Appendix - II

TABLE - 3.2.3.3(d)

CH_3COOH

Strength of CH_3COOH = 0.358N

Strength of NaOH = 0.304N

Volume of CH_3COOH = 50 ml

pH of CH_3COOH = 2.85

Weight of carbon = 1 g.

Temp. of the expt. = 30°C

Blank titration = 59 ml

Time in min.	Volume of alkali required after adsorption	$X \longrightarrow$ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	56.0	0.0547	0.0547	18.2748	1.0	18.2748
2	56.0	0.0547	0.0547	18.2748	0.5	36.5497
3	55.0	0.0729	0.0729	13.7061	0.33	41.1184
5	54.0	0.0912	0.0912	10.9649	0.2	54.8245
7	53.0	0.1094	0.1094	9.1374	0.14	63.9619
10	52.0	0.1276	0.1276	7.8320	0.10	78.3208
15	52.0	0.1276	0.1276	7.8320	0.06	117.4812
20	52.0	0.1276	0.1276	7.8320	0.05	156.6400
25	52.0	0.1276	0.1276	7.8320	0.04	195.8000
30	52.0	0.1276	0.1276	7.8320	0.03	234.9600

Value of γ and δ from the graph

$\frac{1}{\gamma}$ = 0.0400

γ = 25.0

$\frac{1}{\delta}$ = 0.1562

δ = 6.4

Appendix - II

TABLE - 3.2.3.4(a)

CH_3COOH

Strength of CH_3COOH = 0.243N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the expt. = $363^{o}K$
pH of CH_3COOH = 2.95
Weight of carbon = 1 g.
Blank titration = 40.0 ml.

Time in min.	Volume of alkali required after adsorption	X⟶amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	37.0	0.0547	0.0547	18.2748	1.00	18.2748
2	36.0	0.0729	0.0729	13.7061	0.50	27.4122
3	35.0	0.0912	0.0912	10.9649	0.33	32.8947
5	35.0	0.0912	0.0912	10.9649	0.20	54.8245
7	54.5	0.1003	0.1003	9.9681	0.14	69.7767
10	34.0	0.1094	0.1094	9.1374	0.10	91.3742
15	34.0	0.1094	0.1094	9.1374	0.06	137.0614
20	34.0	0.1094	0.1094	9.1374	0.05	182.7485
25	34.0	0.1094	0.1094	9.1374	0.04	228.4356
30	34.0	0.1094	0.1094	9.1374	0.03	274.1228

Value of γ and δ from the graph.

γ = 10.0

δ = 8.5

$\frac{1}{\gamma}$ = 0.1000

$\frac{1}{\delta}$ = 0.1176

Appendix - II

TABLE - 3.2.3.4(b)

CH_3COOH

Strength of CH_3COOH = 0.243N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Weight of carbon = 1 g.
pH of CH_3COOH = 2.95
Temp. of the expt. = $343^{o}K$
Blank titration = 40 ml

Time in min.	volume of alkali required after adsorption	X⟶amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	38.0	0.0364	0.0364	27.4122	1.00	27.4122
2	37.0	0.0547	0.0547	18.2748	0.50	36.5496
3	36.5	0.0638	0.0638	15.6641	0.33	46.9924
5	36.0	0.0729	0.0729	13.7061	0.10	68.5307
7	35.5	0.0820	0.0820	12.1832	0.142	85.2826
10	35.0	0.0912	0.0912	10.9649	0.10	109.6491
15	35.0	0.0912	0.0912	10.9649	0.06	164.4736
20	35.0	0.0912	0.0912	10.9649	0.05	219.2982
25	35.0	0.0912	0.0912	10.9649	0.04	274.1228
30	35.0	0.0912	0.0912	10.9649	0.03	328.9473

Value of γ and δ
from the graph

γ = 18.4

δ = 9.5

$\frac{1}{\gamma}$ = 0.0543

$\frac{1}{\delta}$ = 0.1052

Appendix - II

TABLE - 3.2.3.4(c)

CH_3COOH

Strength of CH_3COOH = 0.243N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Temp. of the expt. = 323°K
Weight of carbon = 1 g.
pH of CH_3COOH = 2.95
Blank titration = 40.0 ml

Time in min.	Volume of alkali required after adsorption.	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	38.1	0.0346	0.0346	28.8550	1.00	28.8550
2	37.0	0.0547	0.0547	18.2748	0.50	36.5497
3	36.5	0.0638	0.0638	15.6641	0.33	46.9924
5	35.5	0.0820	0.0820	12.1832	0.20	60.9161
7	35.0	0.0912	0.0912	10.9649	0.14	76.7543
10	34.0	0.1094	0.1094	9.1374	0.10	91.3740
15	34.0	0.1094	0.1094	9.1374	0.06	137.0610
20	34.0	0.1094	0.1094	9.1374	0.05	182.7480
25	34.0	0.1094	0.1094	9.1374	0.04	228.4350
30	34.0	0.1094	0.1094	9.1374	0.03	274.1220

Value of γ and δ from the graph.

$\gamma = 20.0$ $\qquad \frac{1}{\gamma} = 0.0500$

$\delta = 8.0$ $\qquad \frac{1}{\delta} = 0.1250$

Appendix - II

TABLE - 3.2.3.4(d)

CH_3COOH

Strength of CH_3COOH = 0.243N
Strength of NaOH = 0.304N
Volume of CH_3COOH = 50 ml
Weight of carbon = 1 g.
pH of CH_3COOH = 2.95
Temp. of the expt. = 303°K
Blank titration = 40.0 ml

Time in min.	Volume of alkali required after adsorption	X ⟶ amount of CH_3COOH adsorbed in g.	x/m	1/v	1/t	t/v
1	38.5	0.0273	0.0273	36.5497	1.00	36.5497
2	38.0	0.0364	0.0364	27.4122	0.50	54.5497
3	37.5	0.0456	0.0456	21.9298	0.33	65.7894
5	37.0	0.0547	0.0547	18.2748	0.20	91.3742
7	36.5	0.0638	0.0638	15.6641	0.14	109.6487
10	35.0	0.0912	0.0912	10.9649	0.10	109.6491
15	35.0	0.0912	0.0912	10.9649	0.06	164.4736
20	35.0	0.0912	0.0912	10.9649	0.05	219.2980
25	35.0	0.0912	0.0912	10.9649	0.04	274.1225
30	35.0	0.0912	0.0912	10.9649	0.03	328.9470

Value of γ and δ from the graph

$\frac{1}{\gamma}$ = 0.0283

γ = 35.3
δ = 10.0

$\frac{1}{\delta}$ = 0.1000

TABLE - 3.2.3.5

KINETIC DATA FOR CH_3COOH ADSORPTION (DATA DERIVED FROM LISZI PLOTS)

TEMP°K	Initial concentration C	γ (from the graph	$\frac{1}{\gamma}$ (Initial rate	δ (from the graph)	$\frac{1}{\delta}$ Limiting adsorption
363°K	0.575N	3.2	0.3125	6.3	0.1587
	0.446N	3.3	0.3030	5.4	0.1851
	0.358N	6.6	0.1515	7.6	0.1315
	0.243N	10.0	0.1000	8.5	0.1176
343°K	0.575N	3.3	0.3030	5.4	0.1851
	0.446N	5.0	0.2000	5.5	0.1818
	0.358N	7.2	0.1388	7.5	0.1333
	0.243N	18.4	0.0543	9.5	0.1052
323°K	0.575N	6.6	0.1515	4.8	0.2083
	0.446N	8.46	0.1182	5.8	0.1724
	0.358N	10.4	0.0961	7.4	0.1351
	0.243N	20.0	0.0500	8.0	0.1250
303°K	0.575N	7.8	0.1282	5.6	0.1785
	0.446N	10.76	0.0929	5.0	0.2000
	0.358N	25.0	0.0400	6.4	0.1562
	0.243N	35.3	0.0283	10.0	0.1000

