CHAPTER–III

ADSORPTION OF POLYMERS AND COPOLYMERS ON SOLID SURFACES

3.1 PREVIEW

Synthetic Polymeric materials are among some of the most useful commodities of the modern world meeting basic human needs and improving overall quality of human life. In recent years the emphasis in research, development and production of synthetic macromolecules has been directed towards preparation of cost effective multi-component polymer systems i.e. copolymers, polyblends and composites.

Recent trends in adsorption studies reveal that a large number of polymers with varying chemical structures onto solid surfaces have been performed /33,57,285-287/. These have led to some common and significant conclusions regarding solvent effects, displacement effects, molecular weight effect etc. Not many studies have been carried out to analyse the adsorption properties of random copolymers and a comparative study using the corresponding homopolymers are lacking to our knowledge /49,138/.

As natural rubber could not meet the ever increasing demand for rubber products, the quest for synthetic rubbers led to the discovery of the synthetic elastomer Polybutadiene (PBR). The cis 1,4 PBR is a soft, easily soluble homopolymer with excellent dynamic properties, and good abrasion resistance. The low glasstransition temperature (Tg) is believed to account for its excellent low temperature performance and high resilience. These merits of PBR apart from cost became quickly evident as it soon found world wide acceptance for applcations in both tyre and non tyre products.

In 1940's and 1950's the adsorption of natural /111/ and synthetic rubbers such as poly isoprene and styrene - butadiene (SBR) onto carbon blacks /288-292/ were extensively studied, due to the development of rubber technology. In the recent years Kawaguchi et al. /96/ studied polybutadiene adsorption on nonporous silica (Aerosil 130). From a practical stand point, instead of carbon blacks inorganic fillers like silica /102/ and alumina have been used as a reinforcing material for elastomers; particularly in non black rubber products /8/. Botham and Thies /60/ have studied the adsorption of PBR onto silica surfaces from perchloroethane solutions. Barring few such studies, non black fillers were less investigated and studies with mixed solvent systems are lacking to our knowledge. Hence the adsorption process of PBR on alumina were considered in this study.

The earliest commercial products, poly (ethyl acrylate) and poly (butyl acrylate) are also important elastomers and are placed in the list of speciality rubbers. They exhibit heat and oil resistance and retain their properties even in presence of hot oils and other fluids. Hence these were used in automotive applications seals and gaskets. Polyacrylonitrile has been found to improve the oil resistance of polyacrylates and other similar polymers /208/.

Acrylate-acrylonitrile copolymers have been recommended frequently for binder applications and paper coatings in which they were used to bind inorganic pigments. They posses excellent flexibility, fold resistance, water resistance and printability /201/. Polyacrylonitrile fibers are usually produced in presence of comonomers such as methyl acrylate, methyl methacrylate and vinyl acetate etc., and the amount of these comonomers can be as high as 15%. Moreover, acrylonitrile - methyl acrylate copolymers are very important precursors for the manufacture of carbon fibers /293/.

Adsorption phenomena has a dominant role to play in deciding the ultimate properties in the application of such materials. Therefore in this study the copolymers of acrylonitrile and various acrylates were judiciously chosen to understand their adsorption behaviour. To evaluate the effect of chemical composition the feed ratios of the acrylate monomers were varied in the synthesis as discussed in Chapter II to obtain a series of copolymers.

In copolymers the conformational freedom is considerably restrained because of the dissimilar nature of the monomer segments /27/. The interaction with the interface might be sufficiently disturbing to cause the dominant configurational states in solution and at the surface to be quite different.

The adsorption behaviour of a copolymer at the solid - liquid interface in general is governed by two effects /136/.

[1] The difference in solubility of the components of a copolymer in a solvent i.e. the solvent is better for one component than the other.

[2] The interaction strength between components in a copolymer and the surface i.e. one of the component exhibiting stronger interaction than the other.

Adsorption studios on copolymers of ethylene oxide and propylene oxide from water and benzene /33,49/ and styrene - butadiene rubber /143/ from cyclohexane showed that the amount adsorbed on silica surface at plateau was dependent on the components in the copolymers. Here the results were mainly governed by effect - 1. On the otherhand for adsorption of copolymers of ethylene - vinyl acetate /294/ from various solvents, and styrene - methyl methacrylate /57,141,295/ in several solvents on silica, the plateau amount adsorbed was independent of chemical composition. This was attributed to the overwhelming carbonyl - silanol interactions as methyl methacrylate and vinyl acetate had carbonyl groups. This is the example of effect 2.

In many colloidal dispersions, block copolymers have been extensively used for steric stabilization of the colloidal particles. This process is regulated by the adsorption phenomena. Hence in the recent years much attention has been paid to the adsorption behaviour of block copolymers both experimentally /296-298/ and theoretically /15,299,300/.

In practice random copolymers often have haphazard distribution of different segments along the chain /135/. The primary structure of the chain depends on the synthetic route followed. Generally they are highly polydisperse and this makes the theoretical interpretation of adsorption properties difficult. Marques and Joanny /301/ used a 'blob' model, in which the chains were of uniform length and the adsorbing segments were regularly distributed along the chain. Theodorou /146/ applied lattice model to study the conformation of bulk copolymer at interfaces. In his model since all the chains had same sequence of segments, preferential adsorption was not considered. In a later communication van Lent and Scheutjens /135/ presented a model where the chains were monodisperse in length in presence of all the possible sequences.

As the copolymer contains different components there is competition among the groups towards adsorption. Hence competitive and displacement adsorption phenomena are prevailing in copolymer adsorption studies. Yamagiwa et al. /136/ investigated this by using polystyrene, poly(methyl methacrylate) and copolymer of styrene-methyl methacrylate having a wide range of styrene content onto aerosil silica from trichloroethylene solution. They could discern the preferential adsorption of poly (methyl methacrylate) and the copolymer over polystyrene. Poly(methyl methacrylate) chains completely exchanged polystyrene chains. Howard and McConnel /302/ observed that the specific adsorption of poly (ethylene oxide) is about twice as high as that of poly (propylene oxide) on carbon, with the copolymers giving intermediate values related to their composition. This they attributed to the spatial interference by the methyl side groups.

As it is an arduous task to study the effect of all the variable parameters on the adsorption process, the study was restricted to the determination of adsorption isotherms, temperature effect, effect of composition of the copolymers on adsorption and the effect of adsorbents. The corresponding thermodynamic parameters of the adsorption process were computed and discussed.

Adsorbents have played an important role in the rubber and plastic industries. Infact, the early growth of phenolic plastics would not have been possible without the enhancement of the properties by the use of fillers /303/. The last decade has seen the development of fine silica capable of producing a high degree of reinforcement /304/. For non black rubber products silica gel and alumina are generally used /305/. Precipitated calcium carbonate is one of the most versatile mineral fillers and is consumed in a wide range of products including paper paints, plastics, rubbers, textiles and many more. Hence three adsorbents namely silica gel, alumina and calcium carbonate were chosen for the present study. The characteristics of these are discussed below

SILICA GEL

The nature of the silica surface and interaction with various adsorbates have been extensively studied by Hockey /306/ and Darvdov /307/ et al.. Silica gel consists of globules composed in a disordered manner of SiO_4 tetrahedra /112,308/. This is clearly shown in fig. 3.1. The adsorption properties of Silica gel depend on the mutual orientation of the edges of the surface SiO_4 tetrahedra, to which the hydroxyl groups are bound. Owing to the disordered arrangement of surface SiO_4 tetrahedra, all the surface 'OH' groups bonded to silicon atoms ($\geqslant Si - OH$) are not equivalent in their adsorptivity. Although, the silanol groups ($>S_i - O - S_i<$) also occur on the silicagel surface, the specific adsorptive interaction depends on the number and distribution of 'OH' groups per unit area of adsorbent.

Keselev et al. /117/, Snyder and Ward /309/ and others /310-312/ have shown that there are in principle, four different kinds of hydroxyl groups on the surface of the silica gel as shown in Fig. 3.2. They are:

(1) Free (isolated) OH groups
(2) Bonded OH groups
(3) Active OH groups
(4) Geminal OH groups

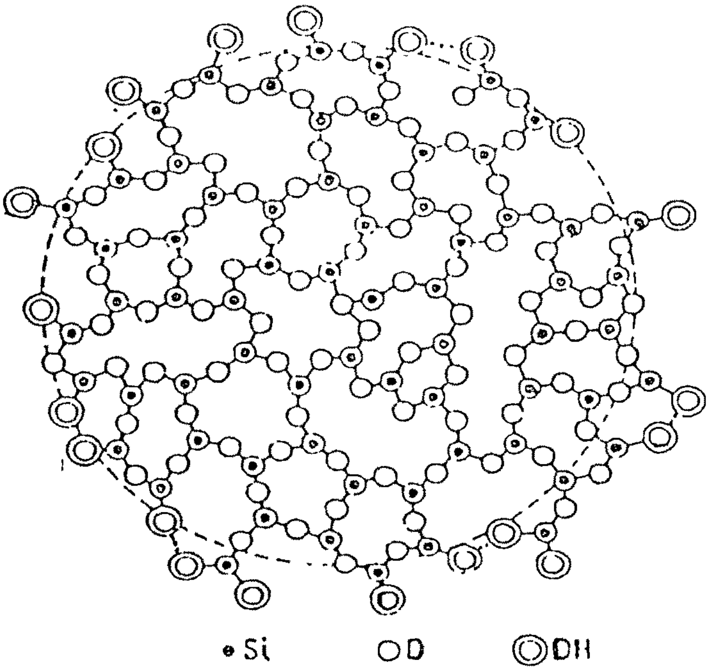
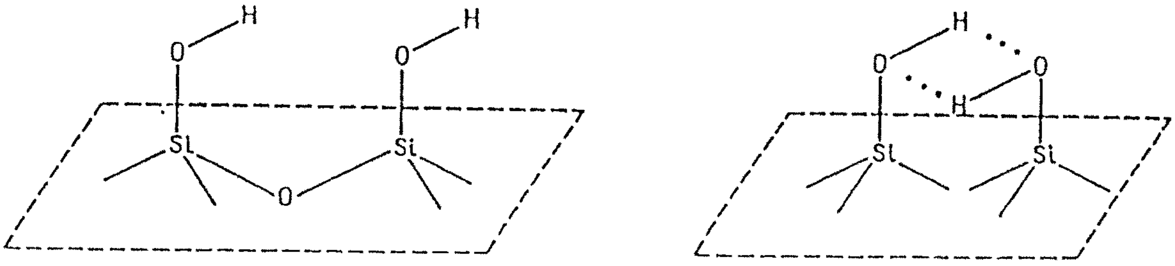
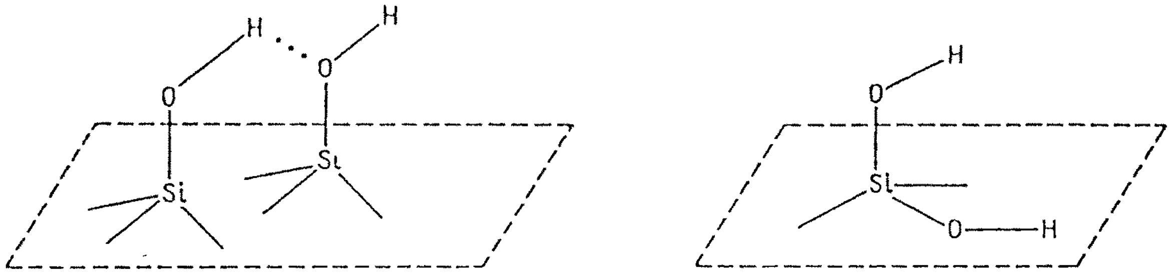


Fig. 3.1 : Globules forming the skleton of silica gel /112/.



free *bonded*



active *geminal*

Fig. 3.2 : Types of hydroxyl groups occuring at the surface of silica gel.

Poly functional adsorbate molecules as well as those possessing Π bonds are strongly adsorbed on active hydroxyl groups /313/. Since the surface hydroxyl groups are responsible for specific adsorption on silica gel, the surfaces of these adsorbents should be hydrated to a maximum degree. The surface concentration of OH groups in hydrated silica gels depend on the temperature of its treatment and not on the specific adsorbent surface area /314/. Activation at 150-200°C is quite sufficient, since most of the water molecules are then desorbed without affecting the number of surface OH groups /315,316/. Activation at 200-400°C causes condensation of most of the bonded (and geminal) OH groups as shown in (fig. 3.3a). At about 400°C, the free hydroxyl groups start shifting on the surface and form active OH groups (fig. 3.3b). Above that temperature the active OH groups undergo condensation, as a result of which the adsorbent molecules also combine with liberation of water and the surface area decreases (fig. 3.3c). At still higher temperature, silica gel is completely dehydrated, thus depriving it of its ability to adsorb unsaturated and polar adsorbate molecules /112/.

ALUMINA

Exhaustive investigations of the alumina surface structure was conducted by Peri et al. /317,318/ some thirty years back. The classification of alumina was proposed by Ginsberg et al. /319/ and modified by Lippens /112/. It was based on the temperature at which it was obtained from hydroxides. The form of alumina most commonly

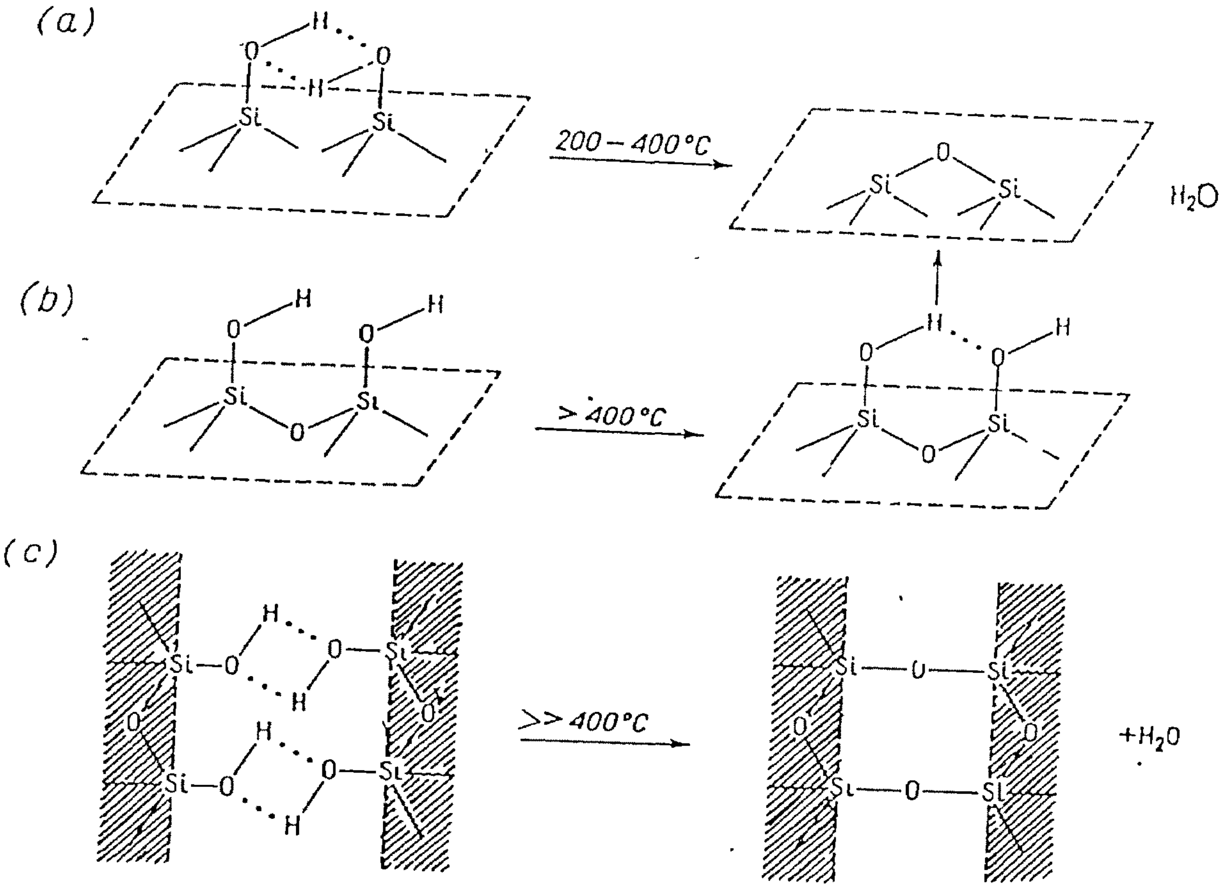


Fig. 3.3 : Effect of temperature on the hydroxylated silica gel surface.

used as an adsorbent is γ alumina with specific surface area between 100-200 m^2/g . γ encompasses low temperature aluminium oxides $Al_2O_3 \times H_2O$ X = 0 to 0.6 obtained at temperature below 600°C. The possible surface sites for adsorption on alumina (γ) include hydroxyls, oxide ions, exposed aluminium ions or protonated vacancies or strong electrostatic fields. This is shown in fig. 3.4 /112/.

A model of the alumina surface layer structure is depicted in 3.5 /112/. Flockhardt et al. /320/ have postulated the existence of two types of defects on the surface of Al_2O_3 heated to temperatures exceeding 773°K. The first type occurs when there is deficiency of two or more oxygen ions in the surface layer. At such sites, Al^{3+} ions are exposed in an anomalous way on the surface (fig. 3.6a). Owing to the accumulation of positive charge such a surface site becomes an electron acceptor (lewis acid). The second type is due to occupation of a surface site by two or more oxygen ions (fig. 3.6b). Such defects are the electron donor types (lewis base).

Four types of active sites occur on the Al_2O_3 surface /321,322/

(1) Al^{3+} ions (acidic)
(2) O^{2-} ions (basic)
(3) ionized hydroxyl groups (basic)
(4) Proton defects (electron acceptor).

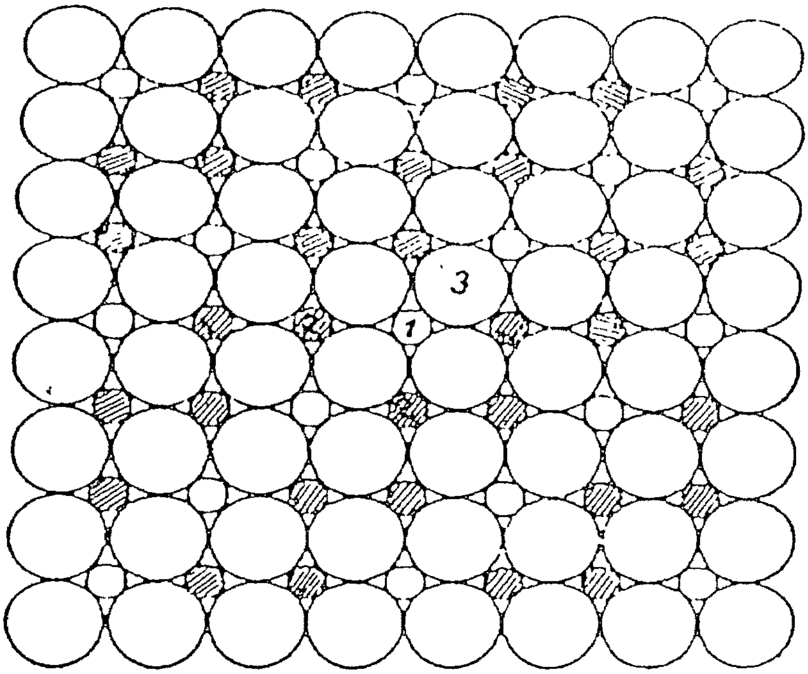


Fig. 3.4 : Model of Al_2O_3 surface structure 1- - surface defects, 2- - Al^{3+} ions, 3- O^{2-} ions.

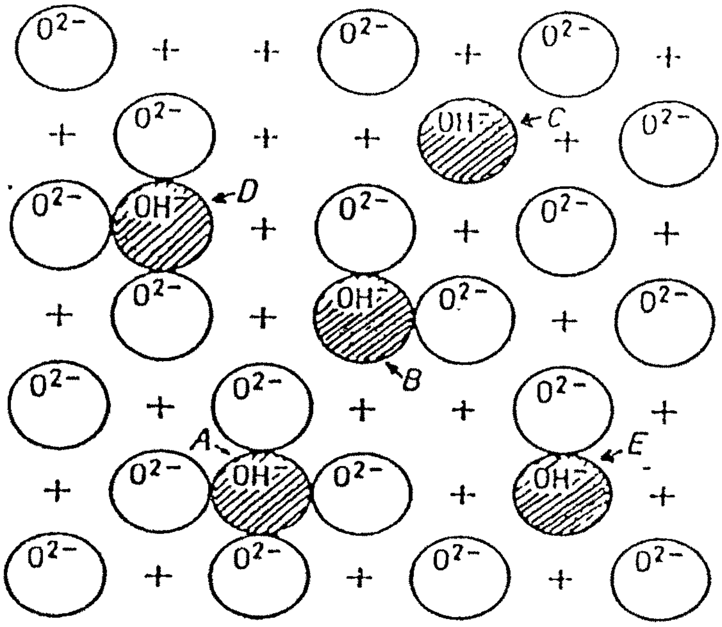


Fig 3.5 : Model of aluminium oxide after strong dehydration.

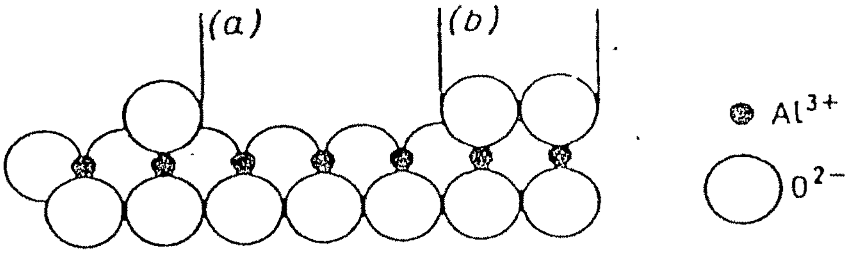


Fig. 3.6 : Surface defects of aluminium oxide heated at 773 K : (a) electron acceptor defects, (b) electron donor defects.

Most substances are adsorbed on Al^{3+} ions around which a strong electric field exists, molecules liable to polarization (unsaturated and aromatic hydrocarbons) are adsorbed particularly strongly. Their weak localization on Al_2O_3 results in general selectivity in adsorption of various aromatic hydrocarbons. Moreover, linear molecules are more stongly adsorbed than non-linear molecules.

It has been shown that some interactions occur between surface hydroxyls of alumina and adsorbing molecules, but this interaction is much weaker than corresponding interaction on silica /323/. Presumably hydroxyl - adosrbate interactions on alumina play a minor role in determining the total adsorption energy of typical organic compounds.

