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ADSORPTION OF POLYVINYL ALCOHOL FROM AQUEOUS SOLUTION ON MONTMORILLONITE CLAY SUBSTRATE

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Abstract

The adsorption of polyvinyl alcohol from aqueous solution on high surface area substrate-montmorillonite clay was examined. At low polymer concentration, the system obey a high affinity type adsorption isotherm. Above a certain coverage, the adsorption of polymer was found to be Langmuirian. Amount of polymer adsorbed per gram of clay was found to be more than 7 times than the amount required for complete coverage of the surface. Adsorption was found to be increased with increase in the temperature and dependent on solution properties like P^H and ionic strength.

Introduction

Interactions between water soluble polymers (W-SP_s) and high surface area solids are of interest from both theoretical and practical view points. Soil scientists use W-SP_s to improve soil quality (resistance to erosion, water retention, air flow etc.) In coatings, W-SP_s are used as thickeners in water borne latex formulations containing pigment, extender (clay), latex and other components. In water purification, the adsorption of W-SP_s on clay particles results in flocculation and sedimentation. In petroleum recovery processes adsorption influences the viscosity of clay drilling fluids and release of drilled solid from such fluids. In the above mentioned processes, the performance is governed by the extent of adsorption of polymers on the substrate which again depends on solution properties (Tewari, 1981) like temperature, ionic strength, solution P^H , solute-solvent ratio etc.

The objective of the present work was to determine the role of solution properties on the adsorption of polyvinyl alcohol on montmorillonite clay substrate. Polyvinyl alcohol is a flexible, uncharged, water soluble polymer and has been used as soil modifier both as a flocculant and as a soil stabilizer (Williams *et al.*, 1968, Kijne, 1967). Montmorillonite is a three layer expanding lattice type clay usually found in most of the representative soils of Bangladesh.

In this study, attempts have been made to identify adsorption isotherms for montmorillonite clay substrate under a wide range of solution conditions.

Materials and Methods

Montmorillonite clay (Panther Creek, Miss. U.S.A.) was purchased from

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Ward's National Science Establishment (Rochester, NY). The clay was ground and sieved. Surface area of the dry clay was obtained by nitrogen adsorption (Brunaur and Emmett, 1937) and elemental analysis by flame ionization (Table I). The clay was identified using the JCPDS powder diffraction files (McClune, 1970). Electron micrograph of the clay is given in fig. 1. Polyvinyl alcohol was supplied by the manufacturer (E. Merck). Molecular weight of the polymer is 72,000 g/mole. All the other reagents were of analytical grade. Both the polymer and the clay were used without further purification.

Aqueous polymer solution was prepared by adding required amount of polymer to 300 ml of distilled water under vigorous agitation for ca 30 sec. The polymer dispersed slurry was immediately added to 700 ml of water and stirred vigorously until dissolution.

The PVA concentration in the supernatant (after the adsorption by clay) was determined colorimetrically by measuring the colour intensity of the complex of PVA with iodine in the presence of boric acid and PVA (Zwick, 1965). Calibration curves were drawn by plotting adsorbance of PVA-iodine complex against PVA concentration (Fig.2).

To 6 ml of PVA solution (10-60 ppm) were added 4 ml of the reagent, containing 0.64 M H_3BO_3 , 0.06 m I_2 and 0.018 M KI. The colour intensity of the complex was measured using a Pye Unicam SP6 series spectrophotometer with 10 mm cell at 670 nm.

To a 100 ml of polymer solutions having concentrations ranging between 30 to 200 ppm, 0.20 g. of clay was added and mixed carefully by shaking for half

Table I. SuLstrate composition and surface area*

Elements	Percent
Al	8.18
Cr	0.05
Fe	4.18
Mg	1.81
Mn	0.07
Ni	0.04
Si	20.90
Ti	0.37
Ca	4.04

*Surface area = 63.20 m²/g

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an hour. Subsequently, the clay was separated by centrifuging the suspension for 10 minutes at 15,000 RPM. The PVA concentration in the supernatant solution was determined by using the previously drawn calibration curve.

The concentration determination method described here has been successfully applied by several workers (Horacek, 1962; Lankveld, 1970). However, the slope of the calibration line changes with electrolyte concentration, hence, for every salt concentration, a new calibration line was determined.

Results and Discussion

The kinetics of PVA adsorption on montmorillonite is illustrated in fig. 3 and 4. Two stage kinetics have been observed viz., (a) initial rapid adsorption

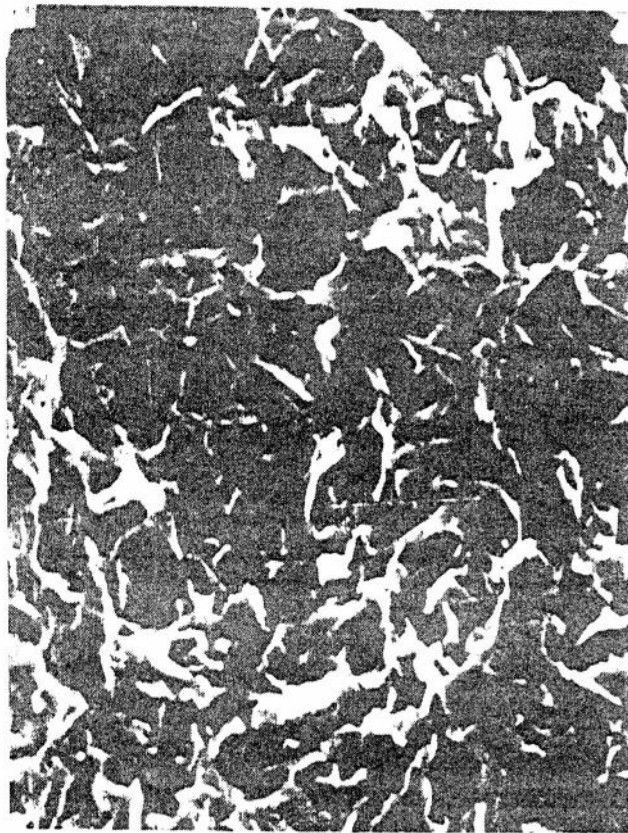


Fig. 1. Electron micrograph of the clay, montmorillonite showing the flake like habit of the mineral magnification 10, 140 X