Appendix - II

TABLE - 3.2.3.6

KINETIC DATA FOR CH_3COOH ADSORPTION

TEMP°K	Initial concentration. C	log C	log C+1	Initial rate $\log \frac{1}{\gamma}$	$\log \frac{1}{\gamma}+2$	'n' Order of adsorption
363°K	0.575N	-0.2403	0.7597	-1.1800	0.8200	1.48
	0.446N	-0.3506	0.6494	-1.3398	0.6602	
	0.358N	-0.4461	0.5539	-1.4782	0.5218	
	0.243N	-0.6143	0.3857	-1.7218	0.2782	
343°K	0.575N	-0.2403	0.7597	-1.2215	0.7785	2.0
	0.446N	-0.3506	0.6494	-1.4415	0.5585	
	0.358N	-0.4461	0.5539	-1.6319	0.3681	
	0.243N	-0.6143	0.3857	-1.9674	0.0326	
323°K	0.575N	-0.2403	0.7597	-0.6231	1.3769	1.07
	0.446N	-0.3506	0.6494	-0.7396	1.2604	
	0.358N	-0.4461	0.5539	-0.8404	1.1596	
	0.243N	-0.6143	0.3857	-1.0179	0.9821	
303°K	0.575N	-0.2403	0.7597	-0.4556	1.5444	1·91
	0.446N	-0.3506	0.6494	-0.6608	1.3392	
	0.358N	-0.4461	0.5539	-0.8385	1.1615	
	0.243N	-0.6143	0.3857	-1.1514	0.8486	

TABLE - 3.2.3.7

DATA FOR (ARRHENIOUS PLOT) ACTIVATION ENERGY(CH_3COOH ADSORPTION)

$T^{o}K$	$\frac{1}{T} \times 10^3$	k	log k	ACTIVATION ENERGY E_a KCals/mole
363	2.7548	6.30×10^{-2}	-1.20 log k+3 = 1.8	5.36 KCal/mole
343	2.9154	4.36×10^{-2}	-1.36 log k+3 = 1.64	
323	3.0959	3.31×10^{-2}	-1.48 log k+3 = 1.52	
303	3.3003	3.01×10^{-2}	-1.52 log k+3 = 1.48	

Appendix - II
TABLE - 3.2.4.1(a)

I_2 adsorption BASIC KINETIC DATA. VARIATION OF I_2 CONCENTRATION WITH TIME DUE TO ADSORPTION OF THE I_2 ON ACTIVATED CARBON.

Strength of I_2 solution = 0.538N
Strength of $Na_2S_2O_3$ solution = 0.177N
pH of I_2 solution = 2.90
Volume of I_2 solution taken = 50 ml
Weight of carbon = 1 g.
Temp. of the expt. = 363°K
Blank titration = 152.2 ml

Time in min.	Volume of $Na_2S_2O_3$ solution	X——Amount of I_2 adsorbed in g.	v or x/m	1/v	1/t	t/v
1	117.0	0.7912	0.7912	1.2638	1.00	1.2638
2	115.0	0.8362	0.8362	1.1958	0.50	2.3917
3	114.5	0.8474	0.8474	1.1799	0.33	3.5399
5	114.0	0.8586	0.8586	1.1645	0.20	5.8227
7	1125	0.8924	0.8924	1.1205	0.14	7.8438
10	112.0	0.9036	0.9036	1.1066	0.10	11.00661
15	110.0	0.9486	0.9486	1.0541	0.06	15.8125
20	110.0	0.9486	0.9486	1.0541	0.05	21.0833
25	110.0	0.9486	0.9486	1.0541	0.04	26.3542
30	110.0	0.9486	0.9486	1.0541	0.03	31.6250

Value of γ and δ from the graph.

$\gamma = 0.18$

$\delta = 1.04$

$\frac{1}{\gamma} = 5.55$

$\frac{1}{\delta} = 0{\cdot}961$

Appendix-II.

TABLE - 3.2.4.1(b)

I_2 adsorption

Strength of I_2 solution = 0.538N
Strength of $Na_2S_2O_3$ solution = 0.177N
pH of I_2 solution = 2.90
Volume of I_2 solution taken = 50 ml
Weight of carbon = 1 g.
Temp. of the expt. = 343°K
Blank titration = 152.2 ml

Time in min.	Volume of $Na_2S_2O_3$ required after adsorption	X⟶Amount of I_2 adsorbed in g.	v or x/m.	1/v	1/t	t/v
1	119.0	0.7463	0.7463	1.3399	1.00	1.3399
2	116.0	0.8137	0.8137	1.2288	0.50	2.4577
3	115.0	0.8362	0.8362	1.1958	0.33	3.5875
5	114.5	0.8474	0.8474	1.1799	0.20	5.8999
7	113.0	0.8811	0.8811	1.1348	0.14	7.9439
10	112.5	0.8924	0.8924	1.1205	0.10	11.2055
15	112.5	0.8924	0.8924	1.1205	0.06	16.8082
20	112.5	0.8924	0.8924	1.1205	0.05	22.4110
25	112.5	0.8924	0.8924	1.1205	0.04	28.0128
30	112.5	0.8924	0.8924	1.1205	0.03	33.6165

Value of γ and δ from the graph

$\gamma = 0.185$

$\delta = 1.12$

$$\frac{1}{\gamma} = 5.405$$

$$\frac{1}{\delta} = \gamma = 0.892$$

Appendix-II

TABLE - 3.2.4.1(c)

I_2 adsorption

Strength of I_2 solution = 0.538N
Strength of $Na_2S_2O_3$ solution = 0.177N

pH of I_2 solution = 2.90

Volume of I_2 solution taken = 50 ml

Weight of carbon = 1 g.
Blank titration = 152.2 ml
Temp. = 323°K

Time in min.	Volume of $N_2S_2O_3$ solution	X⟶Amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	119.0	0.7463	0.7463	1.3399	1.00	1.3399
2	116.0	0.8137	0.8137	1.2288	0.50	2.4577
3	115.0	0.8362	0.8362	1.1958	0.33	3.5875
5	114.0	0.8586	0.8586	1.1645	0.20	5.8227
7	113.0	0.8811	0.8811	1.1348	0.14	7.9439
10	112.0	0.9036	0.9036	1.1066	0.10	11.0661
15	110.0	0.9486	0.9486	1.0541	0.06	15.8125
20	110.0	0.9486	0.9486	1.0541	0.05	21.0833
25	110.0	0.9486	0.9486	1.0541	0.04	26.3542
30	110.0	0.9486	0.9486	1.0541	0.03	31.6250

Value of γ and δ from the graph. $\frac{1}{\gamma} = 5.0$

$\gamma = 0.20$ $\frac{1}{\delta} = 0.952$

$\delta = 1.05$

Appendix-II

TABLE - 3.2.4.1(d)

I_2 adsorption

Strength of I_2 solution = 0.538N
Strength of $Na_2S_2O_3$ solution = 0.177N
pH of I_2 solution = 2.90
volume of I_2 solution taken = 50 ml
Weight of carbon = 1 g.
Temp. of the expt. = 303°K

Blank titration = 152.2 ml

Time in min.	Volume of $Na_2S_2O_3$ required after adsorption	X $\longrightarrow$ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	119.0	0.7463	0.7463	1.3399	1.00	1.3399
2	116.0	0.8137	0.8137	1.2288	0.50	2.6015
3	115.0	0.8362	0.8362	1.1958	0.33	3.5875
5	114.0	0.8586	0.8586	1.1645	0.20	5.8227
7	112.5	0.8924	0.8924	1.1205	0.142	7.8438
10	112.0	0.9036	0.9036	1.1066	0.10	11.0661
15	112.0	0.9036	0.9036	1.1066	0.06	16.5992
20	112.0	0.9036	0.9036	1.1066	0.05	22.1323
25	112.0	0.9036	0.9036	1.1066	0.04	27.6654
30	112.0	0.9036	0.9036	1.1066	0.03	33.1984

Value of γ and δ from the graph

$$\frac{1}{\gamma} = 4.347$$

$\gamma = 0.230$
$\delta = 1.10$

$$\frac{1}{\delta} = 0.909$$

Appendix-II
TABLE - 3.2.4.2 (a)

I_2 adsorption

Strength of I_2 solution = 0.49N

Strength of $Na_2S_2O_3$ = 0.177N

pH of I_2 solution = 3.05

Volume of I_2 solution taken = 50 ml

Weight of carbon = 1 g.