CALCIUM CARBONATE

Precipitated $CaCO_3$ is a commercial type of the compound produced chemically in a precipitation process. The precipitated products are distinguished by a finer, more uniform particle size, a narrower size range and a higher degree of chemical purity. $CaCO_3$ occurs naturally in two crystal structures, calcite and aragonite. Calcite is thermodynamically stable at all investigated pressures and temperatures /324/. The aragonite polymorph is metastable and irreversibly changes to calcite when heated in dry air to about 400°C, the rate of change increasing with temperature. The crystal forms of calcite are in a hexagonal system. Aragonite is in the orthorhombic system. The usual crystal habits are acicular or elongated prismatic.

In the commercial forms of precipitated calcium carbonate where aragonite predominates, crystals have parallel sides and large length to width ratios. Most commercial grades of precipitated calcium carbonate have a dry brightness in excess of 98% and have minimum purity of 98%, the major contaminants being $MgCO_3$ and silica.

Plastic industry is a rapidly growing consumer of precipitated $CaCO_3$ for cost reduction. It is categorized as a non reinforcing filler. However, when used in resins in concentration greater than 10%, improves physical properties such as heat resistance, dimensional stability, stiffness, hardness and processibility /325,326/.

Calcium carbonate is the preferred filler for asphalt pavement because of its strong interaction with the acidic components of asphalt /327/ and its surface basicity is well established. The basicity resides in the carbonate ion, a moderately strong electron donor or hydrogen acceptor. The acid calcium ions are covered by the large carbonate anions.

3.2 MATERIALS AND METHODS

POLYMERS

Polybutadiene rubber (PBR) was obtained from Indian Petrochemicals Corporation Limited, Vadodara, India. According to the manufacturers

/328/ its composition was cis 1,4 (>96%), trans 1,4 (1-2%) and vinyl (1-2%). It has been characterized by various techniques recently /329/. The viscosity average molecular weight was 4.5 x 10^5 and had a molecular weight distribution of 2.52. Polymer purity is a dominant factor in the adsorption studies hence it was imperative to purify this commercial product before the studies were conducted. This was done by dissolving the polymer in toluene, filtering and then reprecipitating in excess quantity of methanol. It was then vaccum dried at room temperature for several hours until the solvents were completely evaporated.

Poly(methyl acrylate), poly(ethyl acrylate), Poly(butyl acrylate) and polyacrylonitrile were synthesized in the laboratory. The synthesis, purification and characterization of these homopolymers were described in Chapter II.

The six copolymers used in the adsorption study were ANMA$_{11}$, ANMA$_{12}$, ANEA$_{11}$, ANEA$_{12}$, ANBA$_{11}$ and ANBA$_{12}$. These were also synthesized, purified and characterized in the laboratory as described in Chapter II.

ADSORBENTS

Alumina (acidic) was obtained from BDH (Glaxo Laboratories) India. To regulate the particle size it was sieved through a standard (ASTM) sieve of mesh size 100. Alumina with mesh size above 100 was taken for this study. The surface area determined by BET method using nitrogen gas was 97.1 m^2/g. The probability of the surface impurities in alumina was checked by X-ray photoelectron spectroscopy (Fig. 3.7) and no impurity was observed. The spectra were recorded on a VG Scientific Escalab MK II Spectrometer using Mg K_α radiation under pressure of about 5 x 10^{-7} m bar /330/. Silica gel (column chromatography grade) was obtained from Glaxo Laboratories India Ltd. Its mesh size ranging from 60-120. The surface area determined by BET using N_2 was 284.2 m^2/g.

Precipitated calcium carbonate was obtained from E.Merck (India) Ltd. The surface area determined by BET (N_2) was 25.2 m^2/g.

Probability of surface impurities in silica gel and alumina were also checked by X-ray photo electron spectroscopy using Al K_α radiation and no impurity was observed (fig. 3.7).

To maintain the reproducibility of the adsorbent characteristics, the adsorbents used were from the same packing. Prior to the study these adsorbents were always activated at 125°C for at least three hours and cooled in a dessicator before use.

SOLVENTS

The solvents used were

[a] methanol, GPR, E. Merck (India);

[b] toluene, synthesis grade, E. Merck (India);

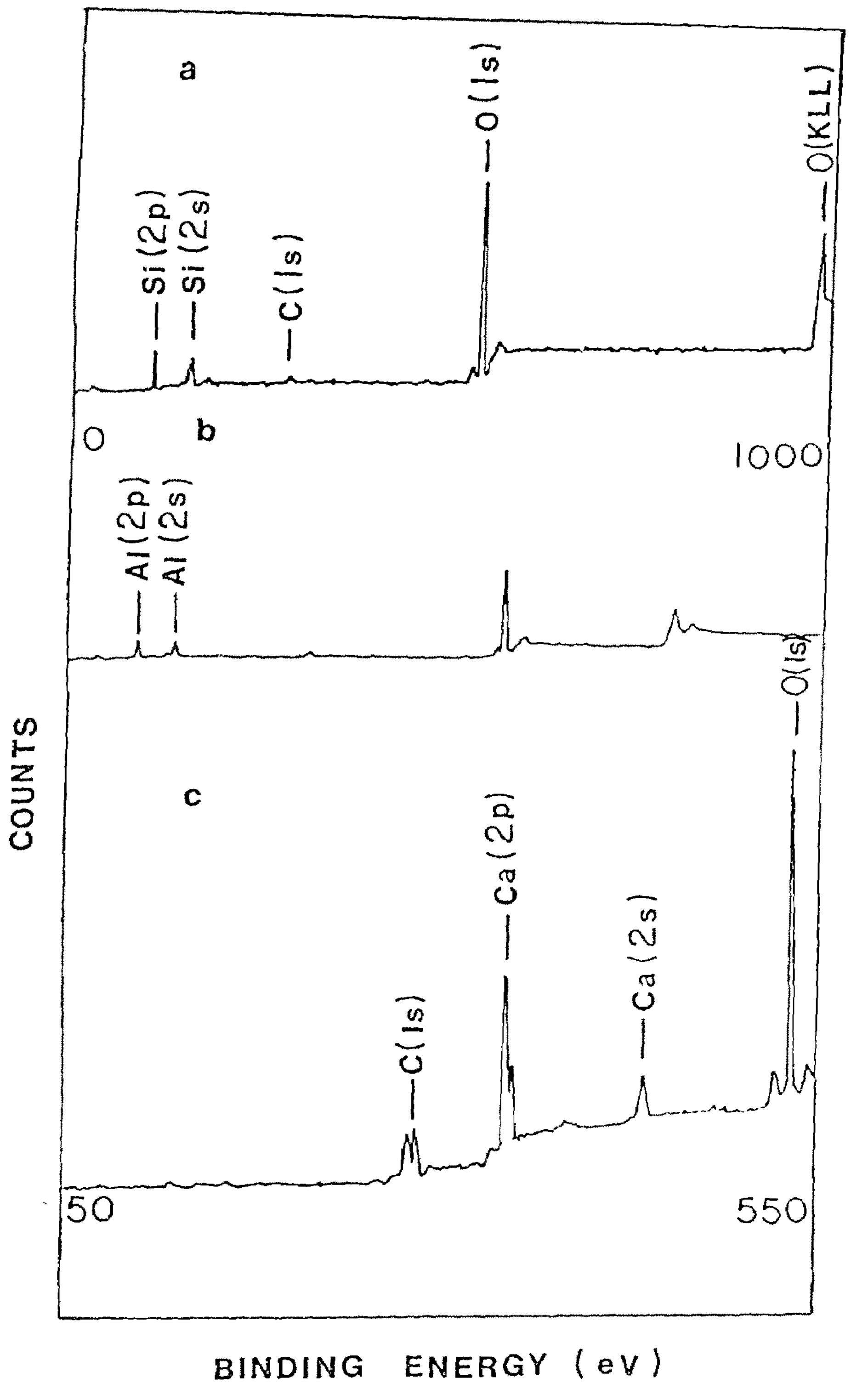


Fig. 3.7 : ESCA of (a) silica gel, (b) alumina, (c) calcium carbonate.

[c] cyclohexane, chromatography grade, E. Merck (India);

[d] NN' Dimethyl formamide, AR, Glaxo lab, India;

[e] Dimethyl sulfoxide, AR, SD fine chem, India

Cyclohexane was pased through a column of actvated silica gel and alumina to remove the traces of any olefinic impurities. All the solvents were freshly distilled and the middle fractions were used.

NN' Dimethyl formamide (DMF) and Dimethyl sulfoxide (DMSO) were stored over 4A° molecular sieves. (Loba Chemie, India) overnight to remove traces of water. This was then distilled under low pressure in dry atmosphere. The distilled fraction was also stored with molecular sieves. The boiling point of the purified DMF was 151°C (literature value 150-152°C). Molecular sieves were washed with conductivity water, dried at 150°C before use.

EXPERIMENTAL METHODS

Polymer solutions at the highest concentration were made by dissolving weighed amount in a known volume of the solvent. Other concentrations were made by dilution of the same. Weighed amount of adsorbents were placed in a series of jacketted bottles and a fixed quantity of the desired solution was added to each bottle. These were then placed on a shaker for continuous shaking and simultaneously thermostated water of experimental temperature (±0.1°C) were pumped through the jacket to have constant temperature while shaking. The estimation of the polymer was done a few times until two consecutive readings were within 2% of each other. The same procedure was followed at all temperatures.

Preliminary runs were performed to determine the equilibration time. It was between 24 to 36 hours. Also, readings were taken at intervals of 3,5 and 7 days to check on the probable quasiequilibrium of the systems and the results showed that such problems were absent in this study.

For mixed solvent systems different mixtures of the two solvents cyclohexane and toluene were prepared in ratios of 80:20, 50:50 and 20:80, by volume respectively. This was considered as the stock solvent and the highest concentration of the polymer solution was made by dissolving weighed amount in the required quantity of solvent. By dilution, solutions of lower concentrations were made Pycnometer was used to determine the solvent density.

The concentration of PBR in cyclohexane was determined by UV spectroscopy at λ max (240 nm) and by gravimtry in toluene and toluene-cyclohexane mixtures due to higher cut off (λ_{max} = 280 nm) of toluene. For the homopolymers of acrylates and acrylonitrile and the copolymer systems the concentrations were estimated at (λ_{max} 272 nm) where DMF was the solvent used. The equilibrium concentrations were computed from a calibration curve obtained earlier.

In the gravimetric procedure /153,331/ 2 ml of the solutions were pipetted out into dry, small, weighed beakers and placed under low vacuum at 50°C until complete evaporation of the solvent. The beakers were then weighed to determine the amount of residual polymer present. The process was repeated until two consecutive weighings gave the same result. Each point was duplicated simultaneously to check the reproducibility of the result. Duplicate blank experiments were also conducted with pure solvents. Concentration of the PBR studied ranged from 0.05% to 1.2% (w/v), for polyacrylates and copolymers from 0.05% to 1% (w/v) and for polyacrylonitrile from 0.05 to 0.8% (w/v) as the isotherms reached plateau region much before the maximum concentration used.

Scanning electron micrographs (SEM) were taken at the Geology Department of this university. The SEM photographs were taken by a JEOL JSM - T3 Scanning electron microscope. The samples were mounted onto aluminium studs with the help of an adhesive. The mounted samples were then gold coated with 100A° thickness. The photographs were taken at different magnifications.

3.3 ADSORPTION OF HOMOPOLYMERS

This section discusses the adsorption of various homopolymers, polybutadiene (PBR), poly (methyl acrylate), poly (ethyl acrylate), poly (butyl acrylate) and poly acrylonitrile. The adsorption has been studied at four different temperatures. PBR adsorption was studied from cyclohexane (C), tolune (T) and various binary mixtures of T and C on alumina. Adsorption of polyacrylates and poly acrylonitrile were studied on three adsorbents, silica gel, alumina and calcium carbonate from NN' Dimethyl formamide solutions.

3.3.1 POLYBUTADIENE (PBR)

The adsorption isotherms for PBR - cyclohexane and PBR - toluene systems on alumina are shown in figs. 3.8 and 3.9. The amount of adsorption is more from cyclohexane than from toluene and decreases as the temperature is increased. The isotherms show maxima, minima and plateau regions. Similar isotherms were also observed earlier /49/. It was suggested /88,152/ that as the polymer gets adsorbed on the surface of the adsorbent a second phenomenon, spreading of the polymer on the surface of the adsorbent starts. The rate of adsorption is expected to be proportional to the concentration of the polymer in solution and the rate of spreading is proportional to the concentration of the adsorbed polymer on the surface. At lower initial concentration, the thickness of the adsorbed layer and the adsorbed polymer mass is large and is distributed randomly. Hence the concentration of the polymer in the adsorbed layer is low. In the lower concentration region, the macromolecules are initially adsorbed in a three dimensional manner and then spreads more and more two dimensionally over the surface with time /28/. At higher initial

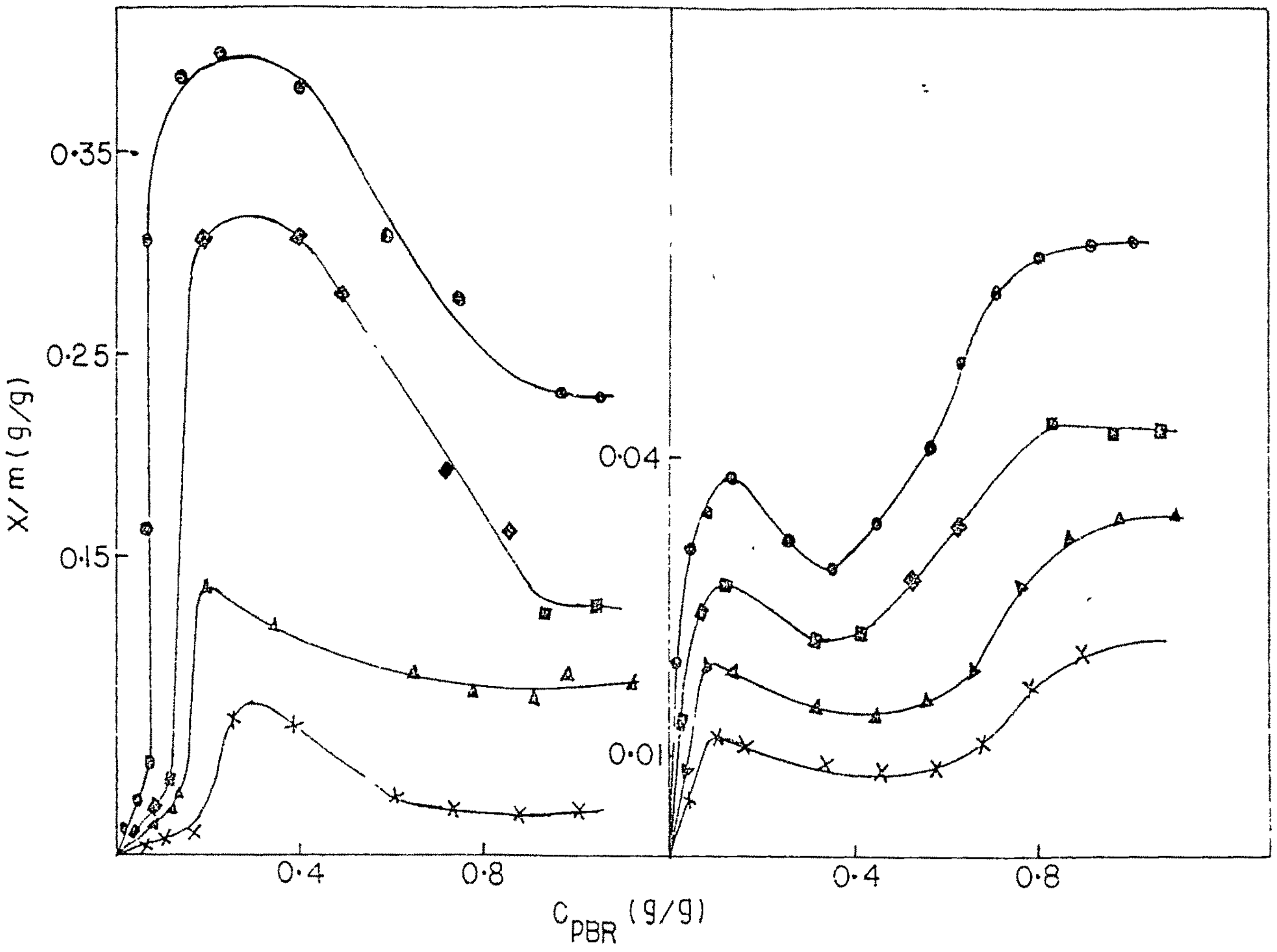


Fig.3.8 Plot of specific adsorption against the equilibrium concentration of PBR from cyclohexane on alumina.

● 25°C ▨ 30°C ▲ 35°C ✕ 40°C

Fig.3.9 Plot of specific adsorption against the equilibrium concentration of PBR from toluene on alumina.

● 25°C ▨ 30°C ▲ 35°C ✕ 40°C

concentration the polymer molecules compete more for the adsorbent surface, adsorbing three dimensionally. This results in greater layer thickness and higher polymer concentration in the adsorbed layer. The layer thickness is known to increase with the square root of the molar mass at higher initial concentration /28/. This spreading starts much before the equilibrium is reached and therefore will determine the amount of PBR adsorbed. Hence, more the polymer spreads on the surface, less is the amount adsorbed. The nature of the observed isotherm is therefore due to these two antagonistic effects, besides others.

The SEM photographs (fig. 3.10a,b,c) of alumina before and after adsorption are shown. The adsorbent was removed from the jacketted bottles after 24 hours, dried and divided into two parts. The SEM of one part was taken immediately and that of the second part was taken after 2 days. It can be easily concluded from the photographs that the system did change with time. One can observe more polymer sheath on the surface and a decrease in the rough edges of the alumina surface taken after two days. This we assume a reasonably good proof of polymer spreading as well as multilayer formation. This has been observed earlier for poly styrene /332/.

The dip observed in the isotherms i.e. the desorption of the adsorbed polymer at higher concentration could also be due to polydispersity of the polymer sample. It is known that the higher molecular weight polymers are preferentially adsorbed /333/. The

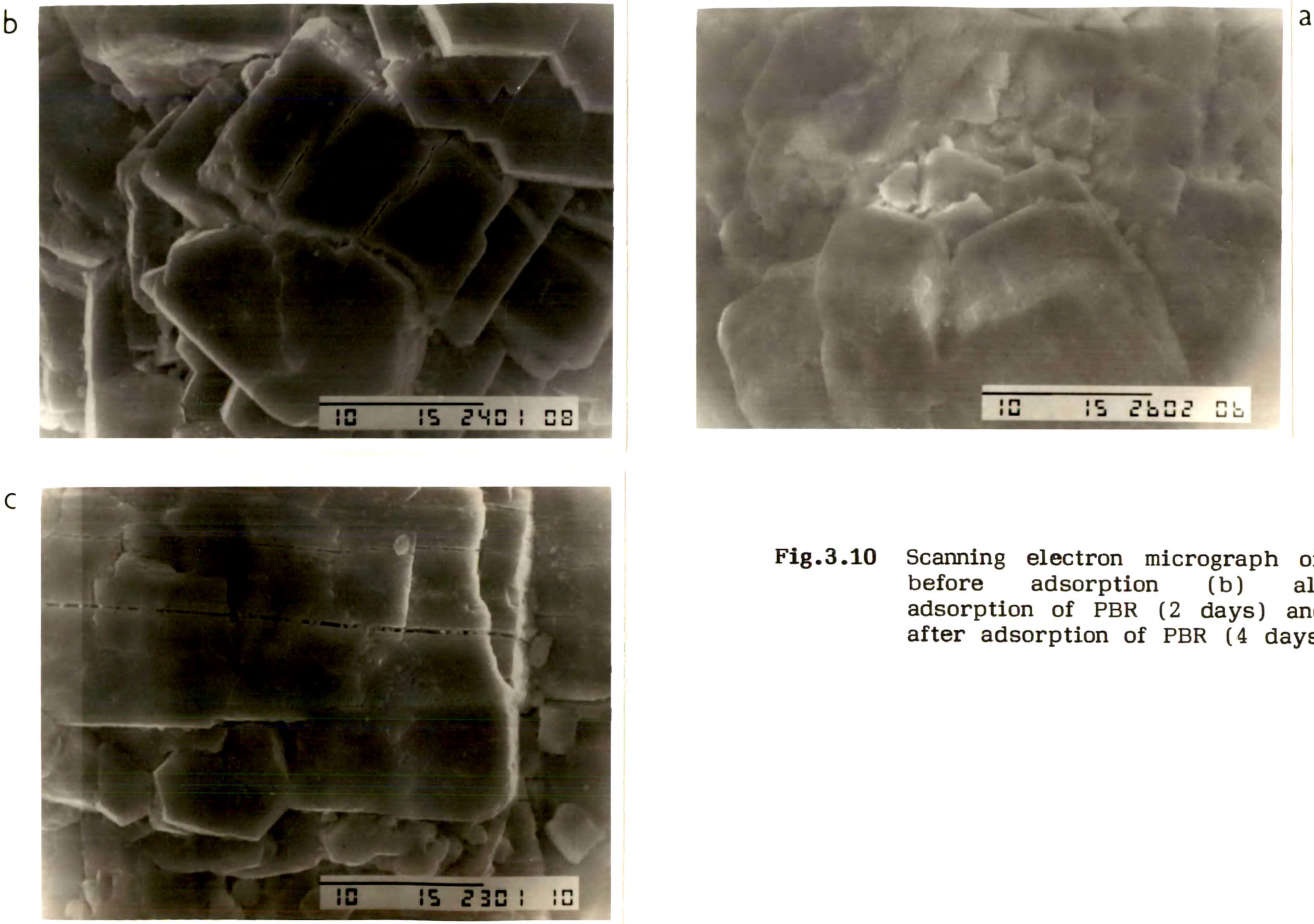


Fig.3.10 Scanning electron micrograph of (a) alumina before adsorption (b) alumina after adsorption of PBR (2 days) and (c) alumina after adsorption of PBR (4 days).

molecular weight distribution of PBR is found to be 2.52 by GPC analysis /334/. This indicates that the polymer sample is polydisperse with various molecular weight species. At lower initial concentration both the high molecular weight and low molecular weight species are adsorbed. The diffusion of the lower molecular weight species are easier on the adsorbent surface, but with time higher molecular weight species replaces the lower ones due to preferential adsorption /333/. When the concentration is increased more larger molecules are available to replace smaller ones. Therefore the molecular weight distribution on the adsorbed layer changes with the amount of adsorption and may differ considerably from that of the polymer in bulk phase /11/. This fractionation continues as long as there are larger molecules in the bulk phase than on the adsorbed layer and the adsorption isotherm is therefore strongly influenced by the molecular weight distribution of the sample /16/. If the adsorption bond is strong such a displacement may not occur and the smaller molecules will also remain adsorbed. Around the concentration at which the dip is observed probably no further adsorption of the polymer happens on the surface. But at a little higher concentration, polymer - polymer interaction becomes important enough, resulting in a higher adsorption, and the dip is more prominent. All these factors taken together are responsible for the nature of the isotherms.