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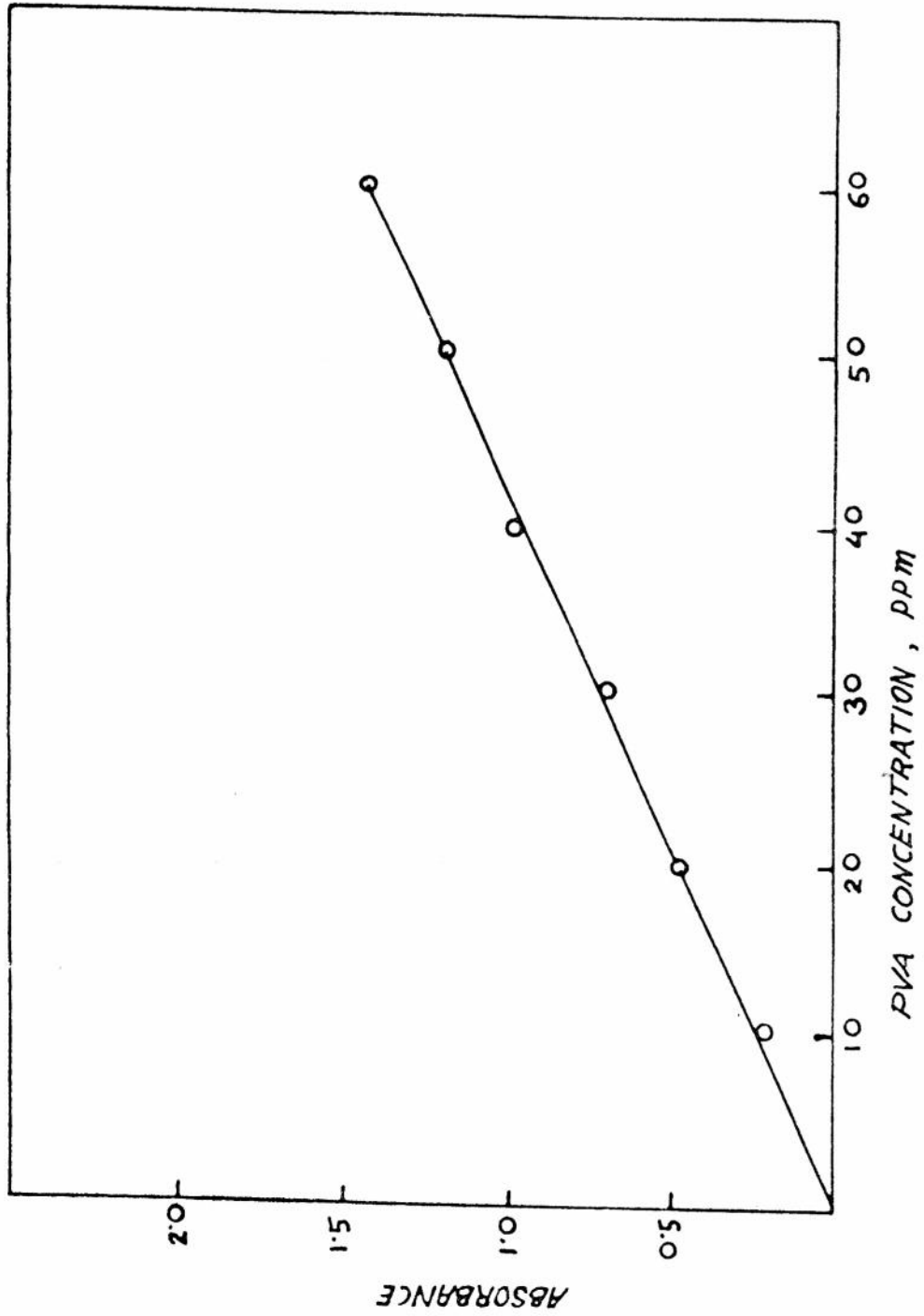


Fig. 2. Calibration line (in the absence of salt) for the determination of PVA concentration