Temp. of the expt. = 363°K

Blank titration = 139.0 ml

Time in min.	Volume of $Na_2S_2O_3$ solution	X → amount of I_2 adsorbed in g.	v or x/m	1/v	1/t	t/v
1	106.0	0.7418	0.7418	1.3480	1.0	1.3480
2	103.5	0.7980	0.7980	1.2531	0.50	2.5062
3	103.0	0.8092	0.8092	1.2357	0.33	3.7071
5	102.5	0.8204	0.8204	1.2187	0.20	6.0939
7	102.0	0.8317	0.8317	1.2023	0.14	8.4162
10	101.5	0.8429	0.8429	1.1862	0.10	11.8629
15	101.0	0.8542	0.8542	1.1706	0.06	17.5602
20	101.0	0.8542	0.8542	1.1706	0.05	23.4136
25	101.0	0.8542	0.8542	1.1706	0.04	29.2670
30	101.0	0.8542	0.8542	1.1706	0.03	35.1204

Value of γ and δ from the graph

$\gamma = 0.19$ $\frac{1}{\gamma} = 5.26$

$\delta = 1.15$ $\frac{1}{\delta} = 0.86$

Appendix - II

TABLE - 3.2.4.2(b)

I_2 adsorption

Strength of I_2 solution = 0. 49N
pH of I_2 solution = 3.05
Volume of I_2 solution taken = 50 ml
Strength of $Na_2S_2O_3$ solutions = 0.177N
Weight of carbon = 1 g.
Temp. of the expt. = $343^{o}K$
Blank titration = 133.00

Time in min.	Volume of $Na_2S_2O_3$ solution	X ⟶ Amount of I_2 adsorption in g.	x/m	1/v	1/t	t/v
1	107.0	0.7193	0.7193	1.3901	1.00	1.3901
2	105.5	0.7755	0.7755	1.2894	0.50	2.5788
3	103.0	0.8092	0.8092	1.2357	0.33	3.7071
5	102.5	0.8204	0.8204	1.2187	0.20	6.0939
7	102.5	0.8317	0.8317	1.2023	0.14	8.4162
10	101.0	0.8542	0.8542	1.1706	0.10	11.7068
15	100.0	0.8766	0.8766	1.1406	0.06	17.1099
20	100.0	0.8766	0.8766	1.1406	0.05	22.8133
25	100.0	0.8766	0.8766	1.1406	0.04	28.5166
30	100.0	0.8766	0.8766	1.1406	0.03	34.2199

Value of γ and δ
from the graph.

$$\frac{1}{\gamma} = 4.34$$

δ = 1.14
γ = 0.23

$$\frac{1}{\delta} = 0.87$$

Appendix - II

TABLE - 3.2.4.2(c)

I_2 adsorption

Strength of I_2 solution = 0.49N Temp. of the expt. = 323°K

pH of I_2 solution = 3.05

Strength of $Na_2S_2O_3$ solution = .177N

Volume of I_2 solution = 50 ml

Weight of carbon = 1 g.

Blank titration = 139.0 ml

Time in min.	Volume of $Na_2S_2O_3$ solution	X ⟶ amount of I_2 adsorbed in g.	v or x/m	1/v	1/t	t/v
1	105.0	0.7642	0.7642	1.3084	1.00	1.3084
2	104.5	0.7755	0.7755	1.2894	0.50	2.5788
3	104.0	0.7867	0.7867	1.2710	0.33	3.8130
5	102.5	0.8204	0.8204	1.2187	0.20	6.0939
7	102.0	0.8317	0.8317	1.2023	0.14	8.4162
10	101.0	0.8542	0.8542	1.1706	0.10	11.7068
15	100.0	0.8766	0.8766	1.1406	0.06	17.1099
20	100.0	0.8766	0.8766	1.1406	0.05	22.8133
25	100.0	0.8766	0.8766	1.1406	0.04	28.5166
30	100.0	0.8766	0.8766	1.1406	0.03	34.2200

Value of γ and δ from the graph

$\gamma = 0.238$ $\frac{1}{\gamma} = 4.20$

$\delta = 1.16$ $\frac{1}{\delta} = 0{\cdot}86$

Appendix - II

TABLE - 3.2.4.2(d)

I_2 adsorption

Strength of I_2 solution = 0.49 N
pH of I_2 solution = 3.05
Volume of I_2 solution = 50 ml
Strength of $Na_2S_2O_3$ solution = .177N
Weight of carbon = 1 g.
Blank titration = 139.0 ml
Temp. of the expt. = 303°K

Time in min.	Volume of $Na_2S_2O_3$ solution	X ⟶ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	107.5	0.7080	0.7080	1.4122	1.00	1.4122
2	106.0	0.7418	0.7418	1.3480	0.50	2.6961
3	103.0	0.8092	0.8092	1.2357	0.33	3.7071
5	102.5	0.8204	0.8204	1.2187	0.20	6.0939
7	102.0	0.8317	0.8204	1.2023	0.142	8.4162
10	101.5	0.8429	0.8429	1.1862	0.10	11.8629
15	101.0	0.8542	0.8542	1.1706	0.06	17.5602
20	101.0	0.8542	0.8542	1.1706	0.05	23.4136
25	101.0	0.8542	0.8542	1.1706	0.04	29.265
30	101.0	0.8542	0.8542	1.1706	0.03	35.118

Values of γ and δ from the graph

$\gamma = 0.24$ $\frac{1}{\gamma} = 4.16$

$\delta = 1.17$ $\frac{1}{\delta} = 0.8547$

Appendix - II

TABLE - 3.2.4.3 (a)

I_2 adsorption

Strength of I_2 solution = 0.36N
pH of the I_2 solution = 3.4
Volume of the I_2 solution taken = 50 ml
Strength of $Na_2S_2O_3$ solution = 0.163N
Weight of carbon = 1 g.
Temp. of the expt. = 363°K
Blank titration = 109.5 ml

Time in min.	Volume of $Na_2S_2O_3$ solution required after adsorption.	$X \longrightarrow$ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	76.5	0.6831	0.6831	1.4638	1.00	1.4638
2	74.0	0.7348	0.7348	1.3607	0.50	2.7215
3	73.0	0.7555	0.7555	1.3234	0.33	3.9704
5	72.5	0.7659	0.7659	1.3055	0.20	6.5280
7	72.0	0.7762	0.7762	1.2881	0.14	9.0172
10	71.5	0.7866	0.7866	1.2712	0.10	12.7123
15	71.5	0.7866	0.7866	1.2712	0.06	19.0684
20	71.5	0.7866	0.7866	1.2712	0.05	25.4246
25	71.5	0.7866	0.7866	1.2712	0.04	31.7808
30	71.5	0.7866	0.7866	1.2712	0.03	38.1369

Value of γ and δ
from the graph.

$\gamma = 0.21$ $\quad \frac{1}{\gamma} = 4.76$

$\delta = 1.25$ $\quad \frac{1}{\delta} = 0.80$

Appendix - II

TABLE - 3.2.4.3(b)

I_2 adsorption

Strength of I_2 solution = 0.36N

pH of I_2 solution = 3.4

Volume of I_2 solution taken = 50 ml

Strength of $Na_2S_2O_3$ solution = 0.163N

Blank titration = 109.5

Temp. of the expt = 343°K

Weight of carbon = 1 g.