Moreover, from viscosity study, voluminosity was calculated and hence the shape factor, which was 2.5 /334/ thereby suggesting that the polybutadiene had a spherical conformation in solution in both the solvents. It is difficult to visualize the conformational nature of the polymer at the solid - liquid interface, but as it is a linear polymer it could show the train, loop and tail segments as suggested by Jenkel and Rumbach /25/, leading to a change in IR frequency of the adsorbed polymer. However, such a change was not detected so the conformation of the polymer on the surface may be same as in solution /77/.

The main objective of the present thesis was to use the fundamental thermodynamics to the adsorption process. Hence the experimental data obtained was used with the thermodynamic principles to get a proper understanding of the process of adsorption.

The adsorption process could be written as

$$A_{(solid)} + PBR_{(solution)} \rightleftharpoons APBR_{(solid)} \qquad \ldots\ldots 3.1$$

Where A is the adsorbent. The equilibrium constant is therefore

$$K = \frac{a_{APBR(solid)}}{a_{A(solid)} \cdot a_{PBR(solution)}} \qquad \ldots\ldots 3.2$$

$$\text{Hence} \quad K = \frac{1}{a_{PBR(solution)}} \simeq \frac{1}{C_{PBR(solution)}} \qquad \ldots\ldots 3.3$$

Where we assume that the activity of the solids (adsorbent and adsorbent - PBR) are unity. Therefore the free energy of adsorption is

$$\triangle G_{ads} = -RT \ln K = -RT \ln C_{PBR} \qquad \ldots\ldots 3.4$$

Where R and T signify universal gas constant and temperature in degree Kelvin.

To obtain free energy of adsorption at infinite dilution $\triangle G^{o}_{ads}$, the $\triangle G^{o}_{ads}$ in the lower concentration region were plotted against original C_{PBR}, linearity was observed and the line was extrapolated to $C_{PBR}=0$. We believe that $\triangle G^{o}_{ads}$ values represent relative variation in the system and indicate the free energy change at a given temperature from a hypothetical solution of unit concentration with the properties of infinitely dilute solution at atmopheric pressure onto a solid surface

The $\triangle G^{o}_{ads}$-T plot showed linearity, the slope and intercept being $\triangle S^{o}_{ads}$ and $\triangle H^{o}_{ads}$ respectively. The thermodynamic values so calculated are presented in Table 3.1. It is obvious from the data that all adsorption processes are exothermic with negative entropy change. These values clearly indicate that the adsorption of PBR on alumina from cyclohexane are enthalpy dominated.

TABLE : 3.1

THE FREE ENERGY (ΔG^{o}_{ads}), ENTHALPY (ΔH^{o}_{ads}) AND ENTROPY (ΔS^{o}_{ads}) OF ADSORPTION OF POLYBUTADIENE AT INFINITE DILUTION FROM DIFFERENT SOLVENTS

(Concentration is expressed in g/100g of solution)

Solvent C:T(v/v)	$-\Delta G^{o}_{ads}$ (kJ mol^{-1})				$-\Delta H^{o}_{ads}$ (kJ mol^{-1})	$-\Delta S^{o}_{ads}$ (J $mol^{-1}K^{-1}$)
	30°C	35°C	40°C	45°C		
100 : 0	9.3	9.0	8.6	8.3	28.7	68.2
80 : 20	8.3	8.0	7.8	7.3	26.4	60.5
50 : 50	12.2	11.7	11.3	10.8	39.1	90.7
20 : 80	11.5	10.9	10.5	9.9	42.1	103.0
0 : 100	11.4	10.6	9.8	9.5	48.0	116.7

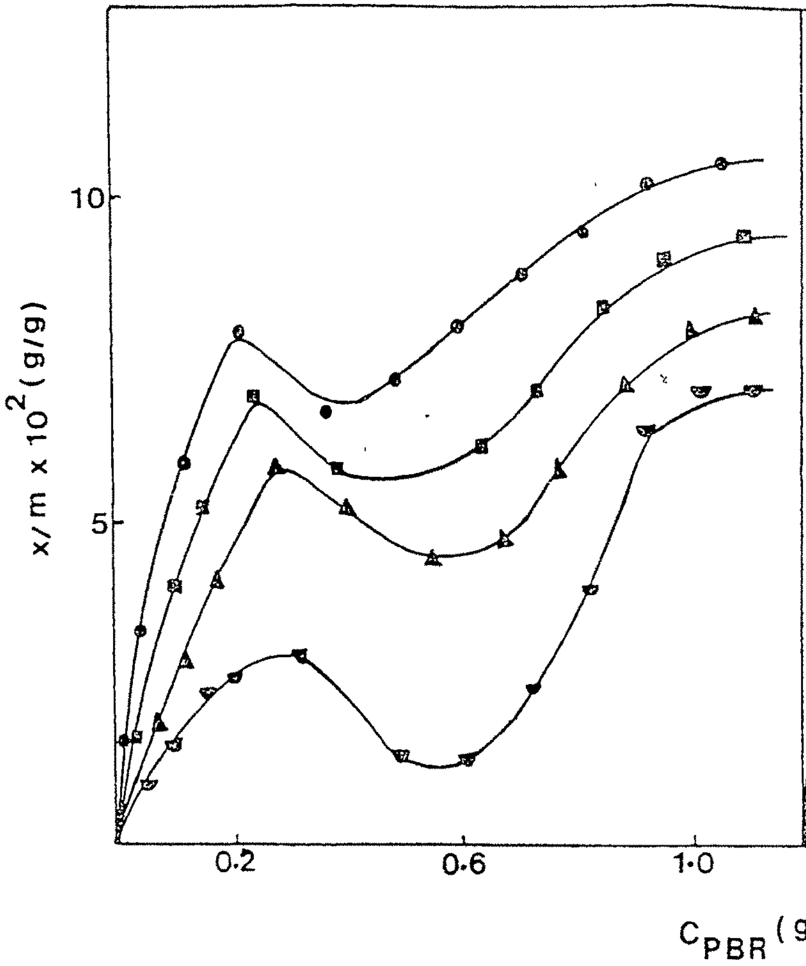
The adsorption process from a solution as in these cases are complicated due to the presence of many different phenomena. Besides the spreading phenomena as mentioned earlier, the polymer - solvent, solvent - adsorbent and the polymer - adsorbent interactions also complicate the system.

It is difficult to compute the interaction parameter of the polymer - solvent system at this juncture. However, from the intrinsic viscosity of the solution one can qualitatively characterize the two solvents as good or poor /87/. It is well known that the adsorption is more from a poor solvent than from a good solvent /85/. The intrinsic viscosity of the cyclohexane - PBR and toluene - PBR systems are 2.38 and 2.48 at 30°C respectively /89/, signifying that toluene is a better solvent and hence there will be less adsorption from this solvent system. The solubility parameter (δ) is another criterion used to characterize the solvent power /91/. The δ values for PBR, cyclohexane and toluene were calculated to be 8.13, 8.2 and 8.9 respectively indicating that cyclohexane should be better solvent for PBR /335,336/ which contradicts the observations of intrinsic viscosity. This type of conflicting observation was also reported earlier /88/.

The other complicating factor is solvent - adsorbent interaction. The characteristic of adsorbent surfaces are important. Aromatics are easily adsorbed on the alumina surface and the adsorption occurs on the Al^{3+} sites of alumina /112/. Hence, qualitatively it was expected that toluene would be competing more for the adsorbent sites than cyclohexane, thereby reducing the polymer adsorption from toluene systems. The experimental observation, the prediction from solvent strength parameter values of eluotropic series and the intrinsic viscosity data all supplement the above contention, though the solubility parameter values belie this. The overall thermodynamic quantities obtained is the contribution from all these different phenomena.

To study the effect of the nature of solvent, which is an important factor in any adsorption process, PBR adsorption was studied from mixed solvent systems of toluene and cyclohexane. Many studies have been done to correlate the nature of the solvent and the adsorbed amount /88, 337-340/ although a clear correlation was not always observed /341,342/.

The adsorption isotherms of the mixed solvent systems are represented in figs. 3.11 to 3.13. The isotherms shows a maxima, minima and a plateau region, similar in nature to that of the pure solvent systems. As discussed earlier the spreading phenoma and polydispersity of PBR accounts for the nature of the isotherms. The adsorption data obatained for mixed solvents is similar to that obtained for pure solvents though the absolute magnitudes differ. Fig. 3.14 shows that the amount of polymer adsorbed per gram of adsorbent decreases with increase in toluene content of the solvent. This indicates that toluene is a better solvent among the two. The



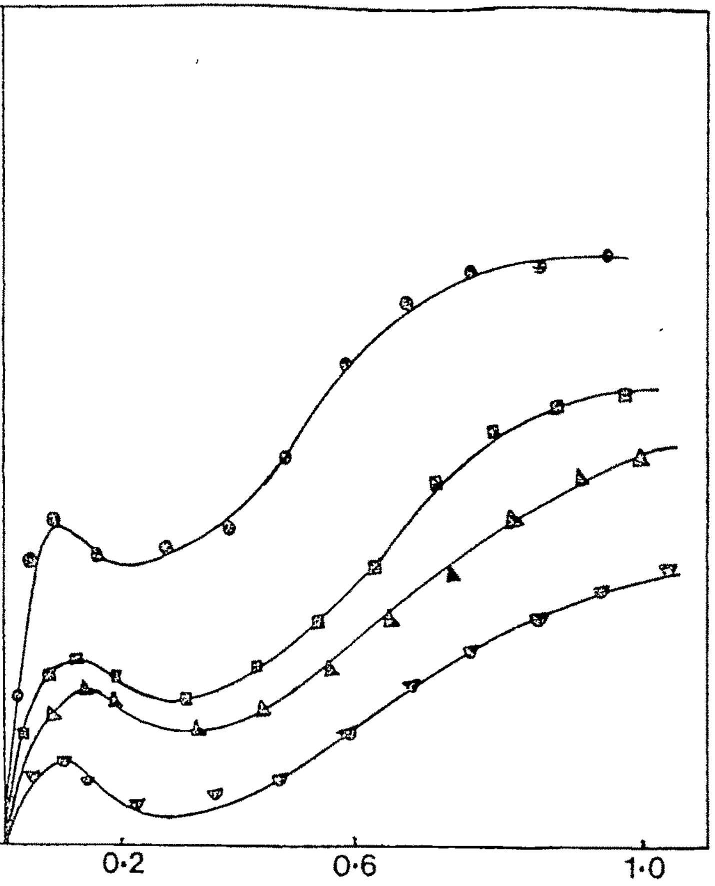


Fig.3.11 Plot of specific adsorption against the equilibrium concentration of PBR from 80C : 20T on alumina.

● 25°C ▨ 30°C ▲ 35°C ▼ 40°C

Fig.3.12 Plot of specific adsorption against the equilibrium concentration of PBR from 50C : 50T on alumina.

● 25°C ▨ 30°C ▲ 35°C ▼ 40°C

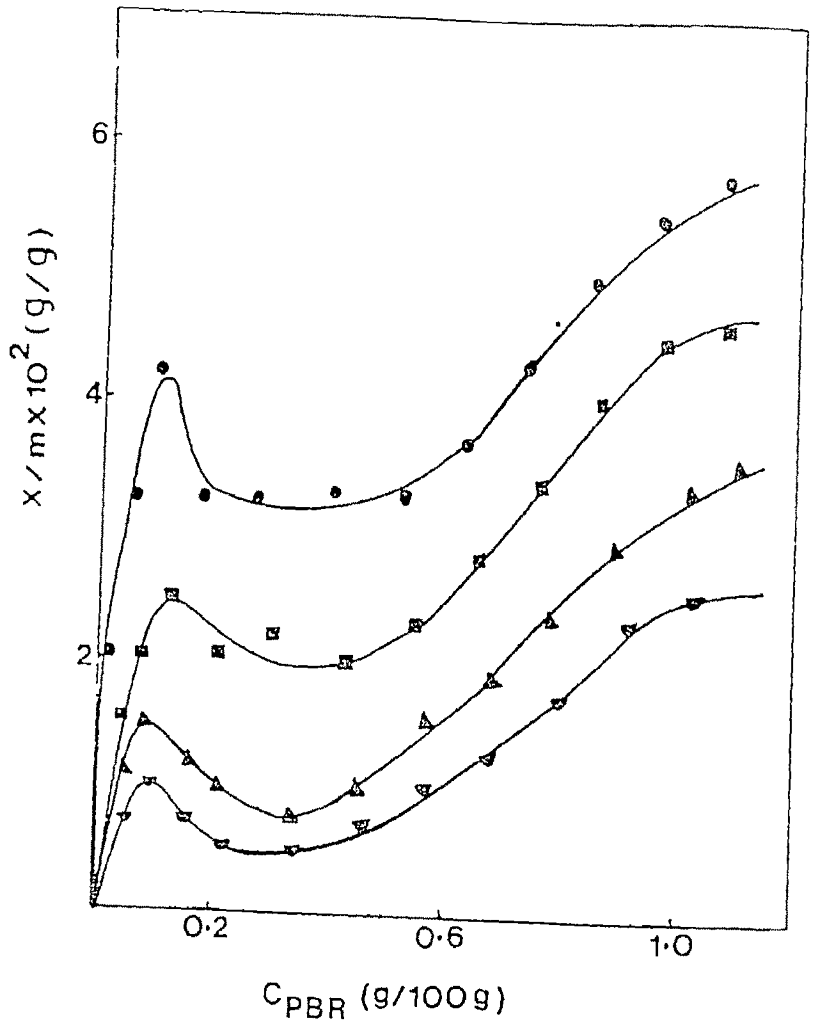


Fig.3.13 Plot of specific adsorption against the equilibrium concentration of PBR from 20C:80T on alumina.

● 25°C ▨ 30°C ▲ 35°C ▼ 40°C

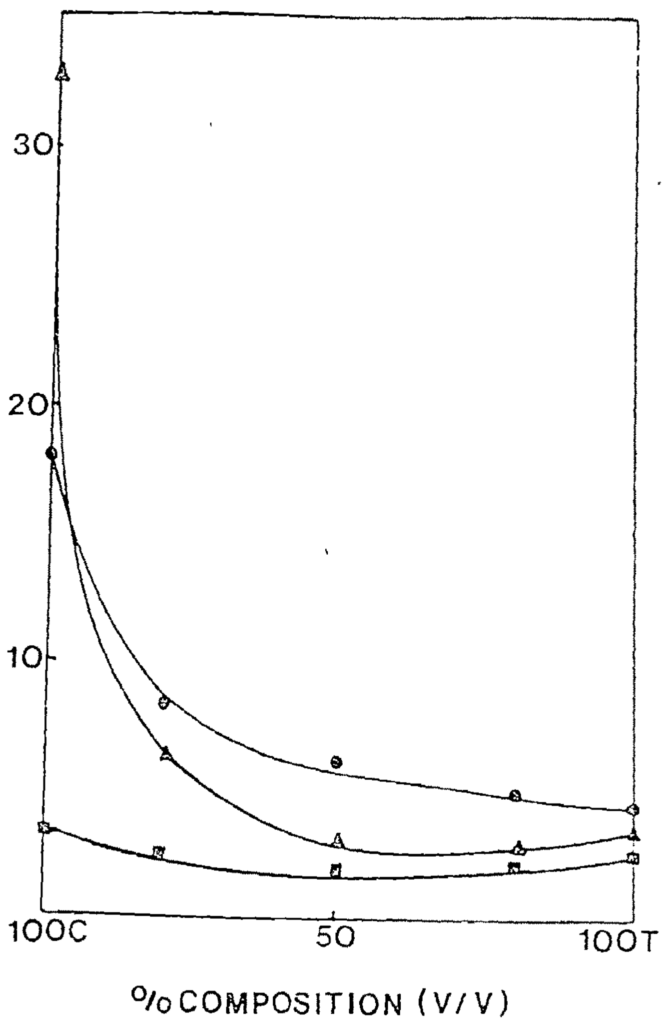


Fig.3.14 Plot of specific adsorption against the percentage composition of solvent mixtures at 30°C and different original concentrations.

● 0.8% ▲ 0.5% ▨ 0.15%

plot also shows a minimum at 20:80 of cyclohexane - toluene solvent system indicating that least amount of adsorption occurs at this solvent composition and hence this mixture can be termed as the better solvent for PBR.

The solubility parameter values of the various mixtures of the liquids can be calculated with the help of Scatchard equation /36,343/.

$$E^{\frac{1}{2}} (n_C V_C + n_T V_T)^{\frac{1}{2}} = n_C (E_C V_C)^{\frac{1}{2}} + n_T (E_T V_T)^{\frac{1}{2}} \qquad \ldots\ldots 3.5$$

Where n_C and n_T are moles, V_C and V_T are molar volumes and E_C, E_T, are cohesive energy densities, C and T represent cyclohexane and toluene respectively. E is the cohesive energy density of the mixture. The solubility parameter values for the various mixtures of liquids are presented in Table 3.2.

The values indicate that 80:20 and 50:50 of C:T should be good solvent for PBR, resulting in lower adsorption from these solvent mixtures. This is contradictory to the observation, where 20:80 of C:T is found to be better solvent for PBR, leading to least adsorption from this mixture.

To account for different amount of adsorption from various mixed

TABLE : 3.2

CALCULATED SOLUBILITY PARAMETER VALUES FOR BINARY SOLVENT MIXTURES

Solvent ratio (v/v)	No. of moles of cyclohexane	No. of moles of toluene	Solubility parameter
C:T	n_C	n_T	δ
80 : 20	0.737	0.187	8.02
50 : 50	0.461	0.467	8.24
20 : 80	0.180	0.75	8.45

solvents, relative solvent strength of the binary mixtures (E_{CT}) were computed as follows :

$$E_{CT} = E_C + (E_T - E_C) [(E_{CT} - E_C) / (E_T - E_C)] \quad . . . . . 3.6$$

E_{CT} obtained for various solvent mixtures is shown in figure 3.15. The plot deviates from linearity, showing almost a saturation in adsorbent - solvent interaction by gradually levelling off with increase in percentage composition of toluene. E_T for pure solvent i.e. toluene calculated with the help of the above equation differes slightly from that in the eluotropic series. This is mainly because of the approximations in the calculations with the above equation for the binary mixture of the liquids. The results obtained above are in agreement with our experimental observation and support the nature of the isotherms. Thus the solvent strength values explain the overall observations even though the solubility parameter values are in contradiction.

Table 3.1 presents the thermodynamic quantitites obtained for the mixed solvent systems. All $\triangle S^{o}_{ads}$ and $\triangle H^{o}_{ads}$ values are negative. This shows that the adsorption process is exothermic and polymer molecules after adsorption on the adsorbents becomes less randomised than in the bulk. It can also be surmised from Table 3.1 that the adsorption process is spontaneous from the solvents over the whole composition range. The variation in the thermodynamic quantities $\triangle H^{o}_{ads}$ and $\triangle S^{o}_{ads}$ with the percentage composition of the mixed

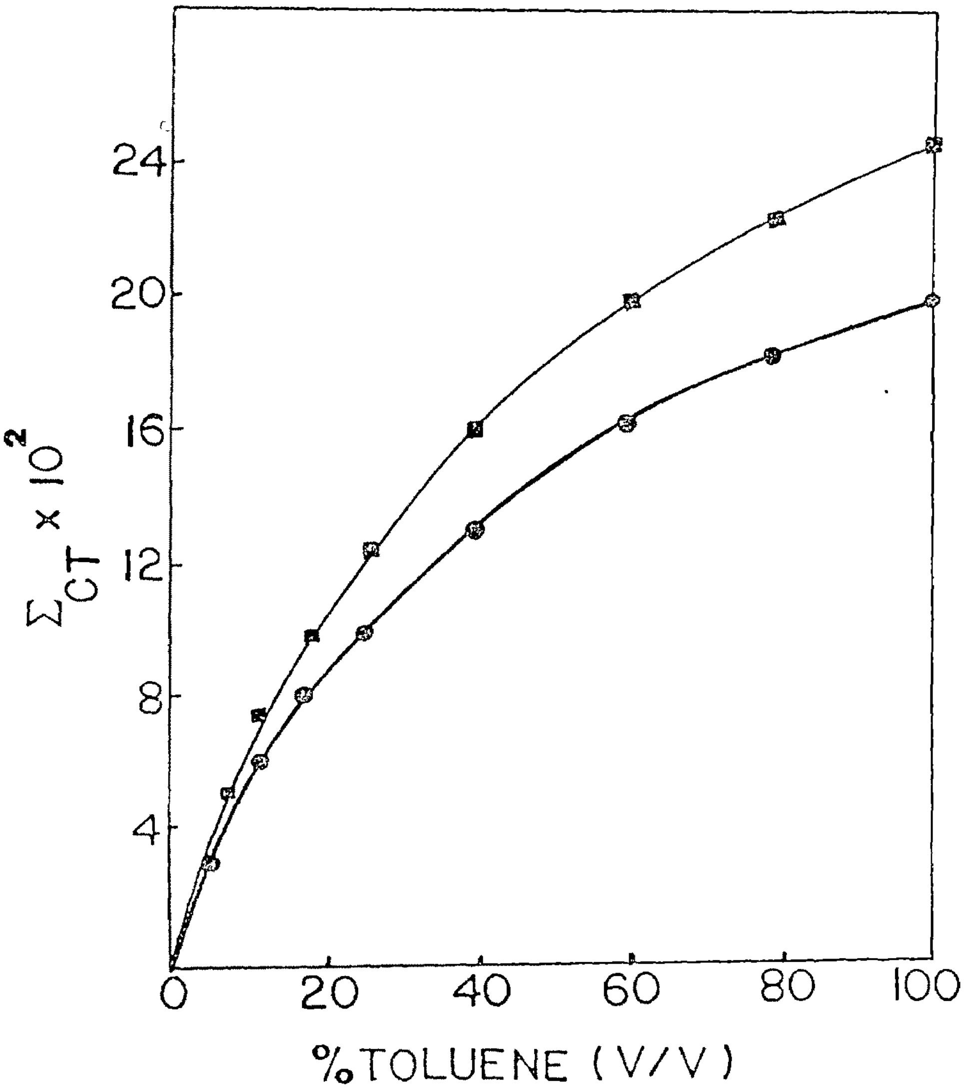


Fig. 3.15 Plot of relative solvent strength parameter of the binary mixture againwt the percentage composition of toluene in solvent mixture.

▨ alumina ● toluene

solvents are shown in fig. 3.16. It is known that heat of mixing of cyclohexane and toluene is a positive quantity i.e. it is an endothermic process /344/. Thus if two liquids are completely miscible and if that process is endothermic, then that mixed solvent system for natural polyisoprenes is a better solvent than the pure ones. This results in lower adsorption from that mixed solvent system. This is in agreement with the earlier observations, that a polymer though not soluble in two liquids, becomes soluble in a mixture of the two liquids, due to unfavourable enthalpy of mixing of the two liquids /14,345/.