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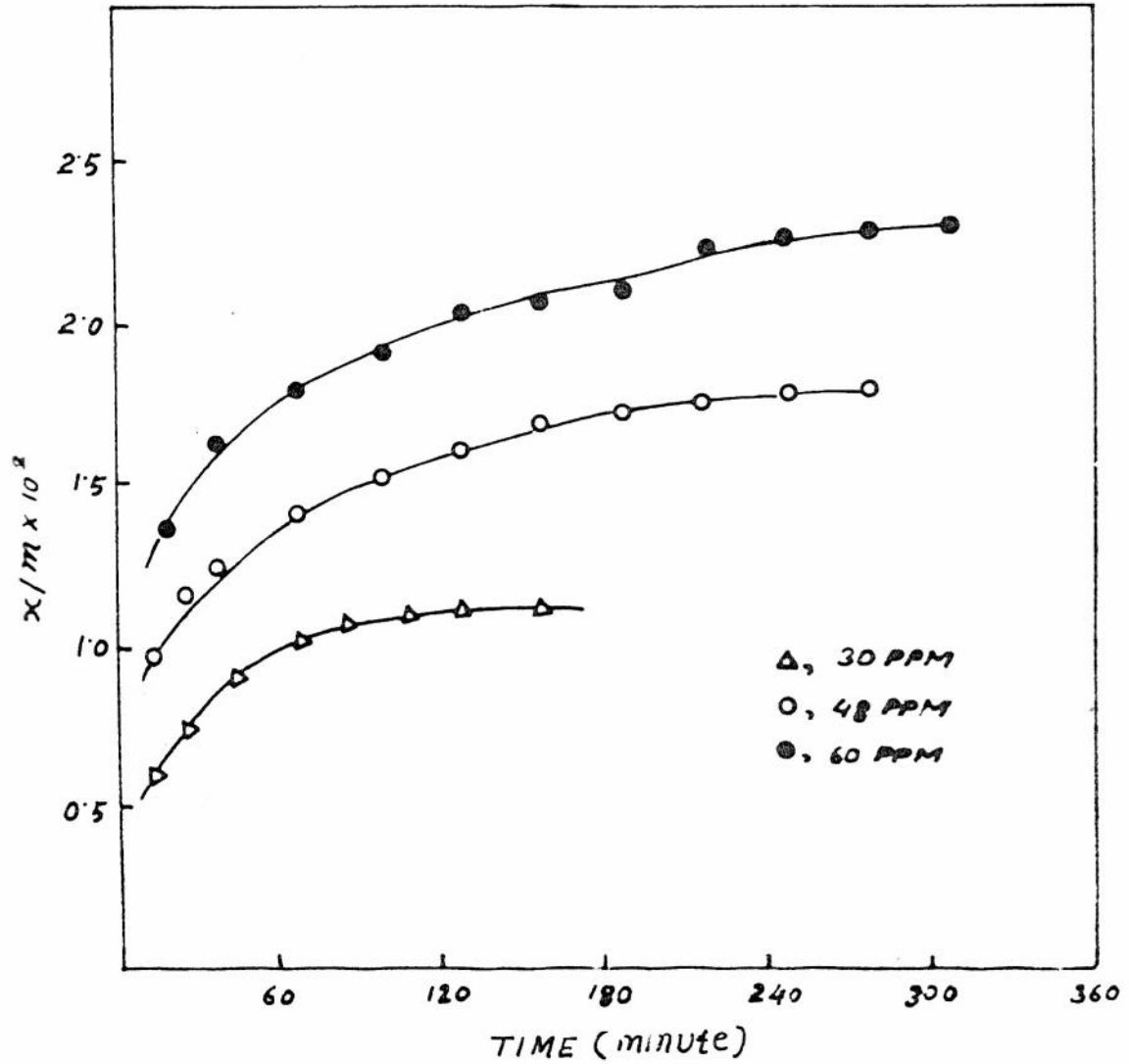


Fig. 3. Adsorption of PVA on montmorillonite as a function of time (initial PVA concentration < 100 ppm)

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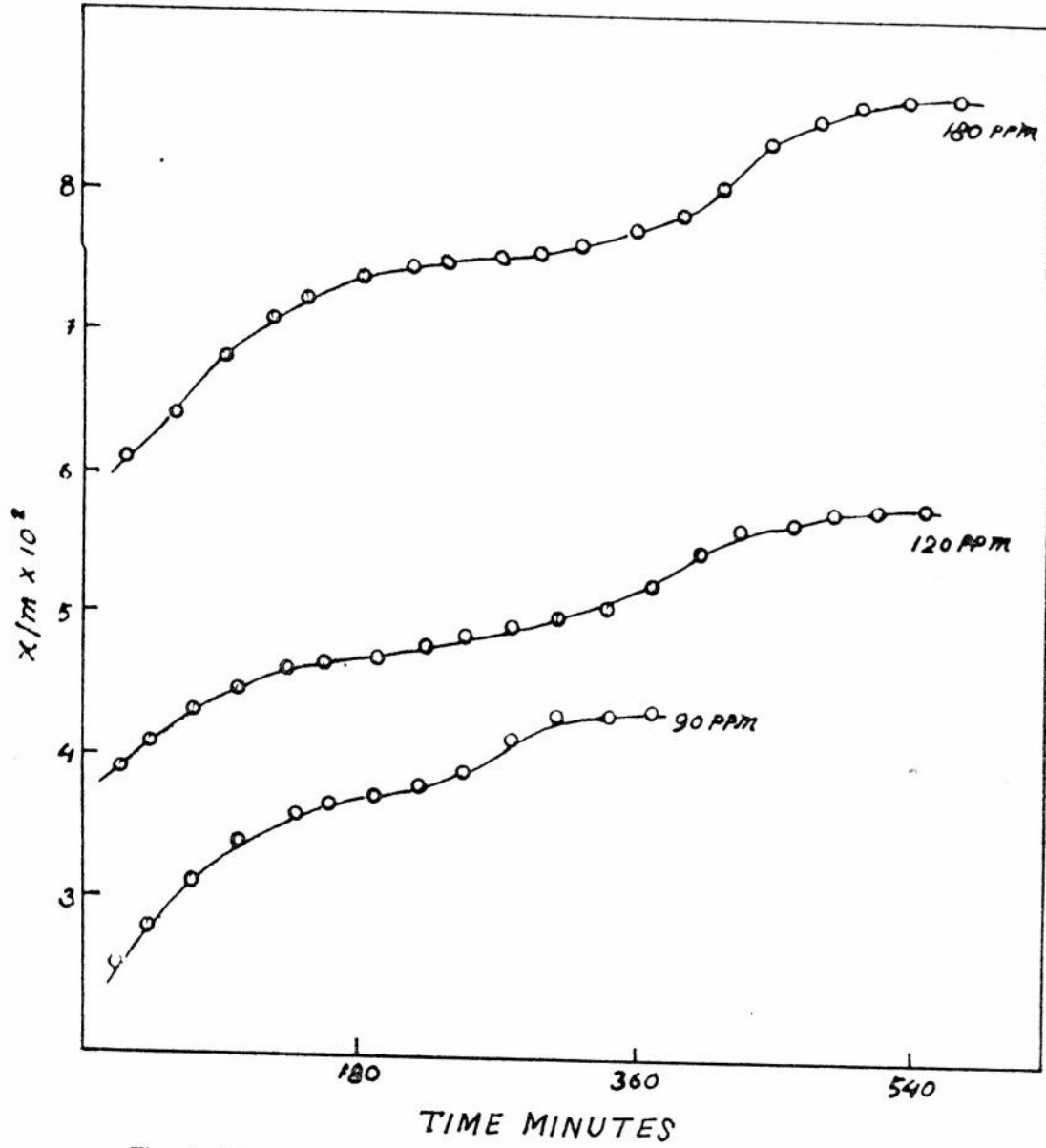