Time in min.	Volume of $Na_2S_2O_3$ required	X ⟶ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	76.5	0.6831	0.6831	1.4638	1.00	1.4638
2	74.0	0.7348	0.7348	1.3607	0.50	2.7215
3	73.0	0.7555	0.7555	1.3234	0.33	3.9704
5	72.0	0.7762	0.7762	1.2881	0.20	6.4409
7	71.5	0.7866	0.7866	1.2712	0.14	8.8986
10	71.0	0.7969	0.7969	1.2547	0.10	12.5472
15	71.0	0.7969	0.7969	1.2547	0.06	18.8208
20	71.0	0.7969	0.7969	1.2547	0.05	25.0947
25	71.0	0.7969	0.7969	1.2547	0.04	31.3684
30	71.0	0.7969	0.7969	1.2547	0.03	37.6420

Value of γ and δ from the graph

$\gamma = 0.25 \quad \frac{1}{\gamma} = 4.00$

$\delta = 1.23 \quad \frac{1}{\delta} = 0.813$

Appendix - II

TABLE - 3.2.4.3(c)

I_2 adsorption

Strength of I_2 solution = 0.36
pH of I_2 solution = 3.4
Volume of I_2 solution taken = 50 ml
Strength of $Na_2S_2O_3$ solution = 0.163N

Weight of carbon = 1 g.
Temp. of the expt. = 323°K
Blank titration = 109.5

Time in min.	Volume of $Na_2S_2O_3$ required after adsorption.	X⟶amount of I_2 adsorption in g.	x/m	1/v	1/t	t/v
1	79.0	0.6313	0.6313	1.5838	1.00	1.5838
2	75.5	0.7038	0.7038	1.4207	0.50	2.8415
3	75.0	0.7141	0.7141	1.4001	0.33	4.2003
5	74.5	0.7245	0.7245	1.3801	0.20	6.9005
7	74.0	0.7348	0.7348	1.3607	0.14	9.5252
10	73.0	0.7555	0.7555	1.3234	0.10	13.2347
15	73.0	0.7555	0/7555	1.3234	0.06	19.8521
20	73.0	0.7555	0.7555	1.3234	0.05	26.4695
25	73.0	0.7555	0.7555	1.3234	0.04	33.0868
30	73.0	0.7555	0.7555	1.3234	0.03	39.7020

Value of γ and δ
from the graph

$\frac{1}{\gamma} = 0.26$ $\qquad \frac{1}{\gamma} = 3.8461$

$\frac{1}{\delta} = 1.32$ $\qquad \frac{1}{\delta} = 0.7575$

Appendix - II

TABLE - 3.2.4.3 (d)

I_2 adsorption

Strength of I_2 solution = 0.36N
pH of I_2 solution = 3.4
Volume of I_2 solution taken = 50 ml
Strength of $Na_2S_2O_3$ solution = 0.163N

Time in min.	Volume of $Na_2S_2O_3$ required	X$\longrightarrow$amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	79.0	0.6313	0.6313	1.5838	1.00	1.5838
2	76.0	0.6934	0.6934	1.4419	0.50	2.8838
3	74.5	0.7245	0.7245	1.3801	0.33	4.1403
5	74.0	0.7348	0.7348	1.3607	0.20	6.8037
7	73.5	0.7452	0.7452	1.3418	0.142	9.3929
10	73.0	0.7555	0.7555	1.3234	0.10	13.2347
15	73.0	0.7555	0.7555	1.3234	0.06	19.8520
20	73.0	0.7555	0.7555	1.3234	0.05	26.4780
25	73.0	0.7555	0.7555	1.3234	0.04	33.0906
30	73.0	0.7555	0.7555	1.3234	0.03	39.7020

Value of γ and δ
from the graph

$\gamma = 0.28 \quad \frac{1}{\gamma} = 3.5714$

$\delta = 1.3 \quad \frac{1}{\delta} = 0.7692$

TABLE - 3.2.4.4 (a)

I_2 adsorption

Strength of I_2 solution =0.264N
pH of ... =4.7
Temp. of the expt. = 363°K
Strength of thiosulphate solution =.203N

m = Weight of carbon = 1 g.
Volume of I_2 solution = 50 ml
Blank titration = 65.0 ml

Time in min.	Volume of $Na_2S_2O_3$ solution required after adsorption	$X \rightarrow$ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	39.5	0.6574	0.6574	1.5211	1.00	1.5211
2	37.0	0.7218	0.7218	1.3852	0.50	2.7705
3	36.0	0.7476	0.7476	1.3375	0.33	4.0125
5	35.0	0.7734	0.7734	1.2929	0.20	6.4647
7	35.0	0.7734	0.7734	1.2929	0.14	9.0505
10	34.5	0.7863	0.7863	1.2717	0.10	12.7174
15	34.5	0.7863	0.7863	1.2717	0.06	19.0761
20	34.5	0.7863	0.7863	1.2717	0.05	25.4349
25	34.5	0.7863	0.7863	1.2717	0.04	31.7936
30	34.5	0.7863	0.7863	1.2717	0.03	38.1523

Value of γ and δ from the graph

$\gamma = 0.30$ $\quad \frac{1}{\gamma} = 3.333$

$\delta = 1.24$ $\quad \frac{1}{\delta} = 0.806$

Appendix - II

TABLE - 3.2.4.4 (b)

I_2 adsorption

Strength of I_2 solution = 0.264N

pH of I_2 solution = 4.7

m = Weight of carbon = 1 g. Temp. of the expt. = 343°K

Strength of thiosulphate solution = .203N

Volume of I_2 solution=50 ml.

Blank titration = 65.0 ml.

Time in min.	Volume of $Na_2S_2O_3$ required after adsorption.	X⟶amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	41.0	0.618744	0.6187	1.6161	1.00	1.6161
2	38.0	0.696087	0.6960	1.4366	0.50	2.8732
3	37.0	0.721868	0.7218	1.3852	0.33	4.1558
5	36.0	0.747649	0.7476	1.3375	0.20	6.6876
7	35.5	0.760539	0.7605	1.3148	0.142	9.2039
10	35.0	0.77343	0.7734	1.2929	0.10	12.9294
15	35.0	0.77343	0.7734	1.2929	0.06	19.3941
20	35.0	0.77343	0.7734	1.2929	0.05	25.8588
25	35.0	0.77343	0.7734	1.2929	0.04	32.3235
30	35.0	0.77343	0.7734	1.2929	0.03	38.7882

Value of γ and δ from the graph.

$\gamma = 0.34$

$\delta = 1.27$

$\frac{1}{\gamma} = 3.333$

$\frac{1}{\delta} = 0.787$

Appendix - II

TABLE - 3.2.4.4(c)

I_2 adsorption

Strength of I_2 solution = 0.264N
pH of I_2 solution = 4.7
Volume of I_2 solution = 50 ml
Strength of $Na_2S_2O_3$ solution = 0.203N
Weight of carbon = 1 g.

Temp. = 323°K
Blank titration = 65.0 ml

Time in min.	Volume of $Na_2S_2O_3$ solution required	X ⟶ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	43.0	0.5671	0.5671	1.7631	1.00	1.7631
2	41.0	0.6187	0.6187	1.6161	0.50	3.2323
3	40.0	0.6445	0.6445	1.5515	0.33	4.6545
5	39.0	0.6703	0.6703	1.4918	0.20	7.4592
7	38.0	0.6960	0.6960	1.4366	0.14	10.0562
10	37.0	0.7218	0.7218	1.3852	0.10	13.8529
15	37.0	0.7218	0.7218	1.3852	0.06	20.7794
20	37.0	0.7218	0.7218	1.3852	0.05	27.7058
25	37.0	0.7218	0.7218	1.3852	0.04	34.6356
30	37.0	0.7218	0.7218	1.3852	0.03	41.5627

Value of γ and δ from the graph

$\gamma = 0.392$ $\quad \frac{1}{\gamma} = 2.5510$

$\delta = 1.39$ $\quad \frac{1}{\delta} = 0.7194$

Appendix - II

TABLE - 3.2.4.4 (d)

I_2 adsorption

Strength of I_2 solution = 0.264N

Strength of $Na_2S_2O_3$ solution = 0.203N Blank titration = 65.0 ml

pH of I_2 solution = 4.7

Temp. = 303°K

Volume of I_2 solution = 50 ml

Weight of carbon = 1 g.