Thermodynamic quantities can also be calculated as a function of surface coverage. The system can be thermodynamically followed as the degree of adsorption reaches saturation. The amount of PBR adsorbed A per 100 g of adsorbent was calculated using the equation /346/.

$$A = (Co - Ceq)\ V.\ 100\ /\ m \qquad \ldots\ldots\ 3.7$$

Where Co and Ceq are the initial and equilibrium concentrations of the polymer solution (g/l). V is the volume of the solution of polymer taken for the adsorption study (0.01 l). m is the weight of the absolutely dry adsorbent (g).

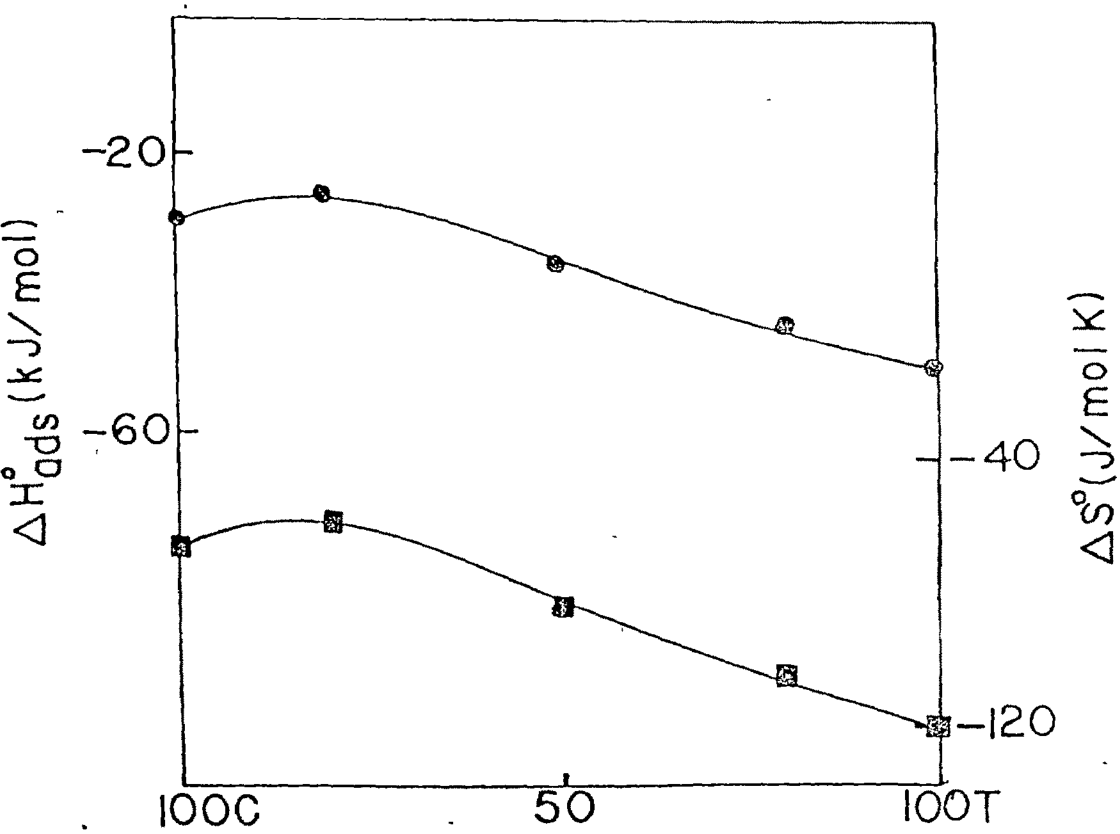


Fig.3.16 Plot of enthalpy ΔH^o_{ads} and entropy ΔS^o_{ads} of adsorption at infinite dilution against the percentage composition of solvent mixtures.

● ΔH^o_{ads} ■ ΔS^o_{ads}

The equilibrium constant K_A were calculated for different amounts of adsorbed polymer using the equation.

$$K_A = 1 / Ceq \qquad \ldots\ldots 3.8$$

This is valid for average filling of the surface. The temperature dependence of the equilibrium constant follows the equation

$$\log K_A = \triangle S_A / 2.3\ R - \triangle H_A / 2.3\ RT \qquad \ldots\ldots 3.9$$

The plot of log K_A Vs T^{-1} was linear, for different values of A and the isosteric heat $\triangle H_A$ was calculated from the slope of the above plot. The values obtained for pure solvent systems, are compiled in Table 3.3, and for the mixed solvent systems are given in Table 3.4.

The values are negative for all the systems and so the process is exothermic i.e. heat is released during the process of adsorption. Isosteric heat linearily decreases with increasing amount of polymer adsorbed according to the relation.

$$(- \triangle H_A) = (- \triangle H_0) - CA \qquad \ldots\ldots 3.10$$

Where $\triangle H_A$ and $\triangle H_0$ are the heat released during the adsorption of A amount of polymer and when $A \rightarrow 0$ respectively. The coefficient C characterizes the energetic heterogeneity of the adsorbent

TABLE : 3.3

THERMODYNAMIC PARAMETERS OF ADSORPTION OF PBR ON ALUMINA FROM PURE SOLVENT SYSTEMS BY SURFACE COVERAGE APPROACH

Solvent	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_c$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
Cyclohexane	0.25	81.6	249.3	6.1	76.1	228.7	6.8
	0.50	86.3	268.4	5.0			
	0.75	92.5	291.5	4.2			
	1.00	97.3	309.6	3.5			
Toluene	0.25	60.8	179.2	6.5	49.9	141.1	7.1
	0.50	74.3	227.3	5.4			
	0.75	85.0	265.2	4.6			
	1.00	95.9	303.4	4.0			

TABLE : 3.4

THERMODYNAMIC PARAMETERS OF ADSORPTION OF PBR ON ALUMINA FROM MIXED SOLVENTS BY SURFACE COVERAGE APPROACH

Solvent (C:T)(v/v)	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
80:20	0.50	72.7	218.7	6.4	62.0	176.9	8.4
	0.75	79.3	244.3	5.3			
	1.00	83.6	261.4	4.4			
	1.25	89.6	284.7	3.3			
50:50	0.50	72.7	218.7	6.4	57.6	162.2	8.5
	0.75	79.3	244.3	5.3			
	1.00	85.9	268.9	4.4			
	1.25	94.9	302.2	3.3			
20:80	0.50	66.5	198.2	6.4	45.2	122.2	8.2
	0.75	75.8	232.9	5.2			
	1.00	87.2	273.3	4.4			
	1.25	97.5	309.8	3.6			

(alumina). The plot of $\triangle H_A$ Vs A were linear and are shown in fig. 3.17 for some systems. The $\triangle H_0$ values hence obtained for pure systems and mixed solvent systems are compiled in Table 3.3 and 3.4 respectively. It is known from the theory of adsorption /346/ that when the isosteric heat decreases with the increase in the amount of the substance adsorbed, the adsorbent surface is treated as uniformly heterogenous. Such a decrease in $\triangle H_A$ values were observed in these systems (Table 3.3 and 3.4) indicating that the alumina surface is uniformly heterogeneous. The change in conformation of the macromolecules of the adsorbed layer could be a reason for this inverse relation between $\triangle H_A$ and A. In such cases the adsorption equilibrium is defined by the logarithmic isotherm of Tjumkin /347/.

$$A = \ln (Ceq.\ K_0) / f \qquad \ldots\ldots 3.11$$

Where f is the coefficient of heterogeneity and K_0 is the equilibrium constant of adsorption at infinite dilution.

This equation can be rewritten as

$$A = 2.3 \log k_0 / f + 2.3 \log Ceq / f \qquad \ldots\ldots 3.12$$

The plot of A vs log Ceq were linear, and the coefficient f and K_0 were obtained from the slope and intercept respectively. The coefficient f is dependent on temperature according to the equation.

$$f = C / RT - f_0 \qquad \ldots\ldots 3.13$$

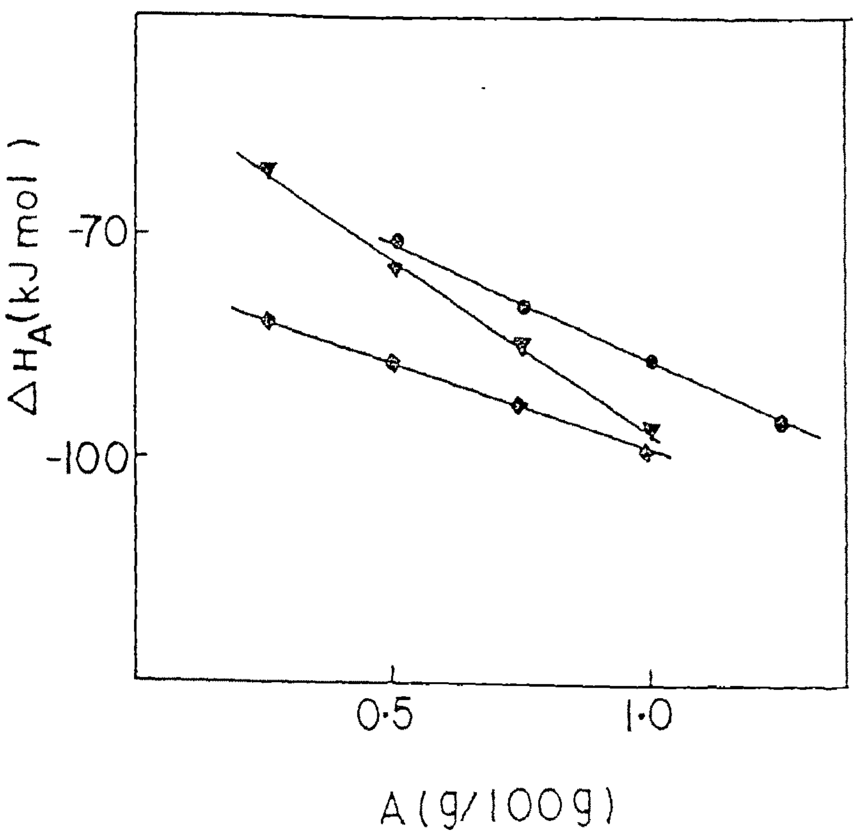


Fig. 17 Change in ΔH_A with the amount of PBR adsorbed, A on alumina from

● 50C:50T ▲ Toluene ▨ cyclohexane

The values of f at different temperatures and f_o obtained from the intercept of the plot of f Vs 1/T are given in Table 3.5. It can be seen that as the temperature rises, the heterogeneity of the adsorbent increases for all systems. The temperature dependence of f is shown in figure 3.18. 'f' is related to the entropy change and is related to 'm' by /348/.

$$m = f_o \cdot R \qquad \ldots\ldots 3.14$$

Entropy change $\triangle S_A$ was calculated from the intercept of the plot of log K_A Vs 1/T using the equation 3.9. The dependence of entropy change on A is expressed by the equation.

$$\triangle S_A = \triangle S_o - mA \qquad \ldots\ldots 3.15$$

Few representative plots of $\triangle S_A$ against A are shown in fig. 3.19. These plots were linear. The value of m so obtained coincides with those obtained from equation 3.14 and are tabulated in Table 3.5.

It is observed that as the amount (A) of polymer adsorbed increases, the degree of freedom of the polymer molecules on the adsorbent surface decreases and the mobility is restricted. The possible reason for this could be the conformational change of the adsorbed polymer molecules on the adsorbent surface. Though Kawaguchi et al. /5/ observed such a change by infrared spectroscopic studies, these systems did not show any change. The infrared spectra of the alumina

TABLE : 3.5

SURFACE CHARACTERISTIC PARAMETERS OF ADSORPTION OF PBR ON ALUMINA FROM DIFFERENT SOLVENT SYSTEM

Solvent System	f (gl^{-1})				$-f_o$ (gl^{-1})	$-m$ ($J\ mol^{-1}K^{-1}$)	$-C$ ($kJ\ mol^{-1}$)
	30°C	35°C	40°C	45°C			
Cyclohexane	1.23	1.33	1.49	1.64	9.7	81.0	21.3
Toluene	1.06	1.28	1.62	1.94	19.7	164.0	50.0
80C : 20T	1.44	1.59	1.76	1.85	10.2	86.1	22.1
50C : 50T	1.44	1.59	1.76	2.01	13.2	110.0	29.3
20C : 80T	1.23	1.49	1.74	2.03	17.6	147.3	41.8

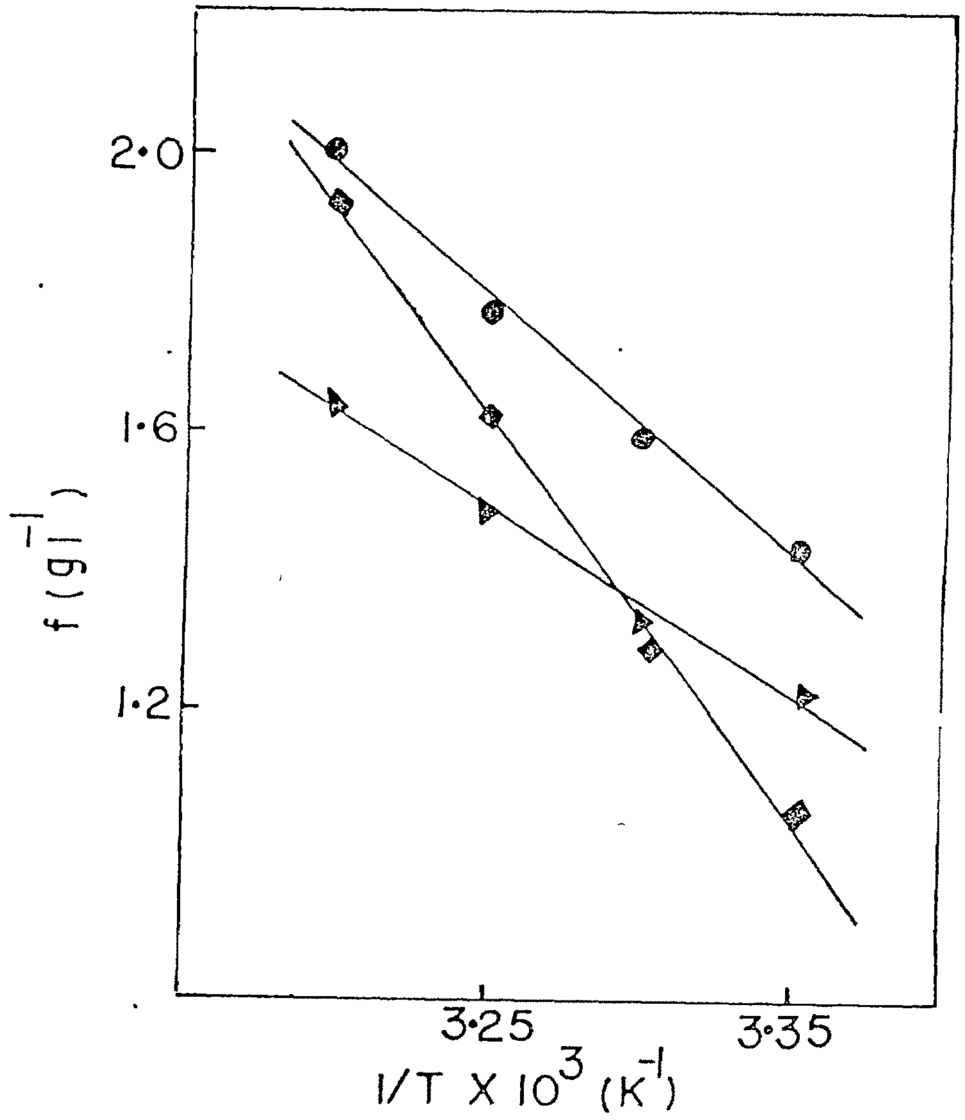


Fig. 3.18 Temperature dependence of 'f' for PBR - alumina system from

● cyclohexane ▨ Toluene ▲ 50C:50T

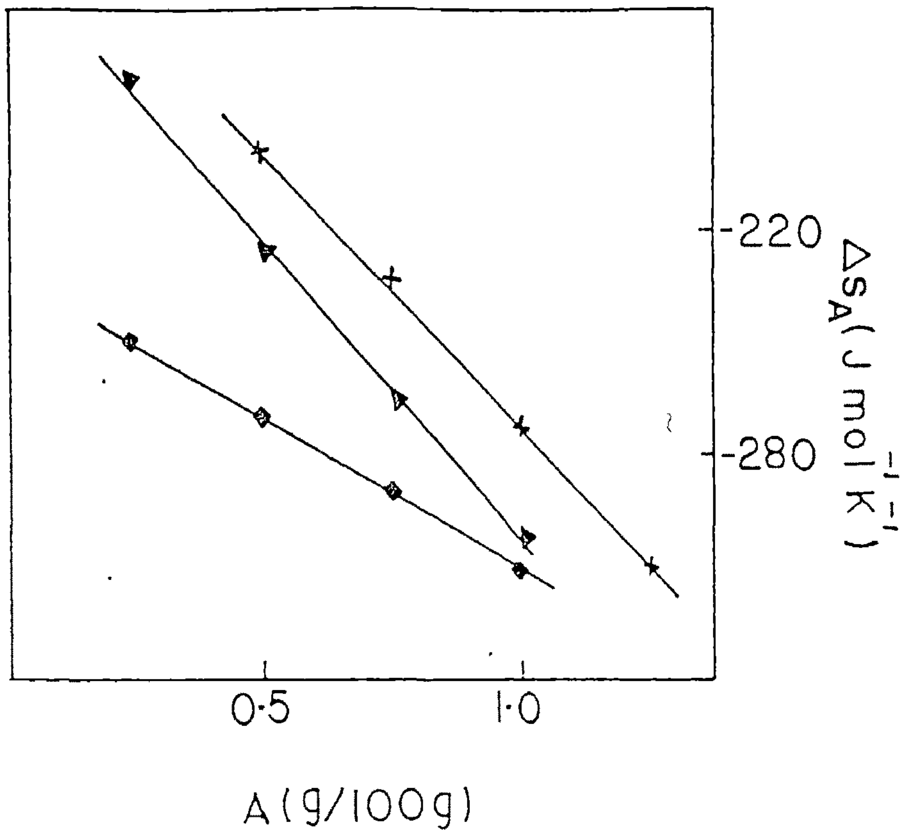


Fig.3.19 Change in Δs_A with the amount of PBR adsorbed A on alumina from

× 20C:80T ▲ Toluene ▨ cyclohexane

samples after the adsorption of the polymer on it did not show any shift in frequency. Hence it could be surmised that the dependence of $\triangle S_A$ on A is due to some other reasons. At this moment we appreciate the possibility that the bands were broader and diffused or the amount of polymer adsorbed was much less than the quantity required for detection.

According to the theory of process of adsorption taking place on a uniform heterogeneous surface the equilibrium constant depends upon the amount adsorbed as follows

$$K_A = K_o \, e^{-f\, A} \qquad \ldots\ldots \; 3.16$$

$$\ln K_A = \ln k_o - f\, A \qquad \ldots\ldots \; 3.17$$

A representative plot of the dependence of log K_A on A at different temperatures is shown in fig. 3.20 for 80C:20T solvent system.

On solving equations 10 and 15, the following dependence is observed.

$$\triangle S_A = \triangle S_o - m \triangle H_o / C + m \triangle H_A / C \qquad \ldots\ldots \; 3.18$$

$$\text{i.e. } \triangle H_A = C \triangle S_A / m - C \triangle S_o / m + \triangle H_o$$

According to this equation $\triangle S_A$ linearily changes with $\triangle H_A$, hence proving the existence of compensation effect. This will be discussed later. This also indicates that the process of adsorption in these systems takes place with the simultaneous change in the entropy and energy factors. These two factors have determining effect on the affinity of the polymer towards the adsorbents, a measure of which is the change in free energy. This is given by the relation.

$$\Delta G_A = \Delta H_A - T \Delta S_A \qquad \ldots\ldots 3.19$$

The value of ΔG_A obtained for different systems at different amount of the polymer (PBR) adsorbed at 303 °K are given in Table 3.3 and 3.4 for pure solvent and mixed solvent systems respectively. The ΔG_A values were plotted against A, the intercept yielding ΔG_0. A representative plot is shown in fig. 20a for PBR-alumina system. These values are given in Tables 3.3 and 3.4.

The ΔG_A values were negative for all these systems, indicating the thermodynamic possibility of the adsorption process.

Hence it is clear that the adsorption process can be treated from the isosteric point of view as well as from the infinite dilution view point. The overall idea about the systems remains same though absolute magnitudes do differ as the nature of the systems are different.

3.3.2 POLYACRYLATES

Adsorption studies of poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA) and poly(butyl acrylate) (PBA) onto silica

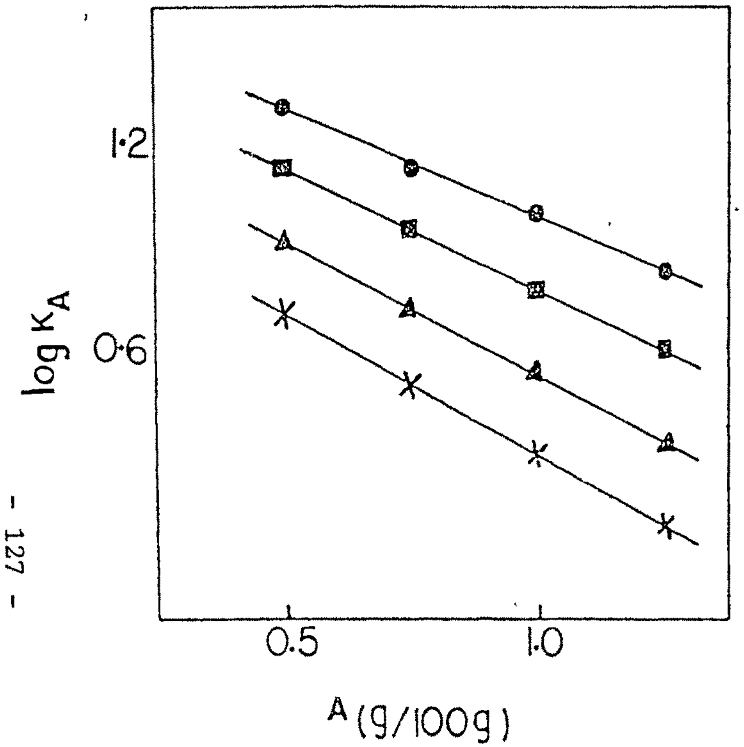


Fig. 3.20 Plot of log K_A against amount of PBR adsorbed on alumina at different temperatures from 80C:20T solvent mixture.