Fig. 4. Adsorption of PVA on montmorillonite as a function of time (initial PVA concentration 100 ppm)

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of polymer followed by (b) slow additional polymer uptake. At low polymer concentration (≤ 100 ppm, fig. 3), almost all the the polymer is removed from the system by clay within 100 minutes. A plateau is obtained indicating the establishment of equilibria. However, the equilibria is not real. All higher polymer concentration and after prolonged exposure of clay to the polymer solution, a second plateau is observed indicating two stage adsorption process. It could be hypothesized that initially PVA is adsorbed in a relatively flat configuration occupying most of the available surface area (first plateau) and in the second process, some desorption takes place which is followed by more polymer adsorption with fewer segments attached.

It should be mentioned that adsorption of PVA on montmorillonite was found to be high affinity type irreversible adsorption. Attempts to desorb the polymer from the clay by replacing the bulk solution containing PVA with pure water was unsuccessful. No polymer could be detected in the water even after prolonged heating (2 hours, 60°C) of the reaction vessel containing polymer adsorbed clay and pure water.

The effect of solution properties like temperature, polymer concentration, added electrolytes on adsorption kinetics were estimated by treating kinetic data according to rate theory developed by Jancovics (1965).

$$\text{Rate} = \frac{1}{t} \ln \frac{a_{\text{eq}} (C_0 - a)}{C_0 (a_{\text{eq}} - a)}$$

Where a_{eq} , a and C_0 are respectively equilibrium adsorption density, adsorption at time t and concentration. The slope of the plot gives the adsorption rate. The adsorption data treated in this manner clearly indicates that adsorption rate is determined by initial polymer concentration—the lower the concentration, the higher is the adsorption rate (Fig.5). At initial polymer concentration, 30 ppm rate constant was $7.5 \times 10^{-4}\text{s}^{-1}$. Whereas at 120 ppm PVA concentration, rate constant was $6.7 \times 10^{-5}\text{s}^{-1}$. Increase in the temperature increases the rate constant to some extent (Fig. 5). Addition of electrolytes increases the rate constant significantly (Fig. 6). The higher the electrolyte concentration, the higher is the adsorption rate. PVA is a non-ionic polymer and hence, it is expected that its solution conformation will remain unchanged in presence of electrolytes. What is happening in this system is probably the salting out of the polymer.

Adsorption isotherms (Temp. 26°C , 36°C and 46°C) of PVA on montmorillonite are illustrated in fig. 7. The isotherms show the characteristic features usually observed in the case of macromolecule adsorption. At low polymer concentration (≤ 100 ppm), the clay virtually removes all the polymer from the system. Only at higher polymer concentration (≥ 120 ppm), a partition of PVA between surface and bulk solution occurs.