Time in min.	Volume of $Na_2S_2O_3$ required	X ⟶ amount of I_2 adsorbed in g.	x/m	1/v	1/t	t/v
1	46.5	0.4769	0.4769	2.0966	1.00	2.0966
2	44.0	0.5414	0.5414	1.8470	0.50	3.6941
3	43.0	0.5671	0.5671	1.7631	0.33	5.2893
5	42.0	0.5929	0.5929	1.6864	0.20	8.4322
7	41.0	0.6187	0.6187	1.6161	0.14	11.3132
10	40.0	0.6445	0.6445	1.5515	0.10	15.5153
15	40.0	0.6445	0.6445	1.5515	0.06	23.2729
20	40.0	0.6445	0.6445	1.5515	0.05	31.0306
25	40.0	0.6445	0.6445	1.5515	0.04	38.7882
30	40.0	0.6445	0.6445	1.5515	0.03	46.5459

Value of γ and δ from the graph

$\gamma = 0.60$ $\frac{1}{\gamma} = 1.66$

$\delta = 1.5$ $\frac{1}{\delta} = 0.66$

Appendix - II

TABLE - 3.2.4.5

KINETIC DATA FOR I_2 ADSORPTION. (DATA OBTAINED FROM LISZI PLOTS).

TEMP°K	Initial concentration C.	γ (from the graph)	$\frac{1}{\gamma}$ (Initial rate)	δ (from the graph)	$\frac{1}{\delta}$ (Limiting adsorption
363°K	0.538N	0.180	5.5550	1.04	0.9615
	0.490N	0.190	5.2631	1.15	0.8695
	0.360N	0.210	4.7619	1.25	0.8000
	0.264N	0.300	3.3333	1.24	0.8064
343°K	0.538N	0.185	5.4054	1.12	0.8928
	0.490N	0.230	4.3478	1.14	0.8771
	0.360N	0.250	4.0000	1.23	0.8130
	0.264N	0.340	2.9411	1.27	0.7874
323°K	0.538N	0.200	5.000	1.05	0.9523
	0.490N	0.238	4.2016	1.16	0.8620
	0.360N	0.260	3.8461	1.32	0.7575
	0.264N	0.392	2.5510	1.39	0.7194
303°K	0.538N	0.230	4.3478	1.10	0.9090
	0.490N	0.240	4.1666	1.17	0.8547
	0.360N	0.280	3.5714	1.30	0.7692
	0.264N	0.600	1.6666	1.50	0.6666

Appendix - II

TABLE - 3.2.4.6

KINETIC DATA FOR I_2 ADSORPTION.

TEMP°K	Initial Concentration C	log C	log C+1	$\log \frac{1}{\gamma}$	Rate constant k min^{-1}	order of adsorption 'n'
363°K	0.538N	-0.2692	0.7308	.6436	14.454×10^{-1}	0.66
	0.490N	-0.3098	0.6902	.6158		
	0.360N	-0.4436	0.5564	.5244		
	0.264	-0.5783	0.4217	.4324		
343°K	0.538N	-0.2692	0.7308	.6905	13.803×10^{-1}	0.76
	0.490N	-0.3098	0.6902	.6600		
	0.360N	-0.4436	0.5564	.5595		
	0.264N	-0.5783	0.4217	.4583		
323°K	0.538N	-0.2692	0.7308	.7361	12.882×10^{-1}	0.87
	0.490N	-0.3098	0.6902	.7009		
	0.360N	-0.4436	0.5564	.5915		
	0.264N	-0.5783	0.4217	.4681		
303°K	0.538N	-0.2692	0.7308	0.8880	10.232×10^{-1}	1.2
	0.490N	-0.3098	0.6902	0.8355		
	0.360N	-0.4436	0.5564	0.6622		
	0.264N	-0.5783	0.4217	0.4878		

Appendix - II

TABLE - 3.2.4.7

DATA FOR (ARRHENIOUS PLOT) ACTIVATION ENERGY. (I_2).

T^oK	$\frac{1}{T} \times 10^3$	k min^{-1}	log k	Activation Energy E_a KCal/mole
363	2.7548	1.4454	0.16	0.4358 KCals/mole
343	2.9154	1.3803	0.14	0.6650 KCals/mole
323	3.0959	1.2882	0.11	1.640 KCals/mole
303	3.3003	1.0232	0.01	2.74 KCal/mole

APENDIX III

TABLE - 3.3.1

a = 2.2606 g. = Initial quantity of Iodine.

m = 1 g.

Volume of I_2 solution taken = 50 ml.

Strength of I_2 solution = 0.356N.

SAMPLE	t Time	Amount adsorbed x(g)	Amount adsorbed (x/m) per gram.	Amount unadsorbed (a - x) g.
$ZnCl_2$ treated activated carbon.	1 min.	0.8892	0.8892	1.3714
	2 "	0.9121	0.9121	1.3485
	3 "	0.9349	0.9349	1.3257
	5 "	0.9464	0.9464	1.3142
	7 "	0.9578	0.9578	1.3028
	10 "	0.9806	0.9806	1.2800
	15 "	0.9806	0.9806	1.2800
	20 "	0.9806	0.9806	1.2800
	30 "	0.9806	0.9806	1.2800
	1 day	1.0149	1.0149	1.2457
	2 day	1.0492	1.0492	1.2114
	7 day	1.0721	1.0721	1.1885
	15 day	1.1064	1.1064	1.1542
	30 day	1.1635	1.1635	1.0971
	60 day	1.2321	1.2321	1.0285

TABLE - 3.3.1 (Contd.)

a = 2.2606 g. = Initial quantity of Iodine.

m = 1 g.

Volume of I_2 solution taken = 50 ml.

Strength of I_2 solution = 0.356N.

SAMPLE	t Time	Amount adsorbed x(g)	Amount adsorbed (x/m) per gram	Amount unadsorbed (a - x) g.
	1 min.	0.8343	0.8343	1.4263
	2 "	0.8458	0.8458	1.4148
	3 "	0.8572	0.8572	1.4034
	5 "	0.8732	0.8732	1.3874
	7 "	0.8915	0.8915	1.3691
Steam activated carbon.	10 "	0.9029	0.9029	1.3577
	15 "	0.9029	0.9029	1.3577
	20 "	0.9029	0.9029	1.3577
	30 "	0.9029	0.9029	1.3577
	1 day	0.9258	0.9258	1.3348
	2 "	0.9486	0.9486	1.3120
	7 "	0.9784	0.9784	1.2822
	15 "	1.0058	1.0058	1.2548
	30 "	1.0698	1.0698	1.1908
	60 "	1.1201	1.1201	1.1405

TABLE - 3.3.1 (Contd.)

a = 2.2606 g. = Initial quantity of Iodine.

m = 1 g.

Volume of I_2 solution taken = 50 ml.

Strength of I_2 solution = 0.356N.

SAMPLE	t Time	Amount adsorbed x(g)	Amount adsorbed (x/m) per gram.	Amount unadsorbed (a - x) g.
Active carbon (E. Merck).	1 min.	0.9144	0.9144	1.3462
	2 "	0.9715	0.9715	1.2891
	3 "	0.9944	0.9944	1.2662
	5 "	1.0287	1.0287	1.2319
	7 "	1.0629	1.0629	1.1977
	10 "	1.0629	1.0629	1.1977
	15 "	1.0629	1.0629	1.1977
	20 "	1.0629	1.0629	1.1977
	30 "	1.0629	1.0629	1.1977
	1 day	1.0858	1.0858	1.1748
	2 "	1.1178	1.1178	1.1428
	7 "	1.1544	1.1544	1.1062
	15 "	1.1932	1.1932	1.0674
	30 "	1.2458	1.2458	1.0148
	60 "	1.2801	1.2801	0.9805

TABLE - 3.3.'2

DATA FOR ADSORPTION MEHCANISM(IODINE)

Initial iodine concentration = 0.538M.