● 25°C ▨ 30°C ▲ 35°C X 40°C

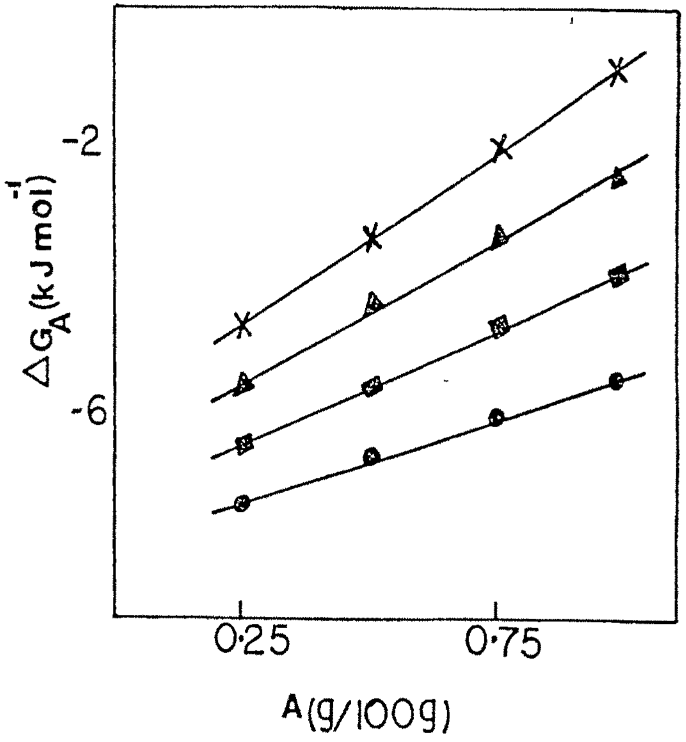


Fig.3.20a Plot of $\triangle G_A$ against amount of PBR adsorbed A on alumina from toluene at different temperatures.

● 25°C ▨ 30°C ▲ 35°C X 40°C

gel, alumina and calcium carbonate from NN' Dimethyl formamide (DMF) were carried out at four temperatures 30°, 35°, 40° and 45°C. The adsorption isotherms obtained are shown in figs. 3.21 to 3.29. The effect of temperature on the amount of adsorption in all these systems are similar, with a decrease in the specific amount adsorbed at a given equilibrium concentration as the temperature is raised. It can also be seen from the isotherms that the amount of polymer adsorbed is higher on silica gel than on alumina and considerably low on $CaCO_3$. This is shown in fig. 3.30 for PEA adsorption on these adsorbents.

The isotherms obtained for alumina and $CaCO_3$ systems are of the usual Langmuir type. The adsorption increases steeply at low concentration and finally levels off to a plateau.

The isotherms of silica gel systems show an inflection after the initial steep rise region (a semi plateau), then increases very steeply at higher concentrations before reaching the plateau region. These reflect either a change in orientation at the surface /64/ or the formation of multilayers /22/.

The nature of these isotherms could also be explained on the basis of polydispersity of the polymer samples and the specific interaction of the adsorbent and polymer. Though a GPC run of these samples could not be obtained to get an idea about the molecular weight distribution, it could be assumed that the polyacrylates were

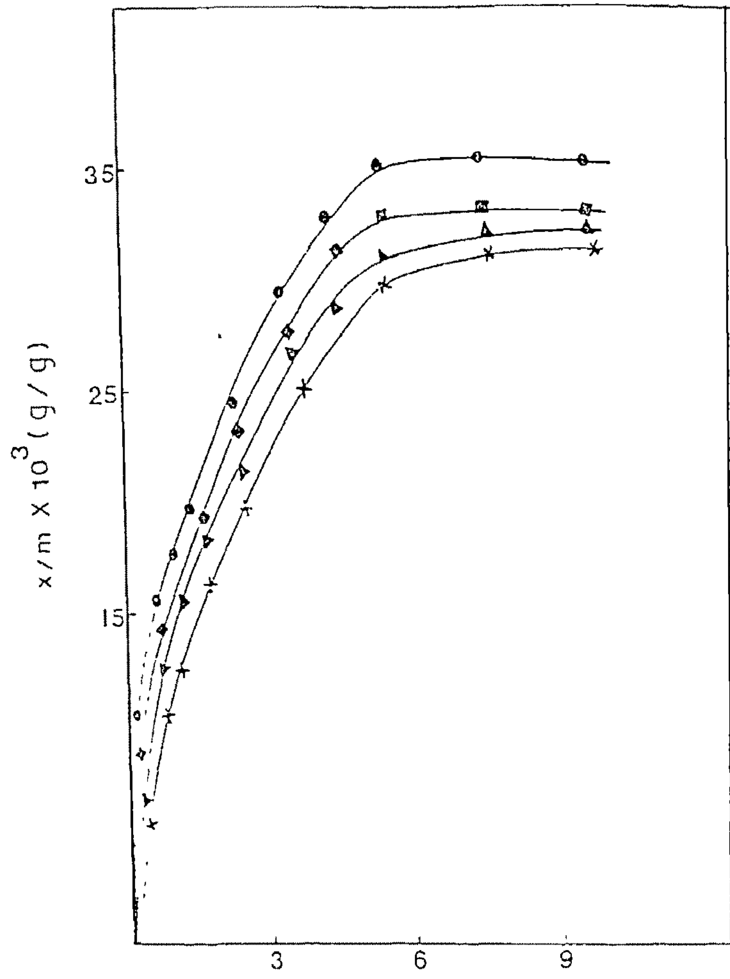


Fig.3.21 Plot of specific adsorption against equilibrium concentration of PMA on alumina.

● 30°C ▣ 35°C ▲ 40°C X 45°C

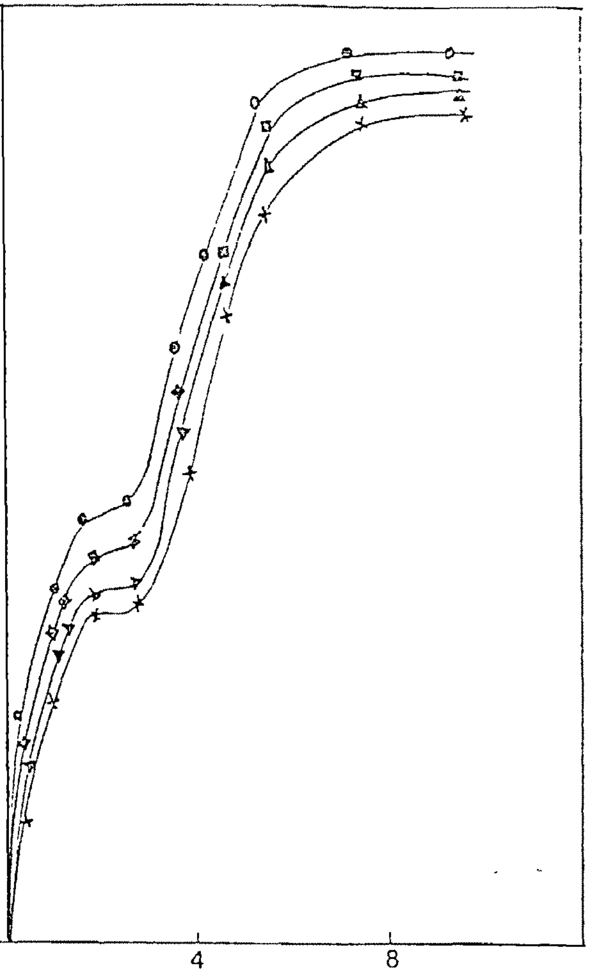


Fig.3.22 Plot of specific adsorption against equilibrium concentration of PMA on silica gel.

● 30°C ▣ 35°C ▲ 40°C X 45°C

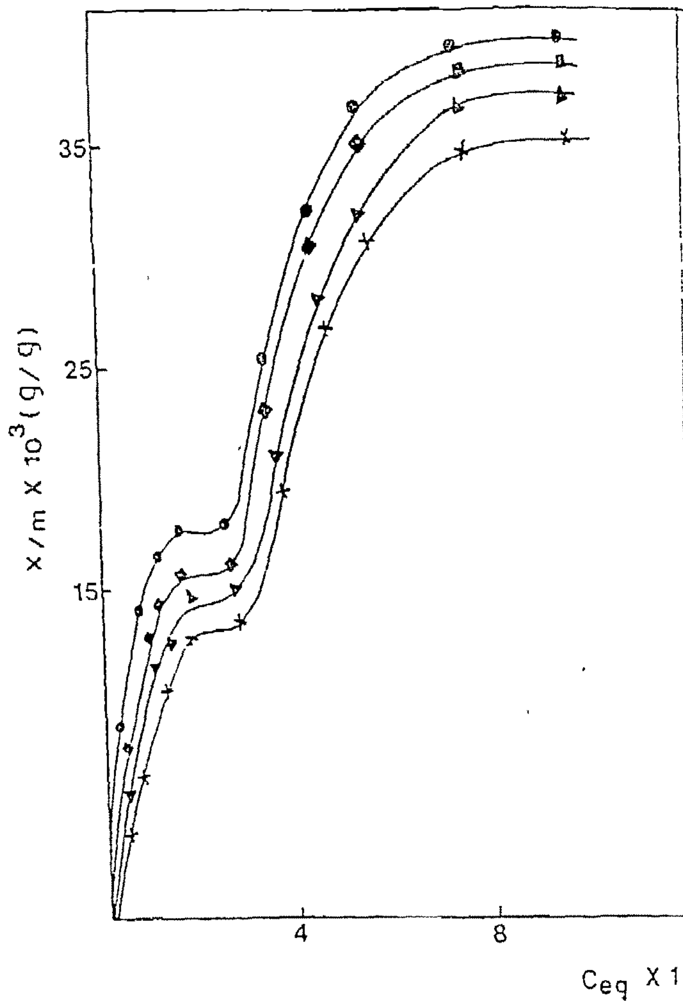


Fig.3.23 Plot of specific adsorption against equilibrium concentration of PEA on silica gel

● 30°C ▨ 35°C ▲ 40°C X 45°C

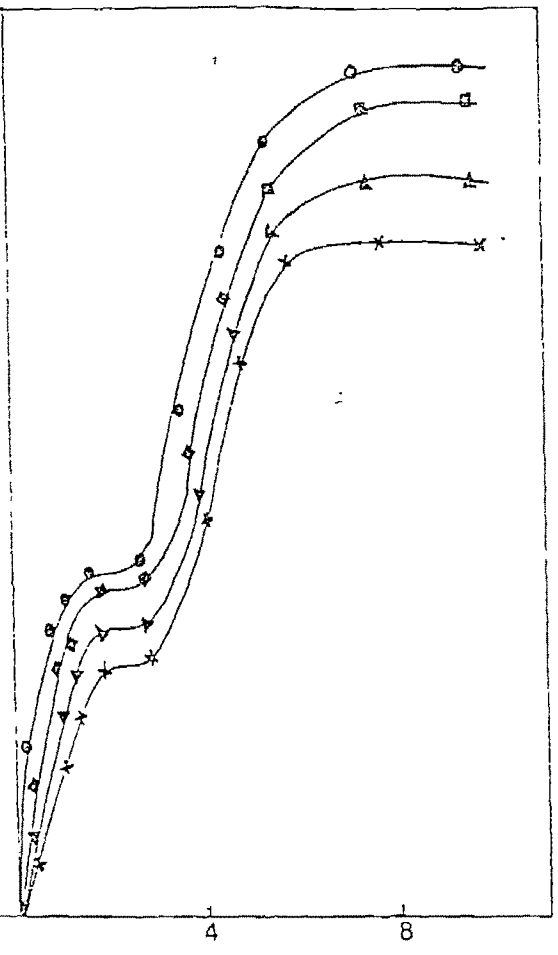


Fig.3.24 Plot of specific adsorption against equilibrium concentration of PBA on silica gel

● 30°C ▨ 35°C ▲ 40°C X 45°C

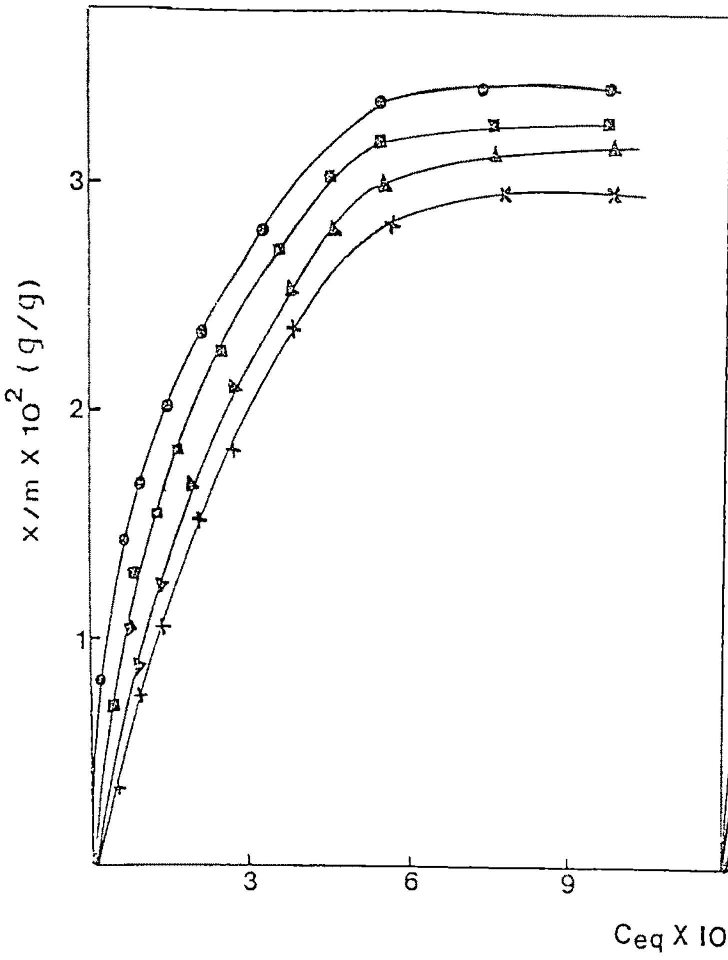


Fig.3.25 Plot of specific adsorption against equilibrium concentration of PEA on alumina

● 30°C ▨ 35°C ▲ 40°C X 45°C

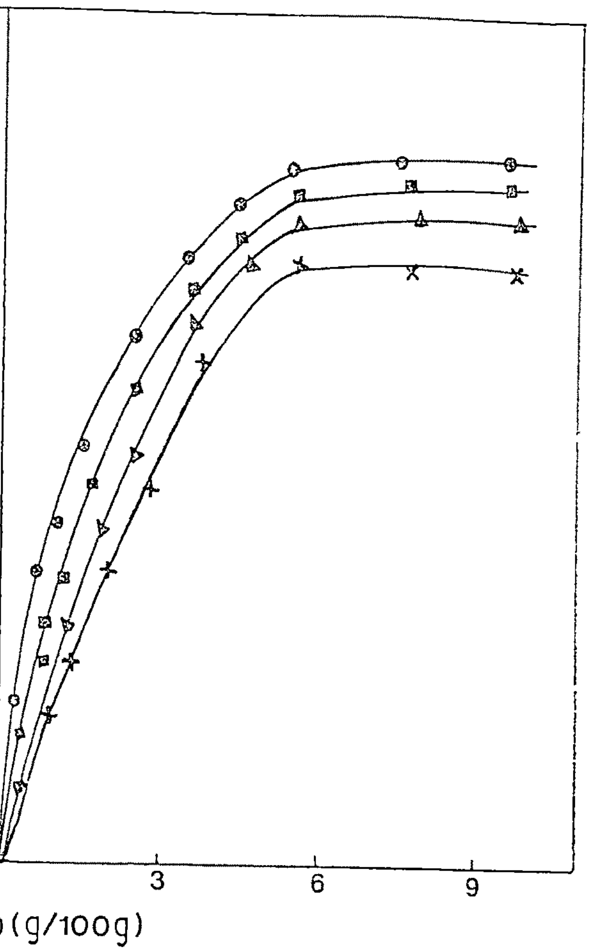


Fig.3.26 Plot of specific adsorption against equilibrium concentration of PBA on alumina

● 30°C ▨ 35°C ▲ 40°C X 45°C

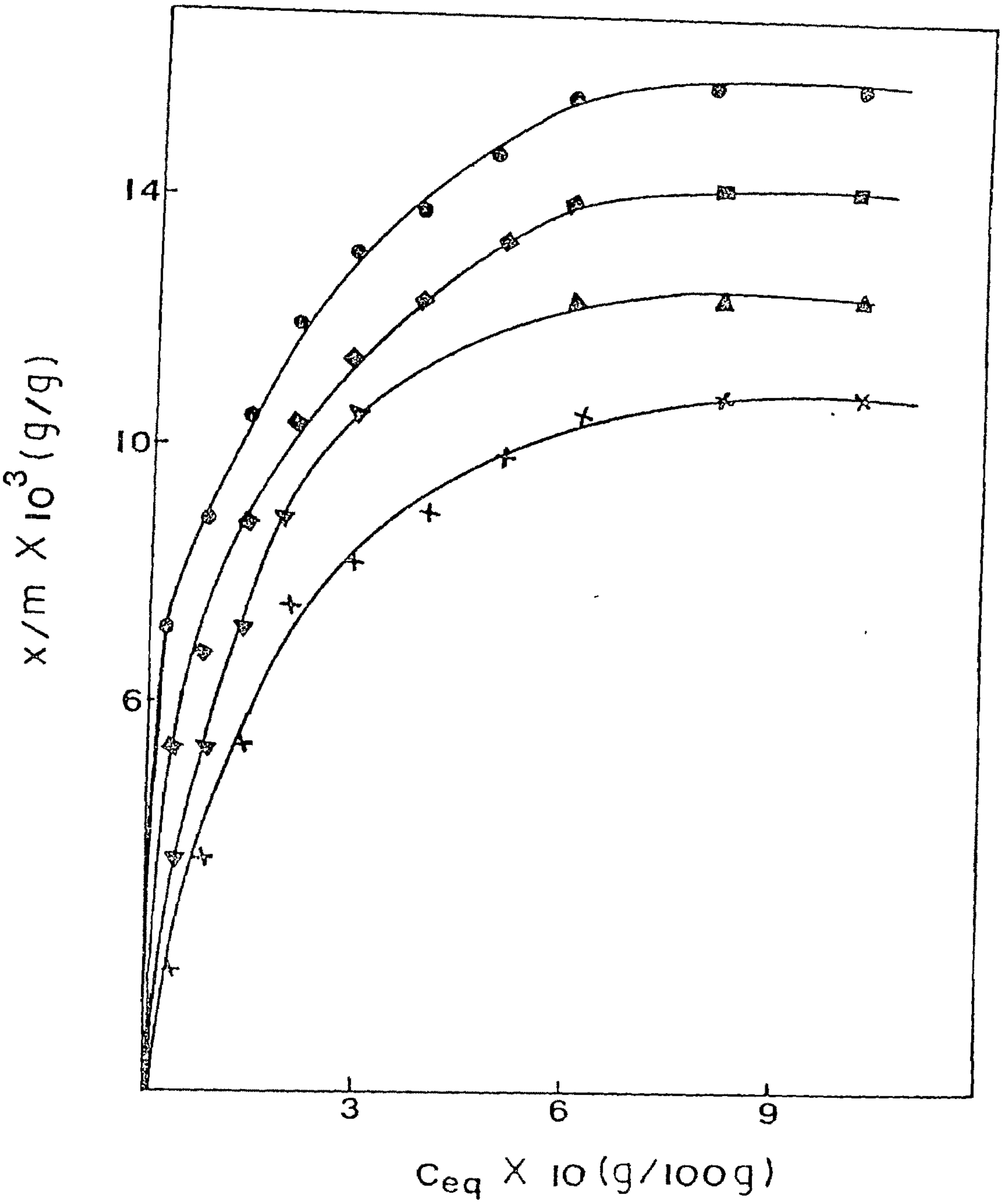


Fig.3.27 Plot of specific adsorption against equilibrium concentration of PMA on $CaCO_3$

● 30°C ▨ 35°C ▲ 40°C X 45°C

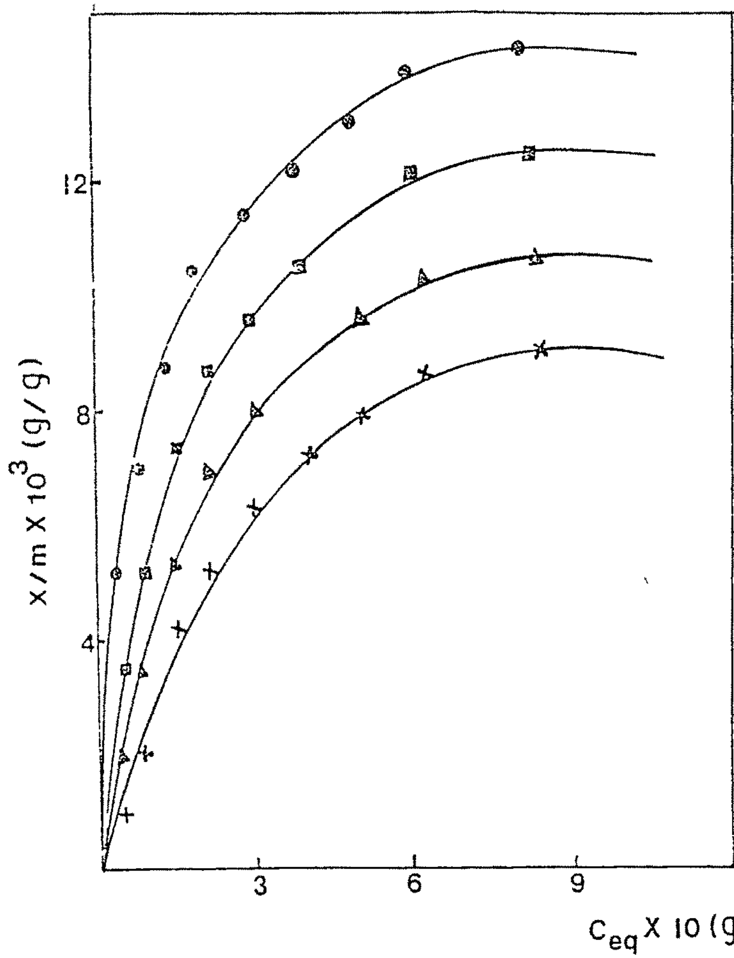


Fig.3.28 Plot of specific adsorption against equilibrium concentration of PEA on $CaCO_3$.