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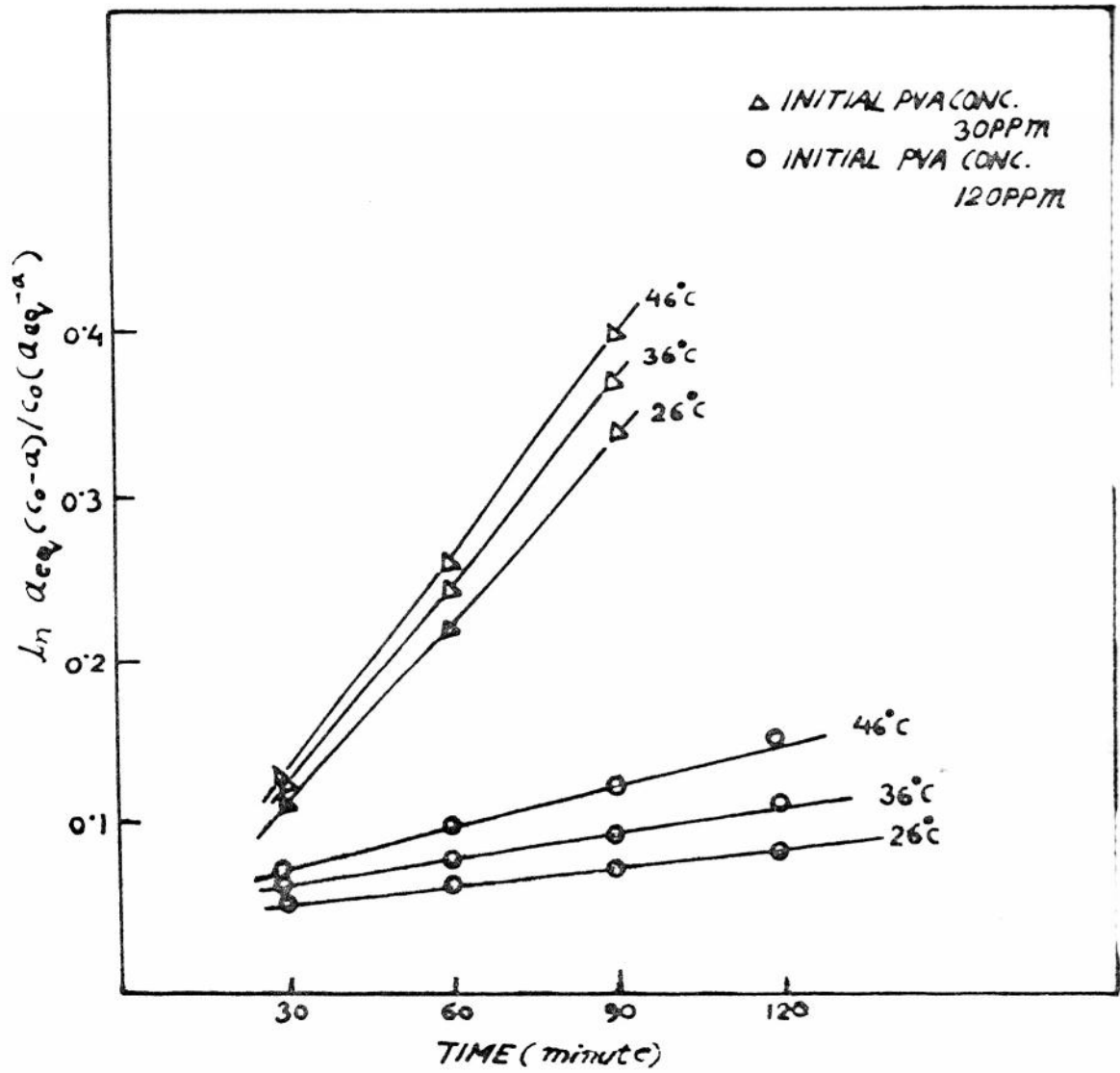


Fig. 5. Jancovics plot. $\ln \frac{a_{eq}(C_0 - a)}{C_0(a_{eq} - a)}$ Vs. time. Effect of temperature and Initial PVA concentration

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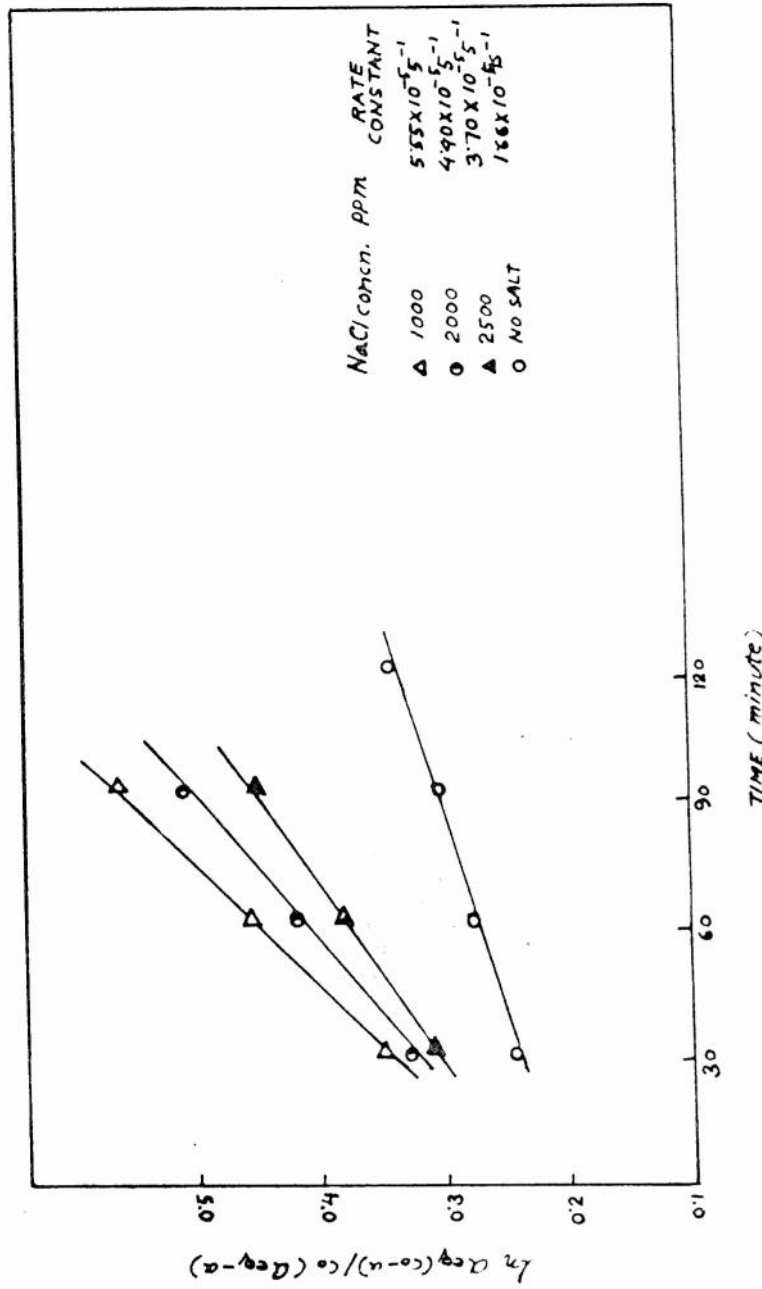