Time in sec.	Temp ^oK	V_t	V_α	$F = \frac{V_t}{V_\alpha}$	log(1-F)	Bt	B sec^{-1}	R or S sec^{-1}
60	363	0.7912	0.9486	0.8340	-0.7798	1.3026	$2.1333x10^{-2}$	0.0299
120		0.8362	0.9486	0.8815	-0.9262	1.6390	$1.3525x10^{-2}$	0.0178
180		0.8474	0.9486	0.8933	-0.9718	1.7453	$0.9500x10^{-2}$	0.0124
300		0.8586	0.9486	0.9051	-1.0227	1.8673	$0.6000x10^{-2}$	0.0078
420		0.8924	0.9486	0.9407	-1.2269	2.4168	$0.5523x10^{-2}$	0.0067
600		0.9036	0.9486	0.9525	-1.3233	2.8209	$0.4166x10^{-2}$	0.0050
900		0.9486	0.9486	1.0000	-	-	-	-
60	343	0.7463	0.8924	0.8362	-0.7856	1.3400	$2.2333x10^{-2}$	0.0301
120		0.8137	0.8924	0.9118	-1.0545	1.9100	$1.5916x10^{-2}$	0.0202
180		0.8362	0.8924	0.9370	-1.2006	2.3200	$1.2888x10^{-2}$	0.0154
300		0.8474	0.8924	0.9495	-1.2967	2.5000	$0.8333x10^{-2}$	0.0099
420		0.8811	0.8924	0.9873	-1.8961	4.1100	$0.9785x10^{-2}$	0.0114
600		0.8924	0.8924	1.0000	-	-	-	-
60	323	0.7463	0.9486	0.7867	-0.6710	1.0730	$1.7883x10^{-2}$	0.0257
120		0.8137	0.9486	0.8577	-0.8467	1.4680	$1.2233x10^{-2}$	0.0162
180		0.8362	0.9486	0.8815	-0.9262	1.6230	$0.9016x10^{-2}$	0.0118
300		0.8586	0.9486	0.9051	-1.0227	1.8000	$0.6000x10^{-2}$	0.0078
420		0.8811	0.9486	0.9288	-1.1475	2.1600	$0.5142x10^{-2}$	0.0063
600		0.9486	0.9486	1.0000	-	-	-	-
60	303	0.7463	0.9036	0.8259	-0.7592	1.2800	$2.1333x10^{-2}$	0.0291
120		0.8137	0.9036	0.9005	-1.0021	1.8000	$1.5000x10^{-2}$	0.0192
180		0.8362	0.9036	0.9254	-1.1272	2.0300	$1.1277x10^{-2}$	0.0144
300		0.8586	0.9036	0.9501	-1.3018	2.5000	$0.8333x10^{-2}$	0.0099
420		0.8924	0.9036	0.9876	-1.9065	4.1100	$0.9785x10^{-2}$	0.0104
600		0.9036	0.9036	1.0000	-	-	-	-

TABLE - 3.3.1.3

a = 1.27 g. . Strength of Iodine solution in Flask F.1 = N/10

m = 1 g . Strength of Iodine solution in Flask F.2 = N/5

Volume of Iodine solution taken in Flask F1 = 100 ml.

SAMPLES	Strength of Iodine solution in normality	x Amount adsorbed (in g.)	(x/m) Amount adsorbed per g.	Amount unabsorbed a - x (g).
Active C (E.Merck)	$\frac{N}{10}$ (F.1)	0.565	0.565	0.705
	$\frac{N}{5}$ (F.2)	0.570	0.570	0.700
$ZnCl_2$ treated activated carbon.	F.1	0.446	0.446	0.824
	F.2	0.450	0.450	0.820
Steam activated carbon.	F.1	0.334	0.334	0.936
	F.2	0.336	0.336	0.934

TABLE - 3.3.2

DATA FOR ADSORPTION MECHANISM(ACETIC ACID)

Initial acetic acid concentration = 0.575N.

Time in sec.	Temp °K	V_t	V_α	$F = \frac{V_t}{V_\alpha}$	log(1-F)	Bt	B sec^{-1}	R or S sec^{-1}
60	363	0.1044	0.1604	0.6508	-0.4569	0.5940	0.9900x10^{-2}	0.0175
120		0.1250	0.1604	0.7793	-0.6561	1.0280	0.8566x10^{-2}	0.0126
180		0.1324	0.1604	0.8254	-0.7579	1.2800	0.7111x10^{-2}	0.0097
300		0.1418	0.1604	0.8840	-0.9355	1.6280	0.5410x10^{-2}	0.0072
420		0.1511	0.1604	0.9420	-1.2365	2.3200	0.5523x10^{-2}	0.0068
600		0.1604	1.0000	-	-	-	-	-
60	343	0.1418	0.1791	0.7917	-0.6813	1.0730	1.7883x10^{-2}	0.0261
120		0.1418	0.1791	0.7917	-0.6813	1.0730	1.8941x10^{-2}	0.0130
180		0.1511	0.1791	0.8436	-0.8057	1.3400	0.7444x10^{-2}	0.0103
300		0.1604	0.1791	0.8955	-0.9808	1.8000	0.6000x10^{-2}	0.0753
420		0.1698	0.1791	0.9480	-1.2839	2.5000	0.5952x10^{-2}	0.0070
600		0.1791	0.1791	1.0000	-	-	-	-
60	323	0.0858	0.1977	0.4339	-0.2471	0.2100	0.3500x10^{-2}	0.0095
120		0.1231	0.1977	0.6226	-0.4231	0.5220	0.4350x10^{-2}	0.0081
180		0.1418	0.1977	0.7172	-0.5485	0.7980	0.4433x10^{-2}	0.0070
300		0.1604	0.1977	0.8113	-0.7242	0.1710	0.3903x10^{-2}	0.0056
420		0.1698	0.1977	0.8588	-0.8501	1.4680	0.3495x10^{-2}	0.0047
600		0.1977	0.1977	1.0000	-	-	-	-
60	303	0.1044	0.1604	0.6508	-0.4569	0.5940	0.9900x10^{-2}	0.0175
120		0.1044	0.1604	0.6508	-0.4569	0.5940	0.4950x10^{-2}	0.0088
180		0.1231	0.1604	0.7674	-0.6333	0.5850	0.5472x10^{-2}	0.0081
300		0.1418	0.1604	0.8840	-0.9355	1.6230	0.5410x10^{-2}	0.0072
420		0.1511	0.1604	0.9420	-1.2365	2.3200	0.5523x10^{-2}	0.0052
600		0.1604	0.1604	1.0000	-	-	-	-

APPENDIX IV

TABLE - 3.4.1

DATA FOR EXPERIMENTAL ISOTHERMS FOR DIFFERENT CARBONS.

SAMPLE	Initial Concentration (in normality)	C Equilibrium Concentration (in normality)	Amount of Iodine adsorbed per gm. x/m
Steam activated carbon (cocoanut shell)	0.538	0.388	0.948
	0.490	0.351	0.876
	0.360	0.241	0.755
	0.264	0.150	0.721
$ZnCl_2$ treated activated carbon (cocoanut shell)	0.428	0.310	0.750
	0.385	0.277	0.683
	0.323	0.225	0.621
	0.204	0.115	0.565
Active carbon. (E. Merck)	0.554	0.390	1.040
	0.447	0.324	0.324
	0.381	0.235	0.930
	0.323	0.180	0.910
Active carbon (B.D.H.)	0.497	0.350	0.9326
	0.329	0.195	0.8473
	0.324	0.192	0.8382
	0.240	0.115	0.7924
Activated carbon. (Sunflower seed)	0.5000	0.3450	0.9814
	0.3240	0.1820	0.9022
	0.2390	0.1050	0.8473
	0.2120	0.0860	0.7985
Activated carbon (Groundnut Husk).	0.5120	0.4250	0.5500
	0.4169	0.3500	0.4250
	0.3590	0.3000	0.3750
	0.2512	0.2000	0.3250

TABLE - 3.4.2

DATA FOR $C/\frac{x}{m}$ vs C plot (for surface area determination)

Temperature = 303°k.