● 30°C ▨ 35°C ▲ 40°C X 45°C

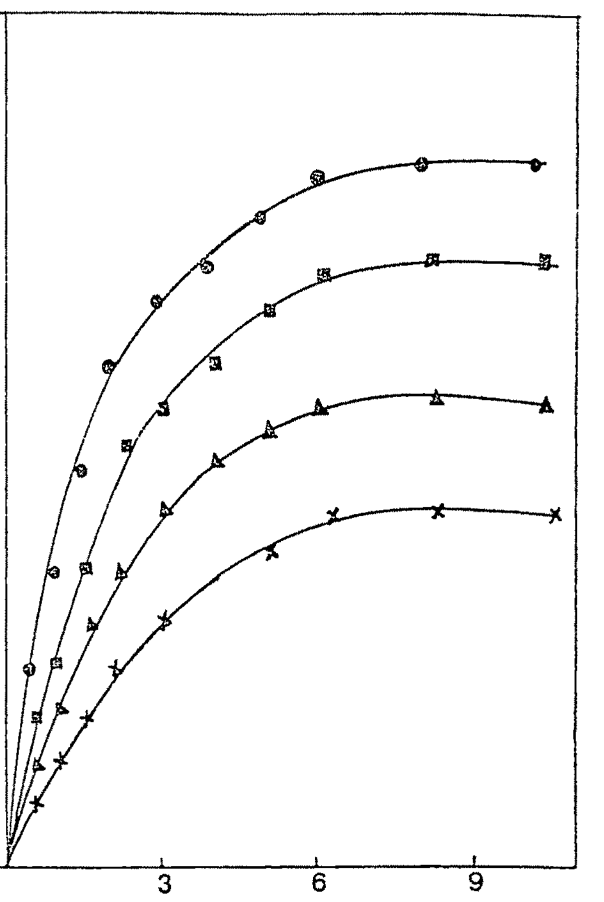
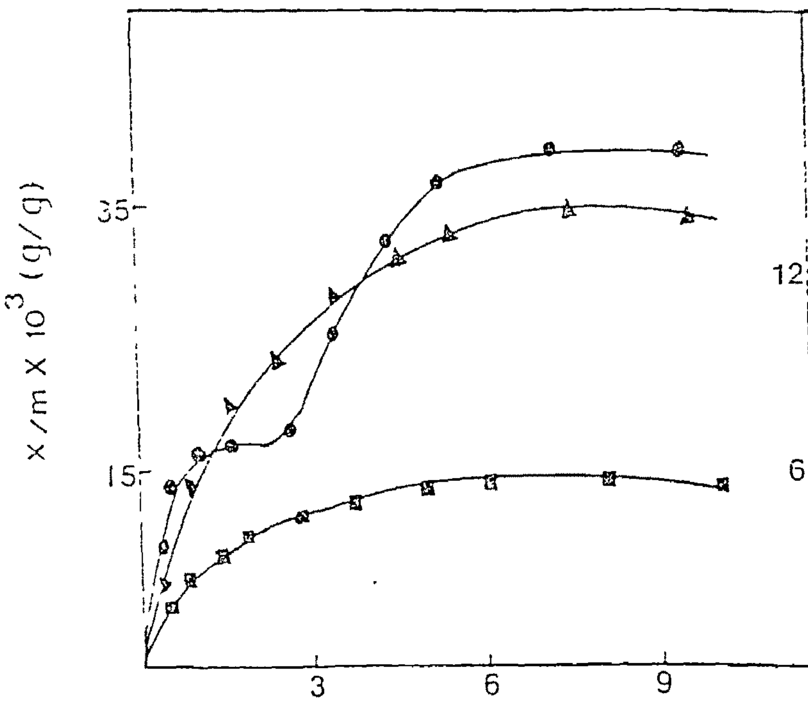


Fig.3.29 Plot of specific adsorption against equilibrium concentration of PBA on $CaCO_3$

● 30°C ▨ 35°C ▲ 40°C X 45°C



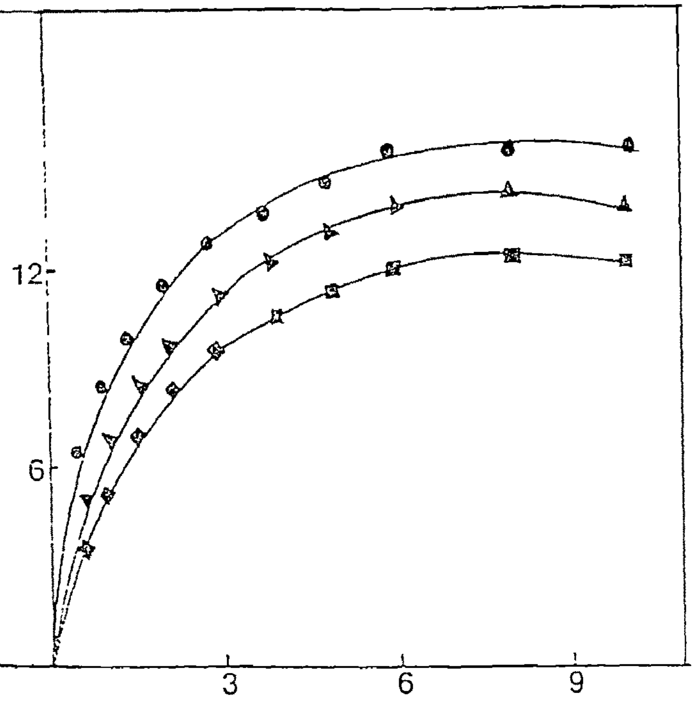


Fig.3.30 Plot of specific adsorption against equilibrium concentration of PEA on adsorbents

● silica gel ▲ alumina ▨ $CaCO_3$

Fig.3.31 Plot of specific adsorption against equilibrium concentration of polyacrylates on $CaCO_3$

● PMA ▲ PEA ▨ PBA

reasonably polydisperse as they were not fractionated and prepared by free radical initiation mechanism. In such systems the low molecular weight fractions are adsorbed initially as diffusion is relatively easier and are later displaced by the larger molecular weight species. The molecular weight distribution on the adsorbed layer changes with the amount of adsorption.

But when the adsorption bond is stronger such displacement may not occur and the smaller molecules will also remain adsorbed. This is dependent on the nature of the adsorbent surface. IR spectra after adsorption though, could not determine any change from the adsorbent. Therefore at the initial concentration region, both the low molecular weight and high molecular weight species of the polyacrylates get adsorbed. It is known that the major adsorption sites of alumina and silica gel are Al^{3+} and surface 'OH' groups respectively /112/. The interaction of the adsorbate with the alumina surface is dominated by electrostatic forces, and should be stronger than the interaction between surface OH and adsorbate as in silica. Hence desorption is easier to occur from the silica gel surface than from alumina surface, giving rise to a condition wherein both adsorption and desorption processes are of similar rate. This hence gives rise to a semi palteau. At a little higher concentration polymer - polymer interaction becomes important enough, as more number of higher molecular weight species are present, resulting in higher adsorption.

It is known that the molecular weight of the polymers have a dominant role in the process of adsorption, where the higher molecular weight polymers get adsorbed more /123-231/. In case of these poly acrylates the molecular weight difference between the polymers is not large (Table 2.2) hence the dependence of molecular weight in the adsorption process is unimportant in these systems.

The ladder type or the S type of isotherms have been observed for adsorption of proteins /349/. This was attributed to the conformational alteration of the proteins during the process of adsorption or due to strong lateral attraction forces existing between adsorbed protein molecules at the interfacial phase or interfacial coagulation by forming multilayers of proteins. Similar isotherms have also been observed for adsorption of surfactants /350-352/.

Polymer adsorption is usually discussed in terms of loop - train - tail conformation, each chain attached to the surface at some site or sites. This is referred to as a monolayer coverage /14/. On the other hand multilayer adsorption is ubiquitous in polymer adsorption. The physical reason being that an intervening multilayer region can lower the free enegy of the interface between the adsorbed layer and the free solution /353/.

Multilayer formation can occur only if macromolecules are present as a part of the surface phase, with none of their segments coming into the actual contact with the surface. In some cases the molecules are treated as a part of the surface phase and their presence would constitute a true macromolecular multilayer formation /354/. Nearly two decades ago calculations by Silberberg /354/ anticipated the possibility of multilayer formation. Priel and Silberberg /355/ observed multilayer formation for polystyrene. The conclusion of multilayer adsorption was drawn from the enchanced (but still microscopic) adsorption observed as non solvent was added to polystyrene solutions /356/.

When the surface area of the adsorbents are higher large number of adsorption sites are available on the surface of the adsorbents. From the surface area determinations by BET method using N_2 gas (section 3.2) the surface areas were found to be 284.2, 97.1 and 25.7 m^2/g for silica gel, alumina and $CaCO_3$ respectively. Hence it is clear that silica gel with the highest surface area has large number of active sites for adsorption, and so accounts for the highest adsorption among these adsorbents.

On the basis of adsorption per unit surface area the adsorption picture changes drastically where adsorption on $CaCO_3$ is maximum and the least on silica gel. This is because at a given total amount of polymer, if the surface area of the adsorbent is small, only the fraction of very high molecular weight can be accommodated on the surface, and the amount adsorbed per unit surface area is high. If at a given volume more area is available smaller molecules also get adsorbed on the surface, the average molecular weight of the adsorbate is lower and so is the amount adsorbed per unit area /24/.

Another important feature was that the amount of polymer adsorbed decreased with the higher alkyl acrylates. Similar observation was also reported by Polonskii /357/ in adsorption of poly alkyl acrylates on glass from toluene. This can be attributed to the effect of the steric factor in the process of adsorption. When the polymeric chains come in contact with the adsorbent surface some of the active sites get covered by the bulkier side chains of the poly acrylates, reducing the number of adsorbent sites available for adsorption, there by reducing the specific adsorption. The effect is more pronounced in higher alkyl acrylates. This effect is shown in fig. 3.31 for polyacrylate - $CaCO_3$ system.

The thermodynamic parameters of adsorption were calculated using the adsorption data obtained at four different temperatures on the adsorbents; alumina, silica gel and $CaCO_3$.

The adsorption process could be written as

$$A_{(solid)} + P_{(solution)} \rightleftharpoons AP_{(solid)} \qquad \ldots\ldots 3.20$$

and therefore the equilibrium constant is

$$K = 1/a_{P(solution)} \simeq 1/C_{P(solution)} \qquad \ldots\ldots 3.21$$

Assuming the activity of the solids as unity the free energy of adsorption is -

$$\triangle G_{ads} = -RT \text{ in } K = -RT \ln C_P \qquad \ldots\ldots 3.22$$

Where R and T have their usual significance. The computation procedure is described in detail in the earlier section 3.3.1.

The values thus obtained are compiled in Table 3.6. It is obvious from the data that the adsorption process on these adsorbents were exothermic with negative entropy change. Both, enthalpy and entropy change follows the order

silica gel $>$ alumina $>$ $CaCO_3$.

The free energy values of adsorption were negative indicating that the process is spontaneous, and these values were found to decrease with higher alkyl acrylates. The observations were similar on all the three adsorbents. In $CaCO_3$ system the free energy change with temperature was nominal and the corresponding enthalpy ($\triangle H^{o}_{ads}$) and entropy ($\triangle S^{o}_{ads}$)values were also much lower than silica gel and alumina systems. These data therefore indicate that the poly acrylate - $CaCO_3$ interaction is much weaker than the interactions of silica gel and alumina adsorbents.

TABLE : 3.6

THE FREE ENERGY $\triangle G^{o}_{ads}$, ENTHALPY $\triangle H^{o}_{ads}$ AND ENTROPY $\triangle S^{o}_{ads}$ OF ADSORPTION OF POLYACRYLATES AT INFINITE DILUTION ON SILICA GEL, ALUMINA AND $CaCO_3$

(Concentration expressed in g/100g of solution)

System	$-\triangle G^{o}_{ads}$ (kJ mol^{-1})				$-\triangle H^{o}_{ads}$ (kJ mol^{-1})	$-\triangle S^{o}_{ads}$ (J mol^{-1}K^{-1})
	30°C	35°C	40°C	45°C		
Silica gel						
PMA	11.6	11.1	10.6	10.0	44.1	107.0
PEA	10.8	10.5	9.8	9.6	37.6	88.4
PBA	10.6	10.2	9.9	9.4	34.5	78.8
Alumina						
PMA	11.6	11.1	10.6	10.2	40.3	94.8
PEA	10.8	10.4	10.1	9.8	32.6	72.0
PBA	10.2	9.9	9.6	9.4	27.3	56.6
$CaCO_3$						
PMA	10.0	9.9	9.9	9.8	13.9	13.0
PEA	9.8	9.7	9.7	9.6	13.1	11.0
PBA	9.4	9.3	9.3	9.2	11.9	8.6

The entropy changes are large in the case of silica gel and alumina systems than in $CaCO_3$ system but it can be seen from Table 3.6 that the adsorption process is enthalpy driven rather than entropy, in all these systems.

The thermodynamic quantities were also calculated as a function of surface coverage. The procedure and the equations used are as described in the previous section 3.3.1. The thermodynamic parameters computed are compiled in Tables 3.7 to 3.9. The negative isosteric heat values obtained indicates, that the adsorption process is exothermic. As the amount of the polymer adsorbed increases the isosteric heat value ($\triangle H_A$) decreases linearly. The entropy values (ΔS_A) also follow a similar order.

The linear relationship of $\triangle H_A$ and $\triangle S_A$ with the amount of surface coverage are shown in figs. 3.32 and 3.33 respectively for few systems.

The energetic heterogeneity of the adsorbent surfaces 'C', the coefficient of heterogeneity 'f' at different temperatures and the coefficient 'f_o' were calculated for all the systems and are presented in Table 3.10. The m and C values increased as the adsorption amount decreased. These values were exceptionally high for the $CaCO_3$ system. The f_o values for the three adsorbents follow the order.

TABLE : 3.7

THERMODYNAMIC PARAMETERS OF ADSORPTION OF POLY ACRYLATE - SILICA GEL SYSTEMS BY SURFACE COVERAGE APPROACH

Polyacrylate	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
PMA	0.25	51.8	151.8	5.8	44.0	123.8	6.5
	0.50	57.8	172.9	5.4			
	0.75	65.8	201.0	4.9			
	1.00	73.7	228.3	4.5			
PEA	0.25	44.5	127.6	5.8	36.8	99.9	6.5
	0.50	56.1	167.1	5.5			
	0.75	64.5	196.6	4.9			
	1.00	71.6	222.4	4.2			
PBA	0.25	40.9	119.3	4.8	27.1	71.0	5.6
	0.50	53.5	163.3	4.0			
	0.65	60.6	187.7	3.7			
	0.75	68.4	214.2	3.5			

TABLE : 3.8

THERMODYNAMIC PARAMETERS OF ADSORPTION OF POLYACRYLATE - ALUMINA SYSTEM BY SURFACE COVERAGE APPROACH

Polyacrylate	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
PMA	0.25	49.6	144.6	5.8	41.8	116.3	6.6
	0.50	56.1	167.1	5.5			
	0.75	64.5	196.6	4.9			
	1.00	71.6	222.4	4.2			
PEA	0.25	46.7	135.3	5.7	34.5	93.2	6.3
	0.50	61.3	185.2	5.2			
	0.75	73.4	226.7	4.7			
	1.00	85.7	269.3	4.1			
PBA	0.25	40.9	119.3	4.8	25.3	66.4	5.2
	0.50	54.9	166.4	4.5			
	0.75	73.3	228.3	4.1			
	0.90	79.6	250.1	3.8			

TABLE : 3.9

THERMODYNAMIC PARAMETERS OF ADSORPTION OF POLYACRYLATE ON $CaCO_3$ BY SURFACE COVERAGE APPROACH

Polyacrylate	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_c$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
PMA	0.20	42.0	119.0	5.9	10.4	7.3	8.2
	0.25	52.5	155.5	5.4			
	0.30	61.5	186.9	4.9			
	0.35	66.4	205.1	4.3			
PEA	0.20	46.3	135.6	5.2	7.7	3.1	6.8
	0.25	52.4	156.9	4.9			
	0.30	62.7	192.3	4.4			
	0.35	73.8	230.3	4.0			
PBA	0.05	17.6	46.4	3.5	5.6	6.0	3.8
	0.10	28.6	83.6	3.3			
	0.15	38.0	115.8	2.9			
	0.20	52.6	164.5	2.8			

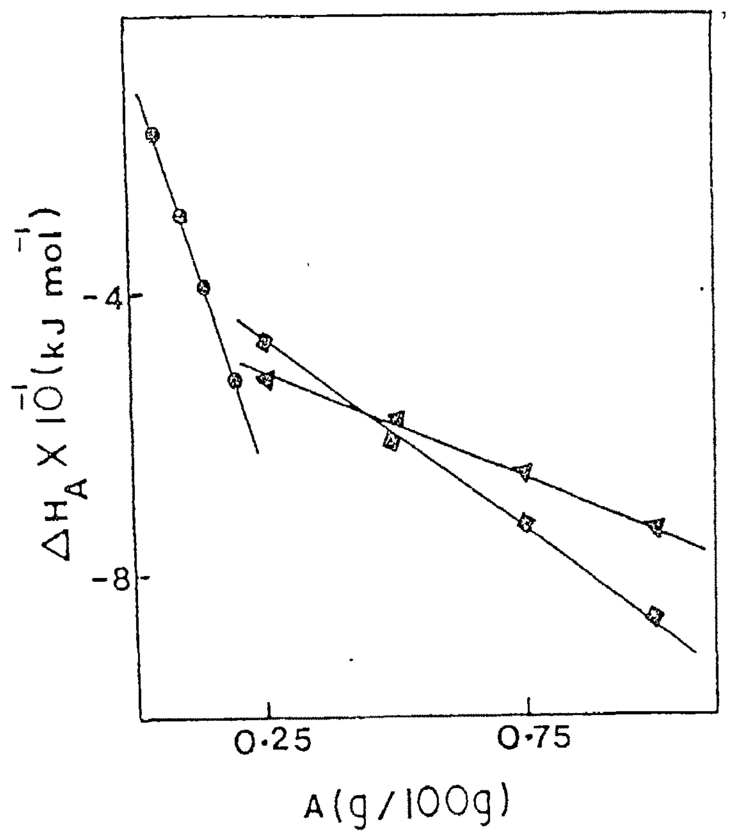


Fig.3.32 Change in $\triangle H_A$ with the amount of polyacrylates adsorbed A

● PBA - $CaCO_3$ △ PMA-silica gel
▨ PEA - alumina

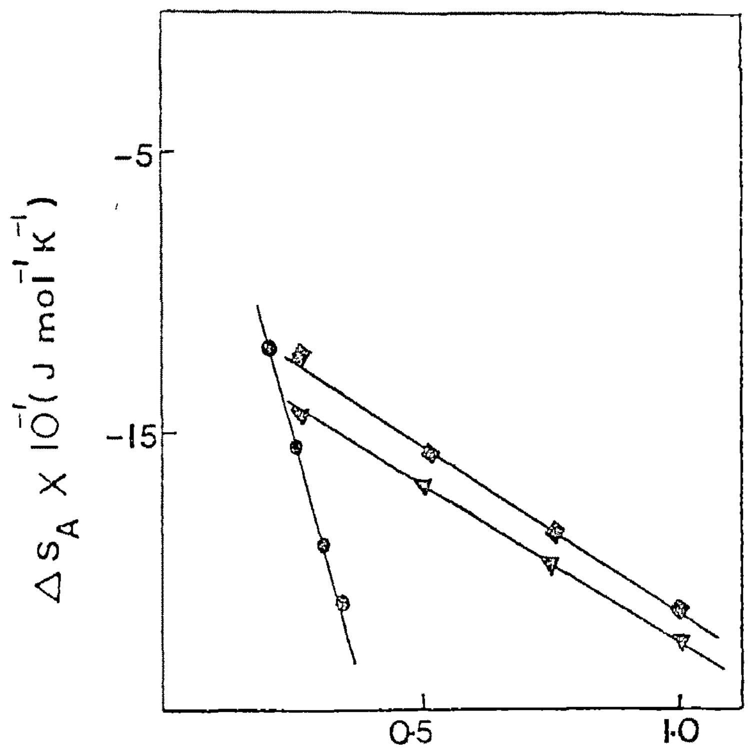


Fig.3.33 Change in $\triangle S_A$ with the amount of polyacrylates adsorbed A

● PEA-$CaCO_3$ △ PMA-alumina
▨ PBA-silica gel

TABLE : 3.10

SURFACE CHARACTERISTIC PARAMETERS OBTAINED FOR POLYACRYLATES ON SILICA GEL, ALUMINA AND $CaCO_3$ BY SURFACE COVERAGE APPROACH

System	f (gl^{-1})				$-f_o$ (gl^{-1})	$-m$ ($J\ mol^{-1} K^{-1}$)	$-C$ ($kJ\ mol^{-1}$)
	30°C	35°C	40°C	45°C			
Silica Gel							
PMA	0.91	1.07	1.23	1.46	12.4	103	29.1
PEA	0.91	1.07	1.26	1.59	15.0	125	35.9
PBA	1.02	1.38	1.74	1.99	21.8	183	53.5
Alumina							
PMA	0.91	1.07	1.26	1.46	12.6	105	29.8
PEA	0.91	1.11	1.55	1.82	21.0	176	51.6
PBA	0.61	0.94	1.34	1.75	24.8	208	61.5
$CaCO_3$							
PMA	4.55	5.37	6.50	7.54	68.5	579	164.4
PEA	3.14	4.23	5.36	6.61	76.4	639	185.6
PBA	2.40	3.60	4.98	6.63	91.7	766	228.8

Silica gel $<$ alumina $<$ $CaCO_3$

and is related to the entropy change during the process of adsorption. From these values the dependence on the ability of the adsorbents to adsorb can be arranged in the following order.

Silica gel $>$ alumina $>$ $CaCO_3$

From the above two comparison orders it can be concluded that the entropy factor produces a definite effect on the process of adsorption of these poly(alkyl acrylates). The f values are linearly dependent with temperature and is shown in fig. 3.34 for some systems.

The $\triangle S_A$ values lenearly decrease with $\triangle H_A$, the change in isosteric heat. This shows that there is a compensation effect. This indicates that the process under study takes place simultaneously with the change in entropy and enthalpy factors and these have determining effect on the affinity of the polymer towards the adsorbents.

The $\triangle G_A$ values calculated show that with the increase in temperature, the negative values decrease. The effect is similar when the amount of polymer adsorbed increases, as shown in fig. 3.34a for PMA - alumina system.

These facts show that the rise in temperature produces no favourable effect on the process of adsorption of the poly alkyl acrylates

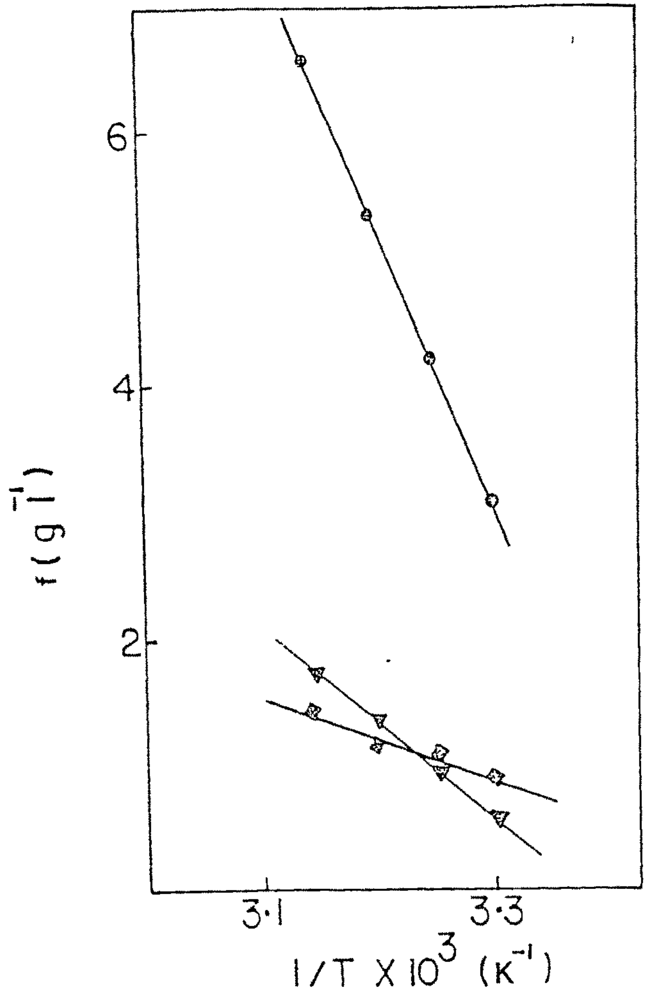


Fig.3.34 Temperature dependence of 'f' for polyacrylate systems.