Fig. 6. Jancovics plot. In $a_{eq} (C_0 - a) / C_0 (a_{eq} - a)$ Vs. time.
 Effect of added electrolytes.
 Initial PVA concentration 90 ppm
 Temperature 26°C

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Adsorption increases with increase in temperature (Fig. 7). Apparently, this seems to be contrary to the general observation. Physical adsorption being an exothermic process should decrease with increase in temperature. However, with macromolecules, the situation is quite complex due to the simultaneous influence of temperature on system properties like solvent power, polymer configuration, hydrogen bonding etc. Higher adsorption with increase in temperature means the process is endothermic. Hence, the entropy change must be positive so that the free energy of the system can decrease. This could occur because during the adsorption of polymers solvent molecules are displaced from the solid and gain more translational entropy than is lost by the polymers. Montmorillonite is an expanding layer type of clay. In aqueous solution, its layer expands facilitating the penetration of macromolecules into the interlayers. The ability W-SP_s to enter into the interlayers of the expanding layer type of clay has been reported in the literature (Glass, 1981).

The process of interpenetration is probably facilitated at higher temperature. With the rise in temperature, uncoiling of the polymers will take place facilitating their entry into the d_{001} spacings of the clay.

Moreover, the expansion of the interlayers at high temperatures should also be taken into consideration.

In presence of the electrolytes, adsorption increases (Fig.8). Electrolytes used were 1:1, 1:2 and 1:3 type (NaCl, CaCl₂ and AlCl₃). Trivalent metal cation was found to be the most effective and monovalent metal cation the least effective in increasing the extent of adsorption. It is expected that PVA will not have any electrostatic interactions with the negatively charged clay. The added salt might increase the acidity of the clay. Montmorillonite has a layer structure composed of alternate sheets of alumina octahedra and silica tetrahedra with the edges possessing oxide characteristics and the surface exhibiting a negative charge. To neutralize this charge, cations are present on the surface and in the interlayers. Cations of the added salt exchange with protons on the platelets. The resultant increase in acidity will lead dissolution of aluminum ions. New adsorption sites will be created increasing the extent of adsorption. This is a slow process but it has been observed that added salt increases the rate of adsorption. Hence, we can rule out the influence of clay acidity factor.

The dependence of the adsorption on the nature and concentration of the salt suggests that the effect is due to the decrease in the solvent power of water. Amount adsorbed depends strongly on solvent quality. A slight difference in solvent power could be responsible for rather a large difference in the amount adsorbed (Fleer, 1971).

Adsorption increases at acidic condition (P^H, 3.5) and decreases at (P^H, 7.6) basic conditions (Table 2). The reason for this observation is not very clear. Obviously, P^H is changing the properties of the clay affecting the extent of

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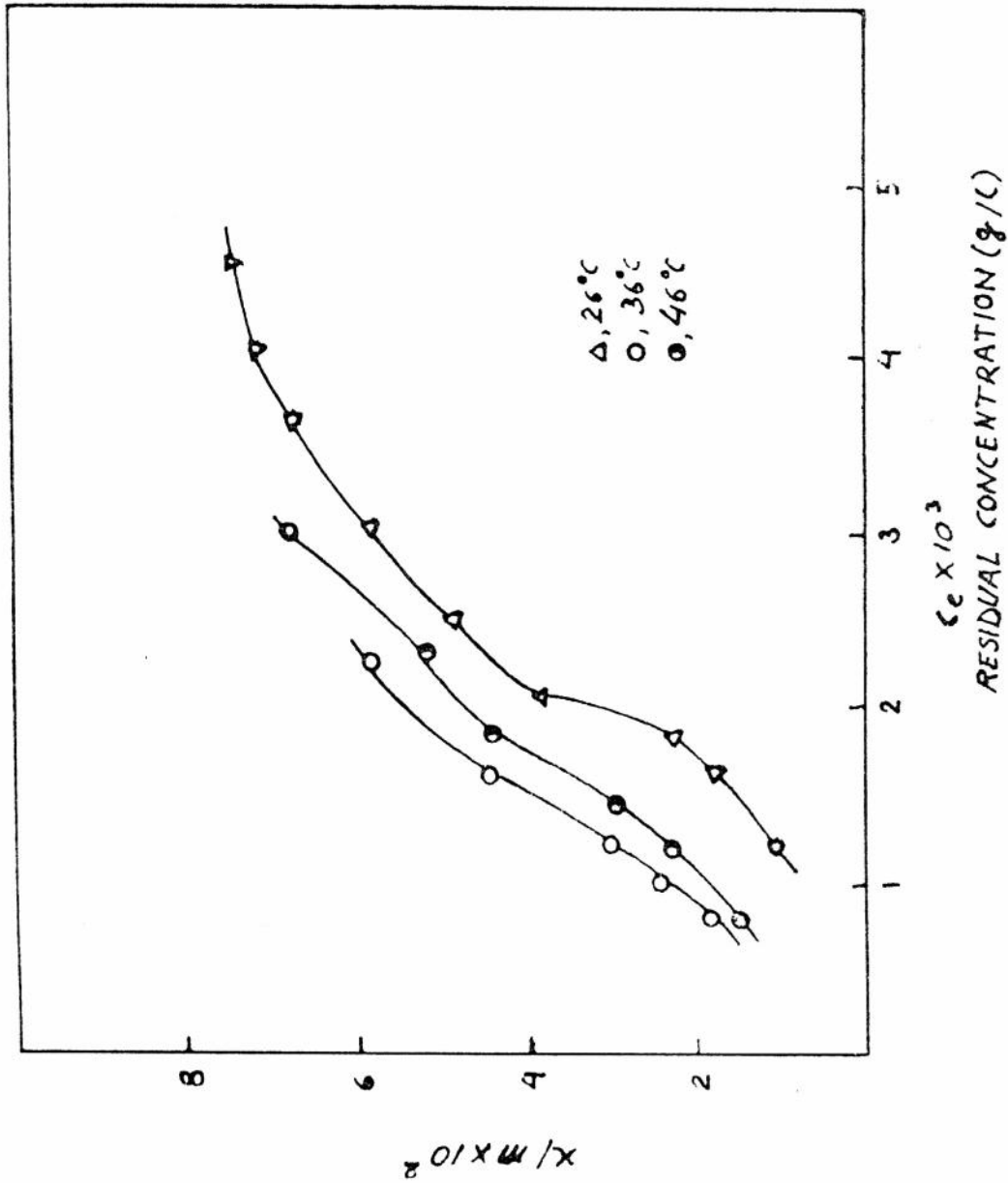