SAMPLES	Equilibrium concentration C(in normality)	Amount of I_2 adsorbed per g x/m	$C/\frac{x}{m}$
Steam activated carbon.	0.170	0.725	0.234
	0.180	0.730	0.246
	0.195	0.735	0.265
	0.215	0.745	0.288
	0.225	0.750	0.300
	0.235	0.755	0.311
	0.250	0.765	0.326
	0.270	0.780	0.346
	0.290	0.800	0.362
	0.300	0.810	0.370
	0.310	0.820	0.378
	0.315	0.825	0.381
	0.340	0.855	0.397
	0.355	0.875	0.405
	0.375	0.900	0.416
	0.380	0.910	0.417
$ZnCl_2$ activated carbon.	0.130	0.570	0.228
	0.145	0.575	0.252
	0.160	0.580	0.276
	0.180	0.590	0.305
	0.190	0.597	0.318
	0.195	0.600	0.325
	0.205	0.605	0.338
	0.210	0.609	0.344
	0.230	0.625	0.368
	0.235	0.630	0.373
	0.240	0.635	0.378
	0.245	0.640	0.382
	0.260	0.657	0.396

TABLE - 3.4.2 (Contd.)

DATA FOR $C/\frac{x}{m}$ vs C plot

Temperature = 303^{o}k.

SAMPLES	Equilibrium concentration C(in normality)	Amount of I_2 adsorbed per gm. x/m	$C/\frac{x}{m}$
$ZnCl_2$ activated carbon.	0.270	0.670	0.403
	0.290	0.700	0.414
Active carbon (E. Merck)	0.185	0.912	0.202
	0.195	0.915	0.213
	0.205	0.917	0.223
	0.210	0.920	0.228
	0.220	0.922	0.238
	0.230	0.925	0.248
	0.235	0.927	0.253
	0.240	0.930	0.258
	0.260	0.937	0.277
	0.275	0.945	0.291
	0.285	0.950	0.300
	0.300	0.960	0.312
	0.315	0.970	0.324
	0.330	0.980	0.336
	0.340	0.987	0.344
	0.350	0.997	0.351
	0.370	1.020	0.362
Active carbon (B.D.H.)	0.105	0.790	0.1329
	0.125	0.802	0.1558
	0.130	0.805	0.1614
	0.140	0.811	0.1726
	0.150	0.816	0.1838
	0.160	0.822	0.1946
	0.165	0.825	0.2000
	0.175	0.830	0.2100
	0.180	0.833	0.2160

TABLE - 3.4.2 (Contd.)

DATA FOR $C/\frac{x}{m}$ vs C plot

Temperature = 303°k.

SAMPLES	Equilibrium concentration C(in normality)	Amount of I_2 adsorbed per g . x/m	$C/\frac{x}{m}$
Active carbon (B.D.H.)	0.190	0.840	0.2260
	0.200	0.845	0.2360
	0.220	0.857	0.2560
	0.225	0.860	0.2610
	0.250	0.875	0.2850
	0.305	0.892	0.3420
Active C (Sunflower seed)	0.0850	0.8125	0.1046
	0.0950	0.8400	0.1130
	0.1000	0.8475	0.1179
	0.1050	0.8550	0.1228
	0.1100	0.8600	0.1279
	0.1200	0.8675	0.1383
	0.1300	0.8750	0.1485
	0.1400	0.8825	0.1586
	0.1450	0.8850	0.1638
	0.1500	0.8875	0.1690
	0.1600	0.8925	0.1792
	0.1650	0.8950	0.1843
	0.1700	0.8975	0.1894
	0.2000	0.9100	0.2197
	0.2200	0.9175	0.2397
	0.2250	0.9200	0.2445
Active C (Ground nut hust)	0.185	0.321	0.5781
	0.210	0.330	0.6363
	0.225	0.335	0.6716
	0.230	0.337	0.6824
	0.240	0.340	0.7058
	0.250	0.345	0.7246
	0.255	0.348	0.7327

TABLE - 3.4.2 (Contd.)

DATA FOR $C/\frac{x}{m}$ vs C plot

Temperature = 303°k.

SAMPLES	Equilibrium concentration C(in normality)	Amount of I_2 adsorbed per g . x/m	$C/\frac{x}{m}$
Active C (Ground nut husk)	0.260	0.352	0.7386
	0.265	0.354	0.7485
	0.275	0.360	0.7638
	0.285	0.367	0.7765
	0.290	0.370	0.7837
	0.305	0.380	0.8036
	0.310	0.385	0.8051
	0.325	0.397	0.8186
	0.340	0.413	0.8232

TABLE - 3.4.3

DATA FOR BET SURFACE AREA

p_o = 760 mm = Atmospheric pressure

p', p'', p''' = Initial pressures.

p_1 , p_2 , p_3 = Final pressures

$$V_M = \frac{p_2 - p_1 / p_o}{p_2 / v_2(p_o - p_2) - p_1 / v_1(p_o - p_1)}$$

$$V_1 = \frac{V_{c_1} - V_{c_3} \cdot (p_1/p_3)}{1 - \frac{p_1}{p_3} \cdot \frac{p_o - p_1}{p_o - p_3}}$$

$$V_2 = \frac{V_{c_2} - V_{c3} \cdot \frac{p_2}{p_3}}{1 - \frac{p_2}{p_3} \cdot \frac{p_o - p_2}{p_o - p_3}}$$

	Steam activated carbon	Zinc chloride treated activated carbon	Active carbon (E. Merck)
1. $T = t + 273$	304	295	295
2. Atmospheric pressure (mm)	752	758	758
3. p' (mm)	393	398	399
4. p_1 (mm)	69	67	69
5. p'' (mm)	448	447	445
6. p_2 (mm)	86	84	83
7. p''' (mm)	500	497	496
8. p_3 (mm)	102	100	99
9. p_1/p_3	0.6764	0.6700	0.6969
10. p_2/p_3	0.8431	0.8400	0.8383
11. $p_o - p_1$	691	693	691
12. $p_o - p_2$	674	676	677

TABLE - 3.4.3 (Contd.)

DATA FOR BET SURFACE AREA

	Steam activated carbon	Zinc chloride treated activated carbon	Active carbon (E. Merck)
13. $p_o - p_3$	658	660	661
14. $p_2 - p_1$	17	17	14
15. $C = \frac{167.5 x 273}{760}$	60.168	60.168	60.168
16. $V_{c1} = \frac{C}{T}(p' - p_1)$	64.126	67.287	67.287
17. $V_{c2} = \frac{C}{T}(p'' - p_2)$	71.6470	74.0371	73.8118
18. $V_{c3} = \frac{C}{T}(p''' - p_3)$	78.7721	80.9717	80.9483
19. $\frac{p_1}{p_3} \times \frac{p_o - p_1}{p_o - p_3}$	0.7103	0.7035	0.7285
20. 1 - (19)	0.2897	0.2965	0.2715
21. $V_{c1} - V_{c3}.\frac{p_1}{p_3}$	10.8450	13.2595	10.8742
22. V_1 (cc)	37.4352	44.7200	40.0523
23. $\frac{p_2}{p_3} \times \frac{p_o - p_2}{p_o - p_3}$	0.8636	0.8603	0.8585
24. 1 - (23)	0.1364	0.1396	0.1415
25. $V_{c2} - V_{c3}.\frac{p_2}{p_3}$	5.2344	6.0209	5.9529
26. V_2 (cc)	38.3746	43.1296	42.0690

TABLE - 3.4.3 (Contd.)