● PEA-CaCO$_3$ ▨ PMA-silica gel

▲ PBA-alumina

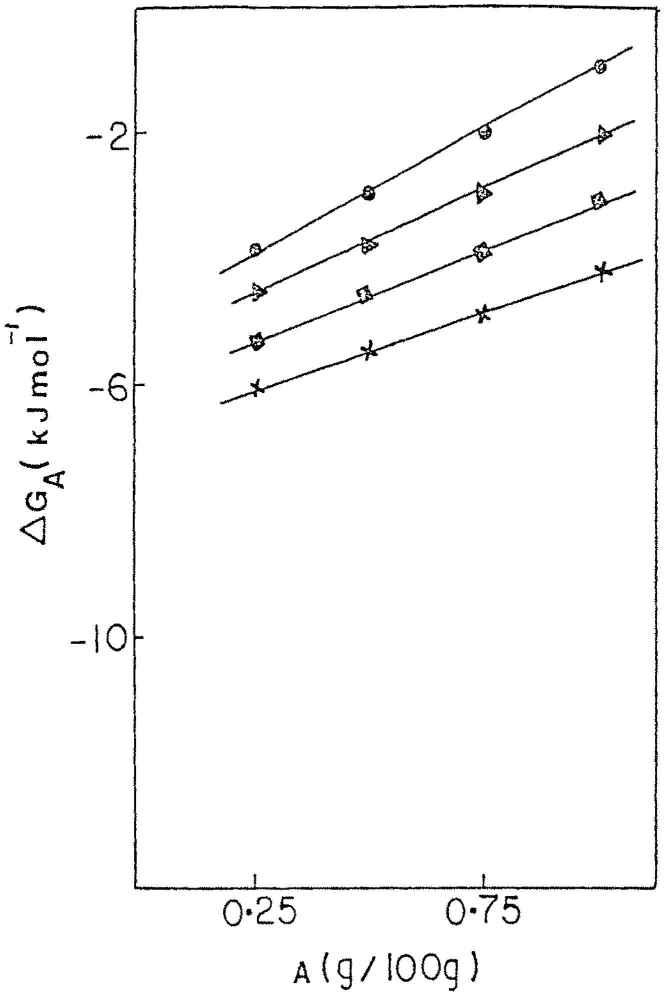


Fig.3.34a Plot of $\triangle G_A$ with the amount of PMA adsorbed on alumina at different temperatures.

● 30°C ▨ 35°C ▲ 40°C X 45°C

considered in this study. Moreover, the negative value of $\triangle G_A$ obtained for all the systems attests to the thermodynamic possibility of the process of adsorption taking place under the conditions specified here.

3.3.3 POLYACRYLONITRILE (PAN)

The adsorption isotherms obtained for PAN on silica gel, alumina and $CaCO_3$ were of general Langmuir type. These are shown in figs. 3.35 to 3.37. However, the amount of polymer adsorbed is much higher compared to the polyacrylates discussed in the previous section 3.3.2. The semi plateau region observed in the case of poly acrylate - silica gel systems are not observed in the acrylonitrile - silica gel systems. This is because an adsorption ← desorption equilibrium sets in in these concentration region for polyacrylate - silica gel system which is reasonably absent in the other case. Moreover, the nitrile moiety is much smaller in size than all acrylate moieties considered here. This results in more surface active sites, available for adsorption in case of PAN. In the acrylate polymers, as discussed earlier the bulkier side groups cover up some of the active sites of the adsorbents. Therefore all the PAN molecules adsorbed can be accommodated in a monolayer, resulting in the high affinity type of the isotherm. This is true for alumina and $CaCO_3$ also. These two effects, taken in combination can account for the difference in the nature of the observed isotherms. The difference in the amount of polymer adsorbed on these adsorbents can be accounted on the basis

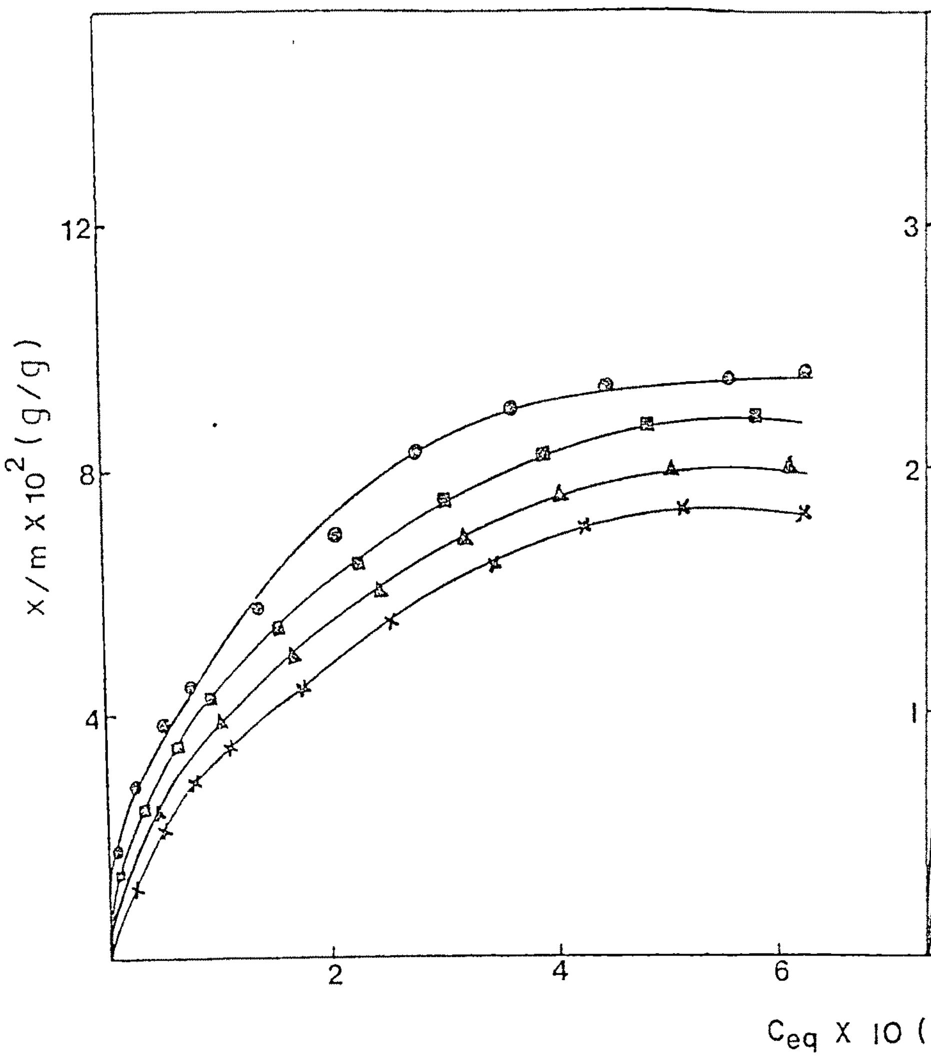


Fig.3.35 Plot of specific adsorption against equilibrium concentration of PAN on silica gel

● 30°C ▨ 35°C ▲ 40°C X 45°C

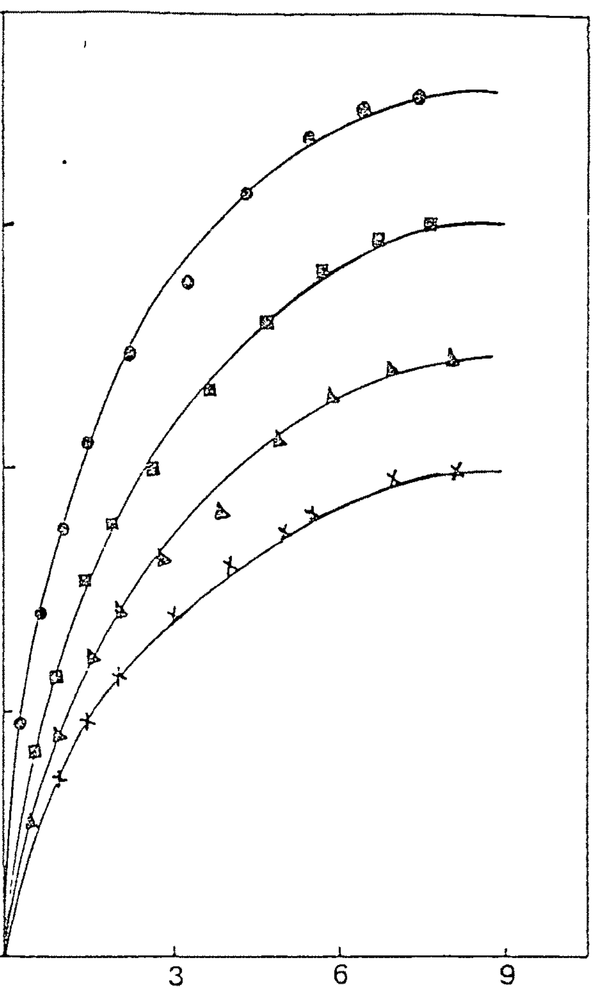


Fig.3.36 Plot of specific adsorption against equilibrium concentration of PAN on $CaCO_3$

● 30°C ▨ 35°C ▲ 40°C X 45°C

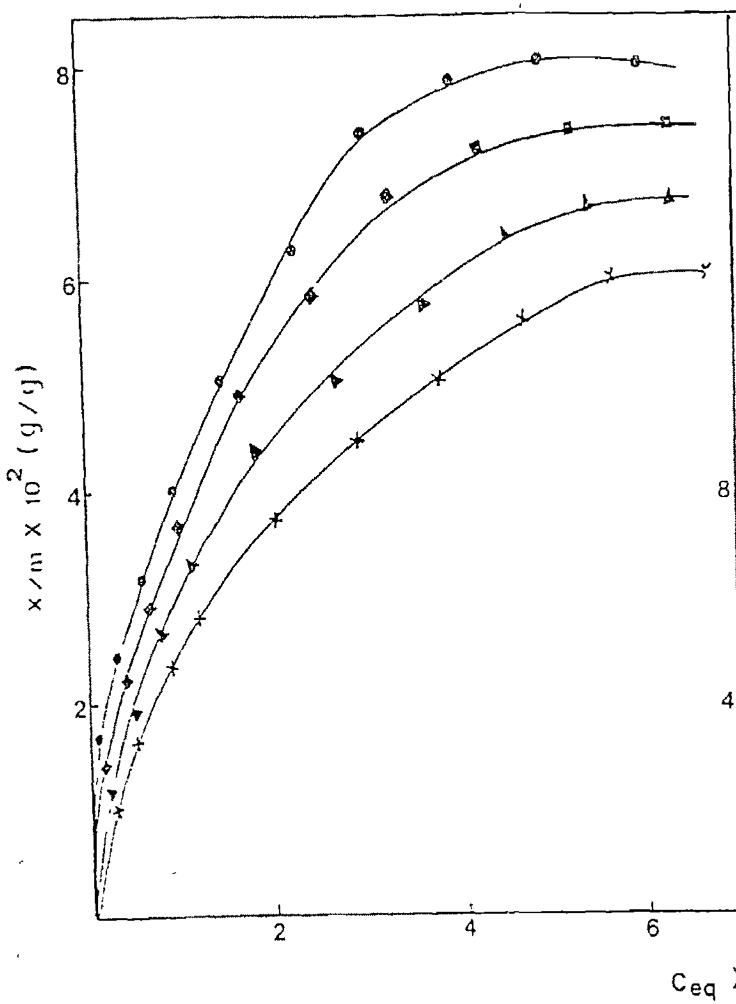


Fig. 3.37 : Plot of specific adsorption against equilibrium concentration of PAN on alumina

● 30°C ▨ 35°C ▲ 40°C X 45°C

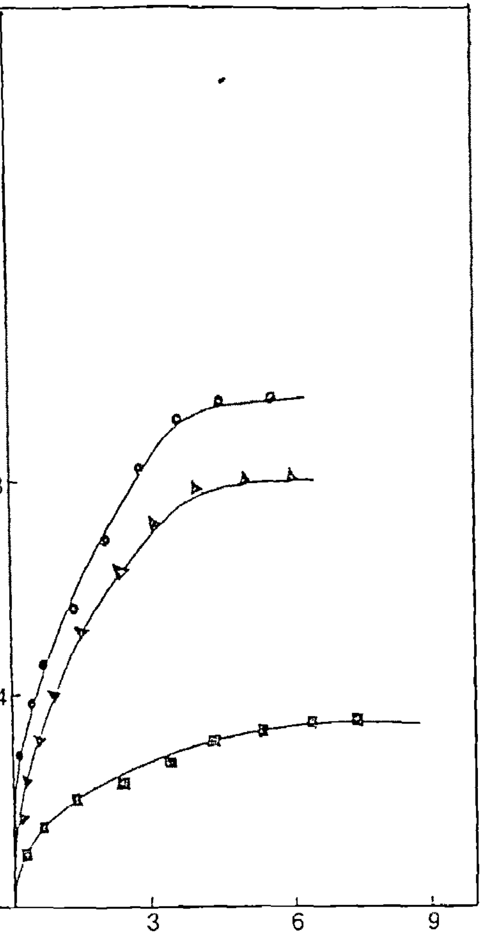


Fig.3.38 Plot of specific adsorption against equilibrium concentration of PAN on adsorbents.

● silica gel ▲ alumina ▨ $CaCO_3$

of polymer - adsorbent interactions alone as the studies were conducted from a single solvent.

As discussed in the previous section (3.3.2) the higher surface area of the silica gel contains more active sites for the polymer molecules to adsorb. Hence more amount of polymer could be accommodated, increasing the specific adsorption on this substrate. The surface area of the adsorbents follows the order silica gel $>$ alumina $>$ $CaCO_3$ (section 3.2). The specific adsorption also follows a similar pattern and is represented in fig. 3.38. The amount of polymer adsorbed is generally a function of molecular weight, and the plateau region for higher molecular weight polymer sometimes extends over the entire experimentally accessible range of concentration /358-360/. The viscosity average molecular weight ($\overline{M}_v$) of PAN is more than double that of the poly acrylates (Table 2.2) and the specific amount adsorbed is much higher than that of polyacrylates. The adsorption of PBR /89/ is again much higher than that of PAN on the adsorbent silica gel. These observations indicate that molecular weight is also a criterion for the changes observed in the specific adsorption amount. The isotherm plateau is observed at a lower equilibrium concentration on all the three adsorbents in comparison to that of all polyacrylates (figs. 3.21 to 3.29).

The thermodynamic quantities at infinite dilution, the free energy ($\triangle G^{o}_{ads}$), enthalpy ($\triangle H^{o}_{ads}$) and entropy ($\triangle S^{o}_{ads}$) computed for different adsorbent systems are presented in Table 3.11. All these

TABLE : 3.11

THE FREE ENERGY ($\triangle G^{o}_{ads}$) ENTHALPY $\triangle H^{o}_{ads}$ AND ENTROPY $\triangle S^{o}_{ads}$ OF ADSORPTION OF POLYACRYLONITRILE AT INFINITE DILUTION ON DIFFERENT ADSORBENTS

(Concentration expressed in g/100g of solution)

Adsorbent	Temp. °C	$-\triangle G^{o}_{ads}$ (kJ mol^{-1})	$-\triangle H^{o}_{ads}$ (kJ mol^{-1})	$-\triangle S^{o}_{ads}$ (J $mol^{-1}K^{-1}$)
Silica Gel	30	18.2	147.6	426.8
	35	16.1		
	40	14.0		
	45	11.8		
Alumina	30	16.2	110.2	311.0
	35	14.0		
	40	12.7		
	45	11.5		
$CaCO_3$	30	10.8	32.1	70.4
	35	10.3		
	40	10.0		
	45	9.7		

values were much higher than those of polyacrylate systems (Table 3.6). The negative enthalpy values obtained indicate that the processes are exothermic. Though the entropy values are also higher, the adsorption process is enthalpy dominated on all the three adsorbent systems. The free energy values as well as the change in free energy with temperature is higher in silica gel systems followed by alumina and the lowest on $CaCO_3$. This shows that PAN - $CaCO_3$ interaction is much weaker.

The thermodynamic parameters by the surface coverage approach as discussed in section 3.3.1 were computed for all the systems and are compiled in Table 3.12. The isosteric heat values ($\triangle H_A$) and entropy ($\triangle S_A$) showed linear dependence with the amount of adsorbed polymer as shown in figs. 3.39 and 3.40. The negative values indicate that heat is released during the process of adsorption and decreases as further amount of polymer gets adsorbed.

Similar studies have also been done with hydrolyzed modified polyacrylonitrile on different types of cellulose /346/. The thermodynamic quantities reported were much lower than the pure acrylonitrile systems discussed here. This difference arises because of the lower surface coverage as the amount adsorbed was less, besides the variation in adsorbate and adsorbent characteristics.

The other parameters like the energetic heterogeneity (C), coefficient of heterogeneity (f), the entropy factor of heterogeneity m and f_0

TAB:E : 3.12

THERMODYNAMIC PARAMETERS OF ADSORPTION FOR PAN SYSTEM BY SURFACE COVERAGE APPROACH

Adsorbents	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_c$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
Silica Gel	1.0	97.3	292.1	8.8	97.1	271.7	14.8
	1.5	100.5	305.1	8.1			
	2.0	102.8	316.1	7.0			
	2.5	104.4	324.5	6.1			
Alumina	1.0	95.6	290.7	7.5	87.2	258.4	8.9
	1.5	98.9	305.1	6.5			
	2.0	103.4	322.2	5.8			
	2.5	107.6	338.0	5.2			
$CaCO_3$	0.2	38.1	108.1	5.3	30.2	80.1	6.0
	0.4	44.5	132.2	4.4			
	0.6	51.9	158.6	3.8			
	0.8	60.2	188.2	3.2			

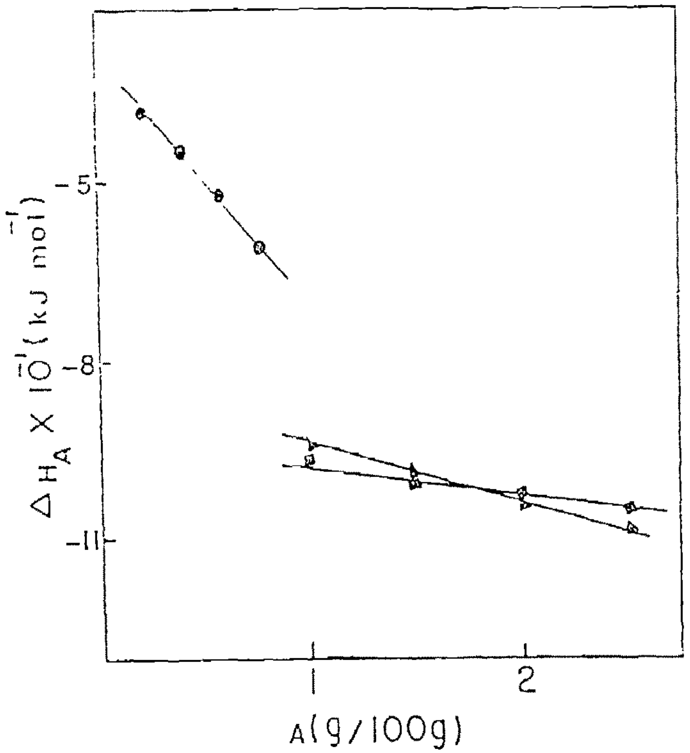


Fig.3.39 Change in $\triangle H_A$ with the amount of Polyacrylonitrile adsorbed A on various adsorbents

● $CaCO_3$ ▨ silica gel ▲ alumina

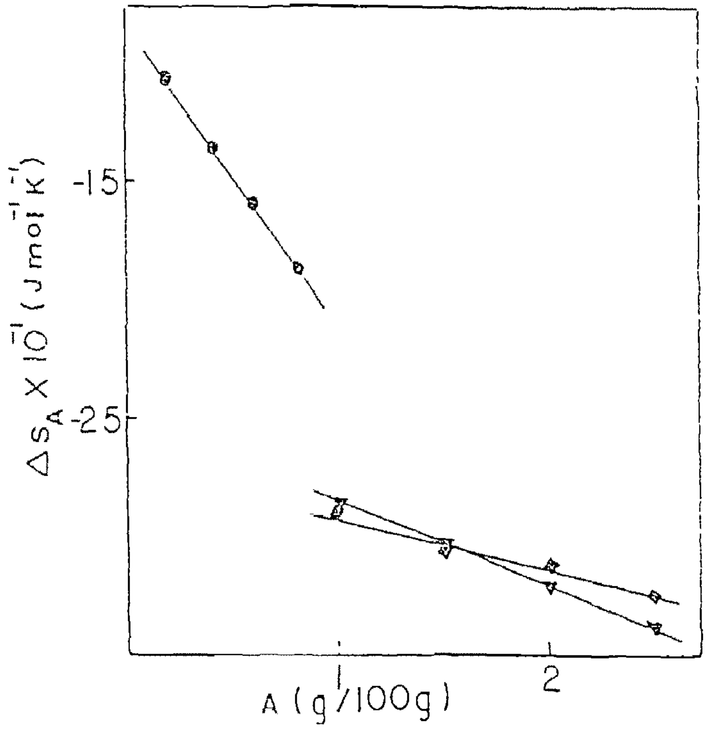


Fig.3.40 Change in $\triangle S_A$ with the amount of Polyacrylonitrile adsorbed A on various adsorbents.

● $CaCO_3$ ▨ silica gel ▲ alumina

(a function of entropy) were also computed for all systems. These values are presented in Table 3.13. It can be seen from the table that the energetic heterogeneity (C) values increase as the amount adsorbed on the adsorbent becomes less. So the value is much higher for the calcium carbonate system than alumina and the least on silica gel.

Temperature dependence of f is shown in fig. 3.41. The dependence is linear and magnitude of f increase as the temperature is raised, indicating an increase in heterogeneity of the polymer - adsorbent system. Among the three adsorbents considered in this study the coefficient f_0 which is related to the entropy change during the process of adsorption, follows the order

$$\text{Silica gel} < \text{alumina} < CaCO_3.$$

Hence their ability to adsorb follows the reverse order. This shows that the entropy factor is also equally important in the process of adsorption of polyacrylonitrile.

The dependence of log K_A as a function of amount adsorbed at all the four temperatures (30°, 35°, 40° and 45°) are linear on all the three adsorbents, and is represented in figure 3.42 for PAN - $CaCO_3$ system. The equilibrium constant at a definite A ie. k_A, decreases with the increase in amount of polymer adsorbed, showing that there are other factors determining the process of adsorption.