Fig. 7. Adsorption isotherms of PVA on montmorillonite as a function of residual monomer concentration

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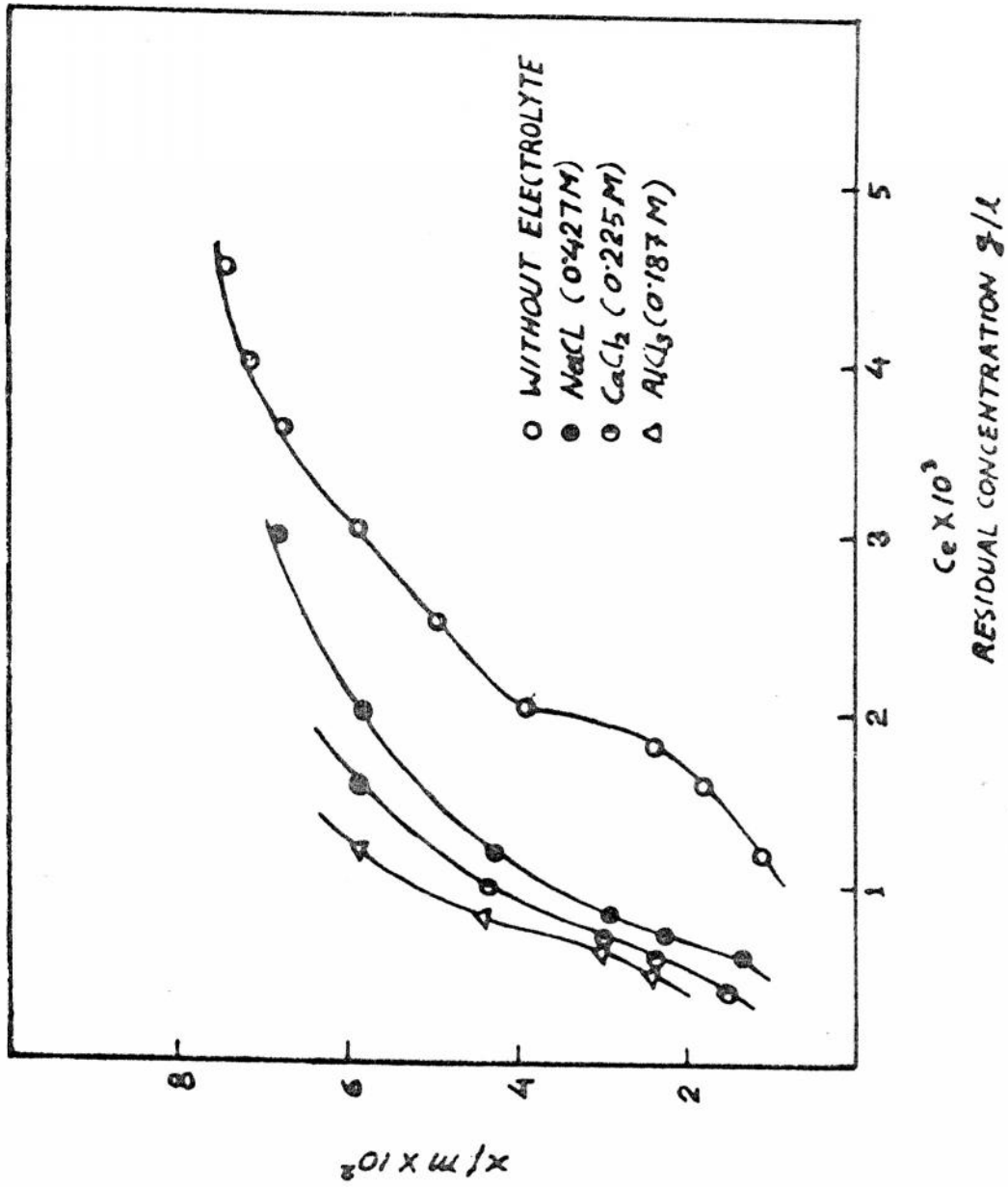


Fig. 8. Adsorption isotherms in presence of electrolytes.
 Temperature 26°C

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Table 2. Effect of solution P^H on the adsorption of PVA on montorillonite

Equilibrium concentration		Adsorption		
g liter ⁻¹ x10 ³		mg polymer g ⁻¹ clay		
C _e	P ^H ,3.5	P ^H ,6.0	P ^H ,7.6	
2	52	40	36	
3	62	58	44	

Initial PVA concentration 120 ppm Temperature 26°C

adsorption. The configuration of PVA in water might be affected by the P^H change. A coiled polymer will be adsorbed to a greater extent than an uncoiled polymer. Another possibility could be the partial ionization of PVA at alkaline condition which will decrease the extent of adsorption due to electrostatic repulsion with the negatively charged clay layers.