DATA FOR BET SURFACE AREA

	Steam activated carbon	Zinc chloride treated activated carbon	Active carbon (E. Merck)
27. $\frac{p_2 - p_1}{p_o}$	0.0223	0.0223	0.0184
28. $\frac{p_2}{V_2(p_o - p_2)}$	0.003325	0.002881	0.002914
29. $\frac{p_1}{V_1(p_o - p_1)}$	0.002667	0.002161	0.002493
30. V_M (cc)	33.8905	31.0672	43.7054
31. $\sigma = \frac{N \times A}{g \times 22.4}$	21.775	21.775	21.775
32. Surface area $S = \sigma \times V_M$ $m^2\ g^{-1}$	737.96	676.48	951.68

	Active carbon (Sunflower seed)	Active carbon (Groundnut husk)	Active carbon (B.D.H.)
1. $T = t + 273$	295	304	295
2. Atmospheric pressure (mm)	763	752	763
3. p' (mm)	392	386	395
4. p_1 (mm0	65	66	68
5. p'' (mm)	450	450	453

TABLE - 3.4.3 (Contd.)

DATA FOR BET SURFACE AREA

	Active carbon (Sunflower seed)	Active carbon (Groundnut husk)	Active carbon (B.D.H.)
6. p_2 (mm)	82	79	85
7. p''' (mm)	558	493	561
8. p_3 (mm)	115	97	118
9. p_1 / p_3	0.5652	0.6804	0.5762
10. p_2 / p_3	0.7130	0.8144	0.7203
11. $p_o - p_1$	695	694	692
12. $p_o - p_2$	678	681	675
13. $p_o - p_3$	645	663	642
14. $p_2 - p_1$	17	13	17
15. $C = \frac{167.5 \times 273}{760}$	60.168	60.168	60.168
16. $V_{c_1} = \frac{C}{T} (p' - p_1)$	66.708	63.3347	66.7080
17. $V_{c_2} = \frac{C}{T} (p'' - p_2)$	75.0720	73.4287	75.0720
18. $V_{c_3} = \frac{C}{T} (p''' - p_3)$	90.3720	78.3767	90.3720
19. $\frac{p_1}{p_3} \cdot \frac{p_o - p_1}{p_o - p_3}$	0.6090	0.7122	0.6208
20. 1 - (19)	0.3910	0.2878	0.3791
21. $V_{c_1} - V_{c_3} \cdot \frac{p_1}{p_3}$	15.6290	10.0072	14.6540

TABLE - 3.4.3 (Contd.)

DATA FOR BET SURFACE AREA

	Active carbon (Sunflower seed)	Active carbon (Groundnut husk)	Active carbon (B.D.H.)
22. V_1 (cc)	39.9718	34.7713	38.6547
23. $\frac{p_2}{p_3} \cdot \frac{p_o - p_2}{p_o - p_3}$	0.7495	0.8365	0.7573
24. 1 - (23)	0.2505	0.1635	0.2427
25. $V_{c_2} - V_{c_3} \cdot \frac{p_2}{p_3}$	10.6330	9.5988	9.9740
26. V_2 (cc)	42.4471	58.7082	41.0960
27. $\frac{p_2 - p_1}{p_o}$	0.0223	0.0171	0.0223
28. $\frac{p_2}{V_2(p_o - p_2)}$	0.002849	0.001975	0.003064
29. $\frac{p_1}{V_1(p_o - p_1)}$	0.002339	0.002735	0.002542
30. V_M (cc)	43.7254	22.5000	42.7203
31. $\sigma = \frac{NXA}{g \times 22.4}$	21.775	21.775	21.773
32. Surface area $S = \sigma \times V_M$ $m^2 g^{-1}$	952.12	489.93	930.14

TABLE - 3.4.4

SURFACE AREA MEASUREMENT BY I_2 ADSORPTION METHOD.

SAMPLE	V_M from the graph	No. of I_2 molecules in V_M (monolayer volume)	Area of I_2 molecule. σ_m	Surface area. $V_M \times \sigma_m = S$. $m^2 g^{-1}$
Steam activated carbon.	0.7518	$\frac{6.06 \times 10^{23}}{254} \times .7518$ $= .01793 \times 10^{23}$	$41.14\ \mathring{A}^2$	737.78
$ZnCl_2$ treated activated carbon.	0.6944	$.01656 \times 10^{23}$	$41.14\ \mathring{A}^2$	685.39
Active C (E.Merck)	1.0483	$.02501 \times 10^{23}$	$41.14\ \mathring{A}^2$	1028.50
Active C (B.D.H.)	0.9375	$.02236 \times 10^{23}$	$41.14\ \mathring{A}^2$	919.89
Active C (Sunflower seed)	0.9883	$.02357 \times 10^{23}$	$41.14\ \mathring{A}^2$	966·79
Active C (Groundnut husk)	0.4688	$.01118 \times 10^{23}$	$41.14\ \mathring{A}^2$	459.94

TABLE - 3.4.5

SURFACE AREA VALUES FOR DIFFERENT CARBONS

	SAMPLES	Surface area by B.E.T. method. N_2 area = 16.2 $A^{\cdot 2}$	Surface area by Iodine adsorption method. I_2 area = 41.14 $A^{\cdot 2}$
(a)	Steam activated carbon. (cocoanut shell)	737.96 m^2g^{-1}	737.78 m^2g^{-1}
(b)	$ZnCl_2$ treated activated carbon (cocoanut shell)	676.48 m^2g^{-1}	685.39 m^2g^{-1}
(c)	Active C (E. Merck)	951.68 m^2g^{-1}	1028.50 m^2g^{-1}
(d)	Active C (B.D.H.)	930.22 m^2g^{-1}	919.89m^2g^{-1}
(e)	Activated carbon. (Sunflower seed)	957.58 m^2g^{-1}	966.79m^2g^{-1}
(f)	Activated carbon. (Groundnut husk)	489.93 m^2g^{-1}	459.94 m^2g^{-1}

CLAIMS TO ORIGINAL RESEARCH

1. Application of Liszi equation in the case of adsorption from solution was done for the first time.
2. Initial rates and limiting adsorption were calculated from the Liszi equation.
3. After initial rapid adsorption slow adsorption was found to continue for weeks and months.
4. It was shown by using Boyd et al. equation that the adsorption of iodine and acetic acid were controlled mainly by mass action. Some contribution from particle diffusion was observed. Film diffusion was found to be completely absent.
5. The adsorption of iodine and acetic acid were studied in the temperature range 303^{0}K to 363^{0}K and it was found that the orders of adsorption changed from 0.66 to 1.2 in case of iodine and from 1.48 to 2.00 in case of acetic acid.
6. Heats of adsorption for iodine varied from 0.4919 KCal/mole at high coverage to 3.0926 KCal/mole at low coverage and for acetic acid from 0.44 KCal/mole to 7.45 KCal/mole at high and low coverages respectively.
7. Above results showed that the carbon surface was heterogeneous with respect to adsorption of iodine and acetic acid.
8. Mechanisms for adsorption of iodine and acetic acid on active carbon consistent with the kinetic data were suggested. These mechanisms could explain satisfactorily all the experimental facts. This was for the first time that this type of mechanism was applied for adsorption phenomena.

9. On a heterogeneous surface, the heat of adsorption should normally decrease with increase of adsorption, because the more active sites would be occupied earlier. In the present case, we observed an initial decrease in the heat of adsorption as expected, followed by an increase. We explained this unusual behaviour by assuming that activated carbon consisted of bottle-shaped macro and micro pore structures. The origin of the bottle-shaped macro and micro pores in activated carbon was ascribed to the mechanism of activation. In the course of activation, the carbonized carbonaceous raw material was in a plastic state. By thermal decomposition , released gases might form hollows in the plastic matter, from which they escape through small passages. This might be the cause of the creation of the bottle-shaped pores.
10. Our experimental findings show that foreign materials tenaciously remain adsorbed on the carbon surface confer specificity on the activated charcoal.
11. It was found while studying the adsorption of perchlorate, zinc amalgam reduction method of determination of perchlorate gave rather irreproducible results, and that the order of addition of reagents had a significant influence on the accuracy of the method.

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