Above a certain coverage (40 mg of polymer/g clay), adsorption of PVA was found to be Langmuirian (Fig. 9). The fit to the Langmuirian equation up to a certain extent is quite good. However, it should be mentioned that PVA adsorption does not satisfy the conditions required for Langmuir type of adsorptions. It has already been pointed out that PVA adsorption is irreversible, and exact equilibrium between the adsorbate and the bulk solution is not attained within the time intervals indicated. However, assuming the model, some useful information could be obtained. The slope of the Langmuir plot is a measure of polymer required for complete coverage of the substrate surface which was found to be 220 mg/g of clay. The surface area of each segment of PVA determined by Lankveld (1970) from the compressibility of PVA in the water paraffin interface was 25Å² in a closed packed monolayer. Assuming the same value on clay, the amount of PVA required for complete coverage would be 0.48 mg per m² of the surface. Surface area of montmorillonite clay is 63.2 m²/g. From this, it follows that 31 mg of polymer is necessary for complete coverage which is about 7 times less than the actual amount adsorbed and which is equivalent to seven monolayers. Thus at maximum adsorption, one seventh of the total number of segments, at most, is adsorbed on the surface and the polymer layer must be very thick. At low coverage, a high proportion of segments can be adsorbed giving a thinner layer.

The empirical formula of the clay (Al_{3.2}Mg_{0.79}Fe_{0.8})Si₈O₂₀(OH)₄CA_{1.1} obtained from the elemental analysis suggests some substitution of Nontronite and Beidellite to the ideal montmorillonite composition.

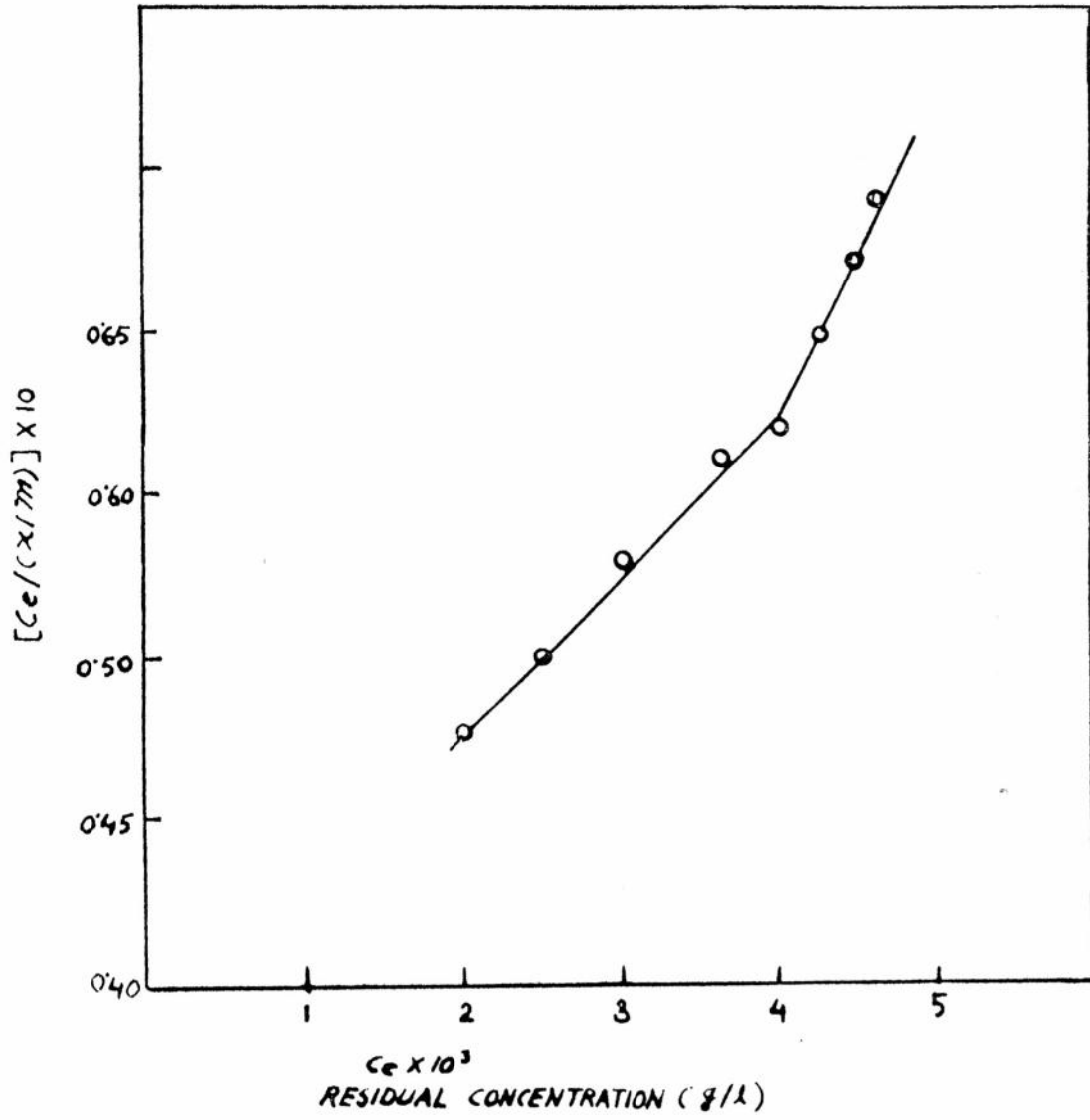


Fig. 9. Langmuir plot $C_e/(X/m)$ Vs. C_e .
Temperature 26°C

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