TABLE : 3.13

SURFACE CHARACTERISTIC PARAMETERS OF ADSORPTION OF PAN BY SURFACE COVERAGE APPROACH

Adsorbents	$f\ (gl^{-1})$				$-f_o$ (gl^{-1})	$-m$ $(J\ mol^{-1}K^{-1})$	$-C$ $(kJ\ mol^{-1})$
	30°C	35°C	40°C	45°C			
Silica Gel	0.74	0.77	0.81	0.83	2.6	21	2.8
Alumina	0.62	0.67	0.72	0.78	3.9	33	8.1
$CaCO_3$	1.44	1.62	1.86	2.12	15.8	132	36.9

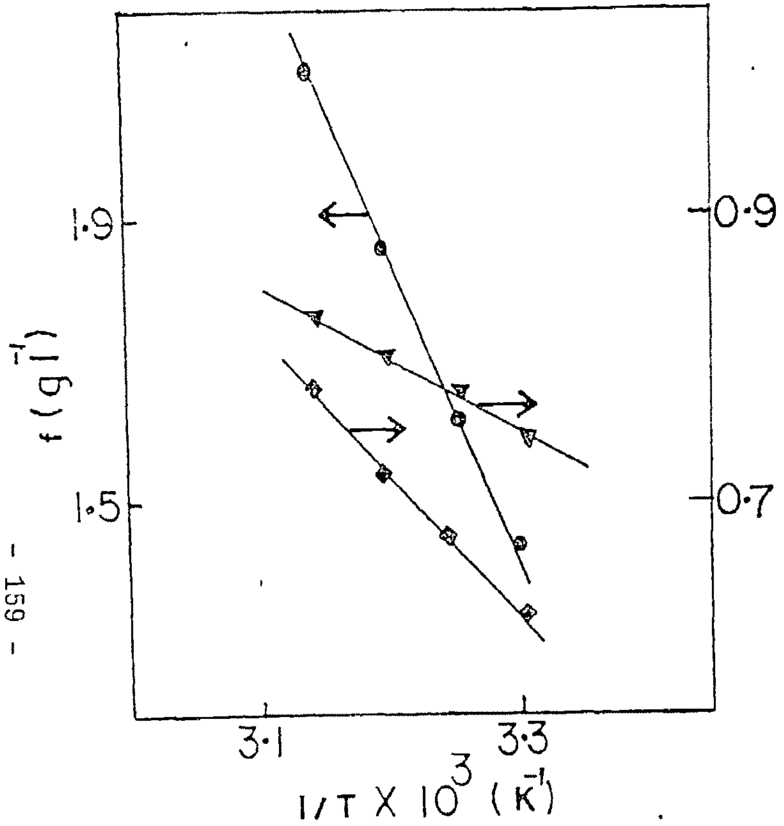


Fig.3.41 Temperature dependence of 'f' for Polyacrylonitrile - adsorbent systems.

● $CaCO_3$ ▲ silica gel ▨ alumina

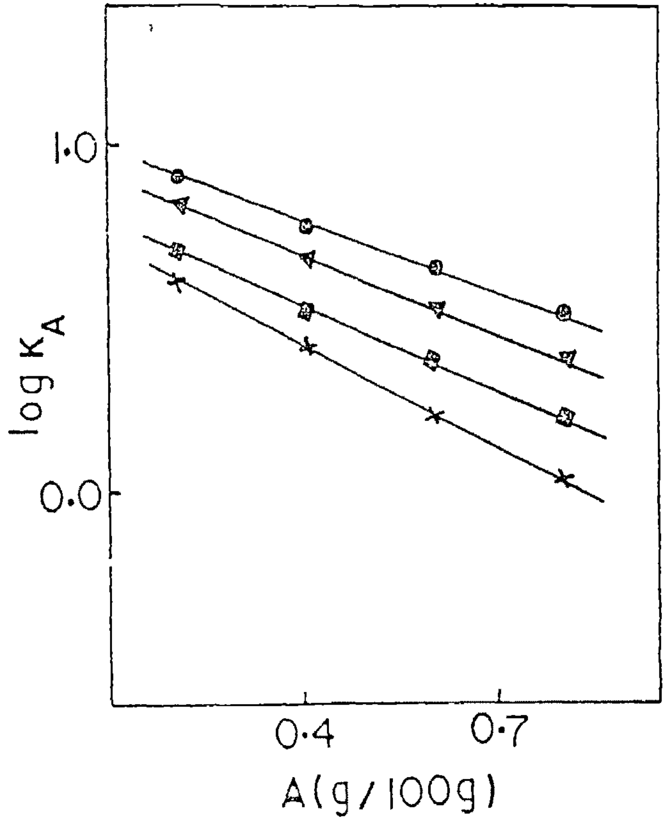


Fig.3.42 Plot of log K_A against amount of polyacrylonitrile adsorbed on $CaCO_3$ at different temperatures

● 30°C ▲ 35°C ▨ 40°C × 45°C

The existence of a compensation effect are also noticed from the linear relationship of isosteric heat and $\triangle S_A$ in all the systems. These factors i.e. the entropy and enthalpy determine the effect of the affinity of the polymer towards the adsorbents.

The $\triangle G_A$ values for all systems were also negative at all temperatures. The relative spontaneity of adsorption increases as the temperature is lowered. Moreover, similar type of behaviour is also observed as the amount adsorbed decreases. This indicates that the adsorption process is not favoured when the temperature is raised or when the amount of polymer is increased. And adsorption takes place regardless of the type of adsorbents considered in this study under the conditions specified.

3.4 ADSORPTION OF COPOLYMERS

The adsorption of various copolymers of acrylonitrile - methyl acrylate ($ANMA_{11}$, $ANMA_{12}$), acrylonitrile-ethyl acrylate ($ANEA_{11}$, $ANEA_{12}$) and acrylonitrile-butyl acrylate ($ANBA_{11}$, $ANBA_{12}$) on silica gel, alumina and calcium carbonate were studied at four temperatures, 30°, 35°, 40° and 45°C from NN' Dimethyl formamide solutions. The effect of the chemical composition in the copolymers were also considered by changing the acrylate concentration in the copolymers. The adsorption behaviour of the copolymers were also compared with that of the corresponding homopolymers.

The adsorption isotherms obtained are shown in figs. 3.43. to 3.60. The effect of temperature on adsorption in all systems are similar, with a decrease in the specific amount adsorbed at a given equilibrium concentration as the temperature is raised. As in the case of homopolymers of acrylates and acrylonitrile on these adsorbents, specific adsorption of copolymers was also more on silica gel than on alumina and least on $CaCO_3$. The nature of the isotherms were similar to that obtained for the polyacrylate systems on the respective adsorbents.

The semiplateau regions observed in the case of copolymer - silica gel systems arise because of polydispersity, multilayer adsorption and reasonably weak interaction which leads to adsorption-desorption equilibrium between the surface hydroxyls of silica gel and carbonyl of acrylate group, as discussed in section 3.3.2.

In the semiplateau region polymer - adsorbent interactions dominate, preventing the preferential adsorption of the higher molecular weight species. After this stage the polymer - polymer interactions becomes important enough as the concentration in the bulk phase is increased. This results in more adsorption on the substrate i.e. the multilayer adsorption. The second rise region of the copolymer - silica gel systems are not so steep as in the case of polyacrylate - silica gel systems. This is due to the effect of the second component, acrylonitrile. The interaction between the surface hydroxyls with the nitrile group is weaker compared to the interaction with carbonyl of

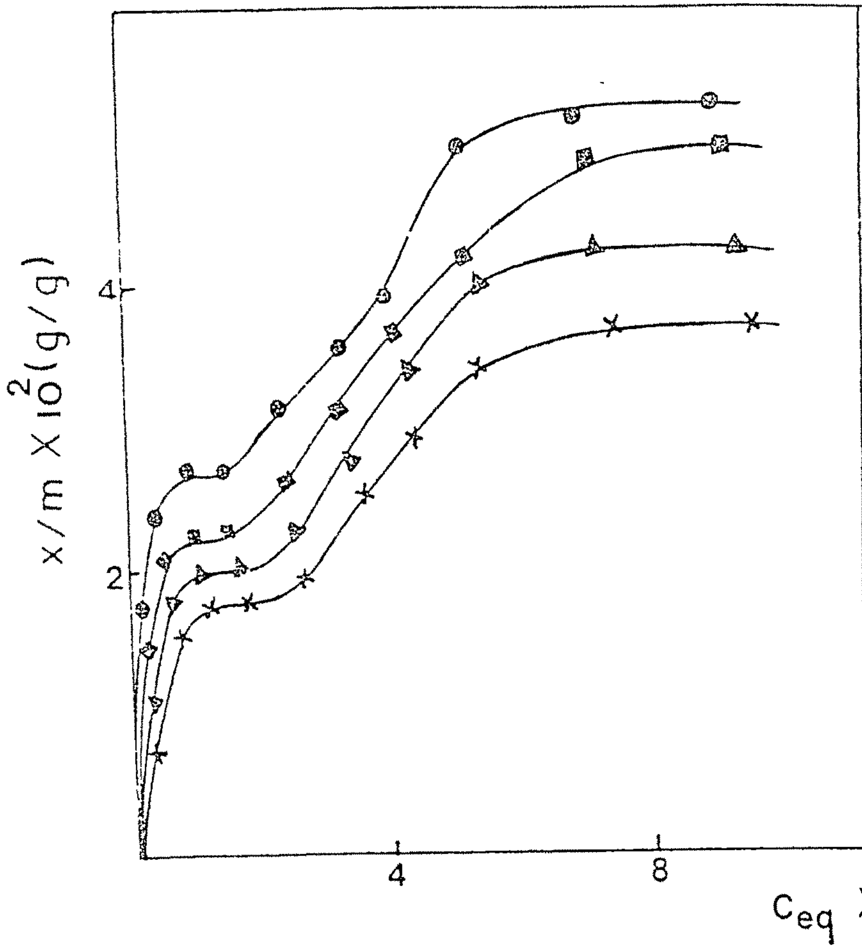


Fig.3.43 Plot of specific adsorption against equilibrium concentration of $ANMA_{11}$ on silica gel.

● 30°C ▨ 35°C △ 40°C X 45°C

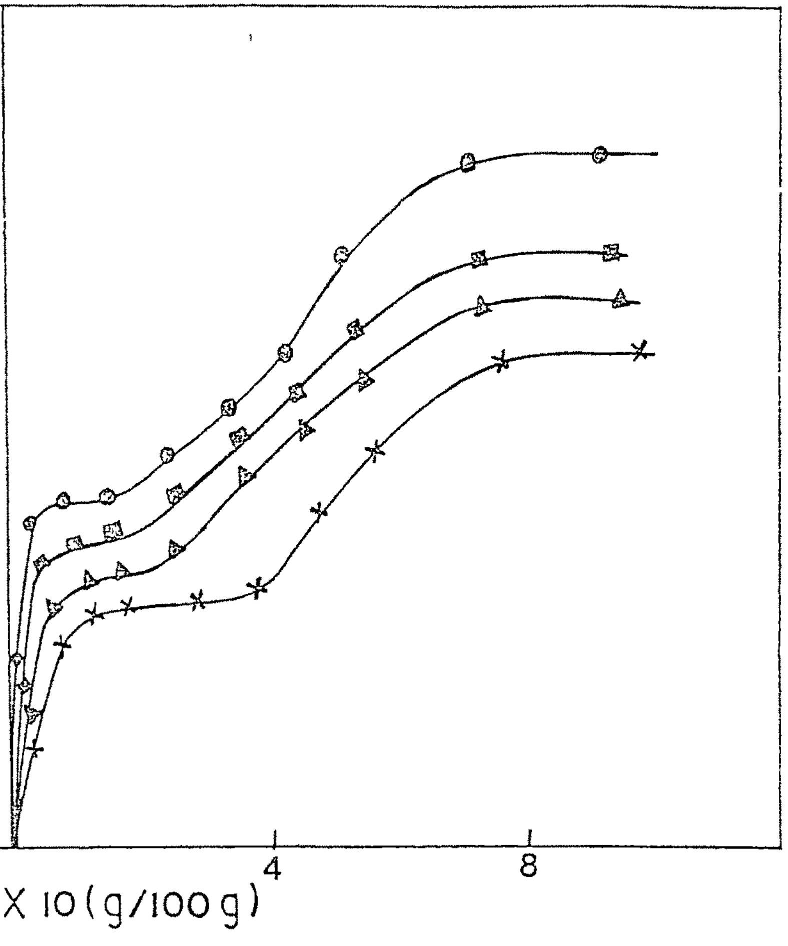


Fig.3.44 Plot of specific adsorption against equilibrium concentration of $ANMA_{12}$ on silica gel.

● 30°C ▨ 35°C △ 40°C X 45°C

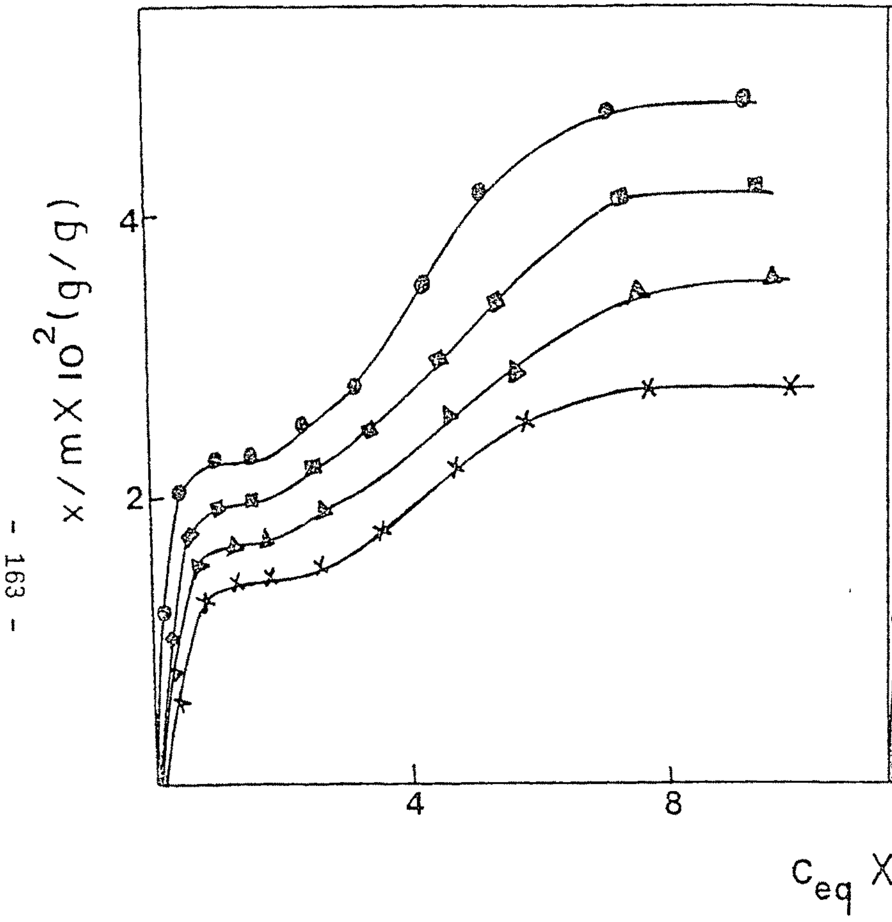


Fig.3.45 Plot of specific adsorption against equilibrium concentration of $ANEA_{11}$ on silica gel.

● 30°C ▨ 35°C ▲ 40°C X 45°C

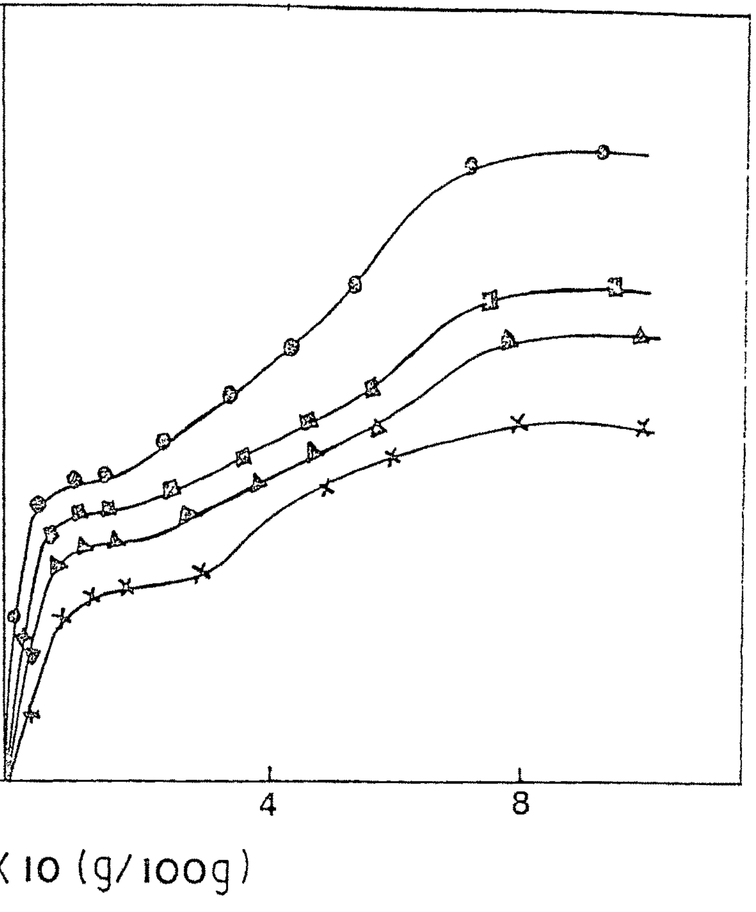


Fig.3.46 Plot of specific adsorption against equilibrium concentration of $ANEA_{12}$ on silica gel.

● 30°C ▨ 35°C ▲ 40°C X 45°C

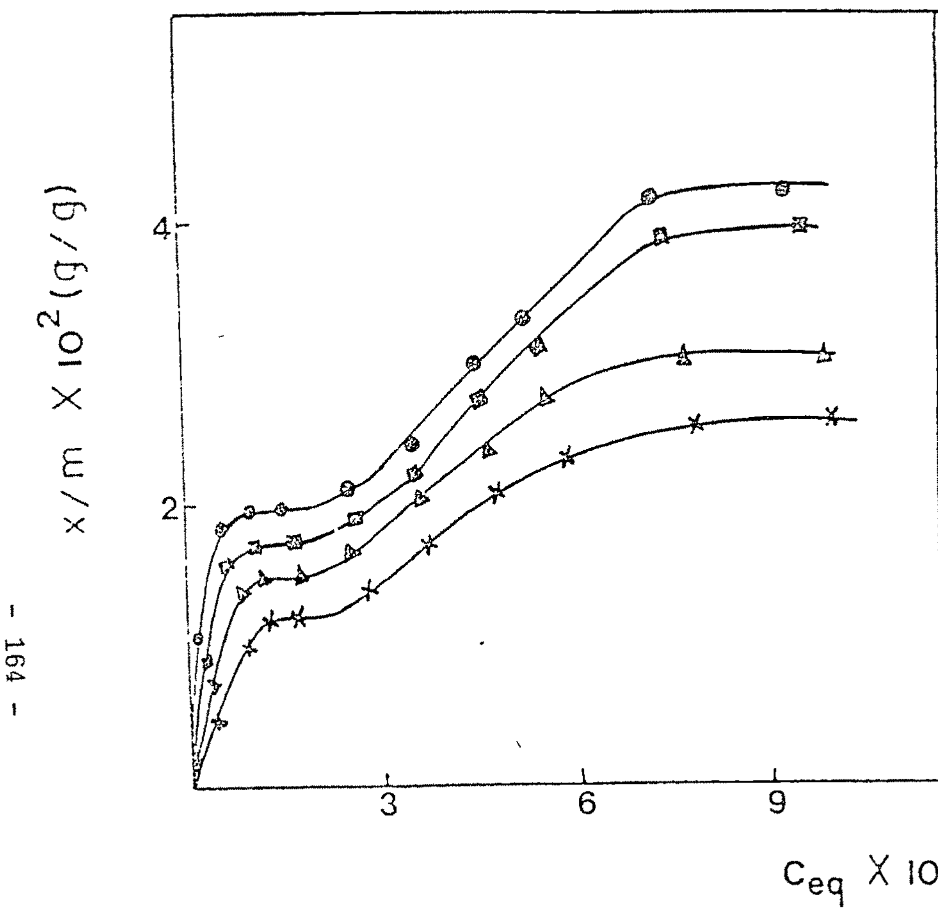


Fig.3.47 Plot of specific adsorption against equilibrium concentration of $ANBA_{11}$ on silica gel.

● 30°C ▨ 35°C ▲ 40°C X 45°C

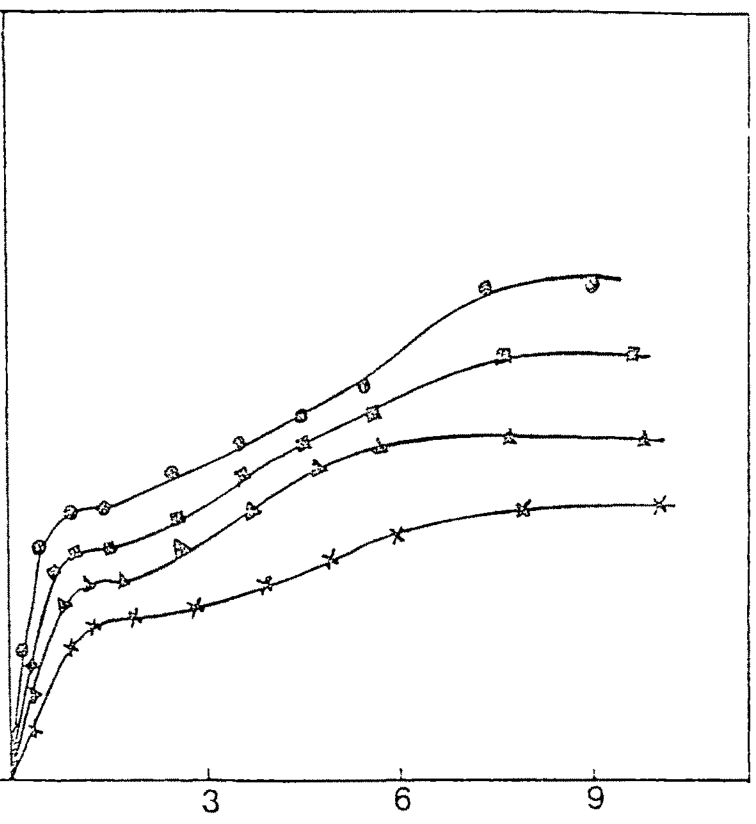


Fig.3.48 Plot of specific adsorption against equlibrium concentration of $ANBA_{12}$ on silica gel.

● 30°C ▨ 35°C ▲ 40°C X 45°C

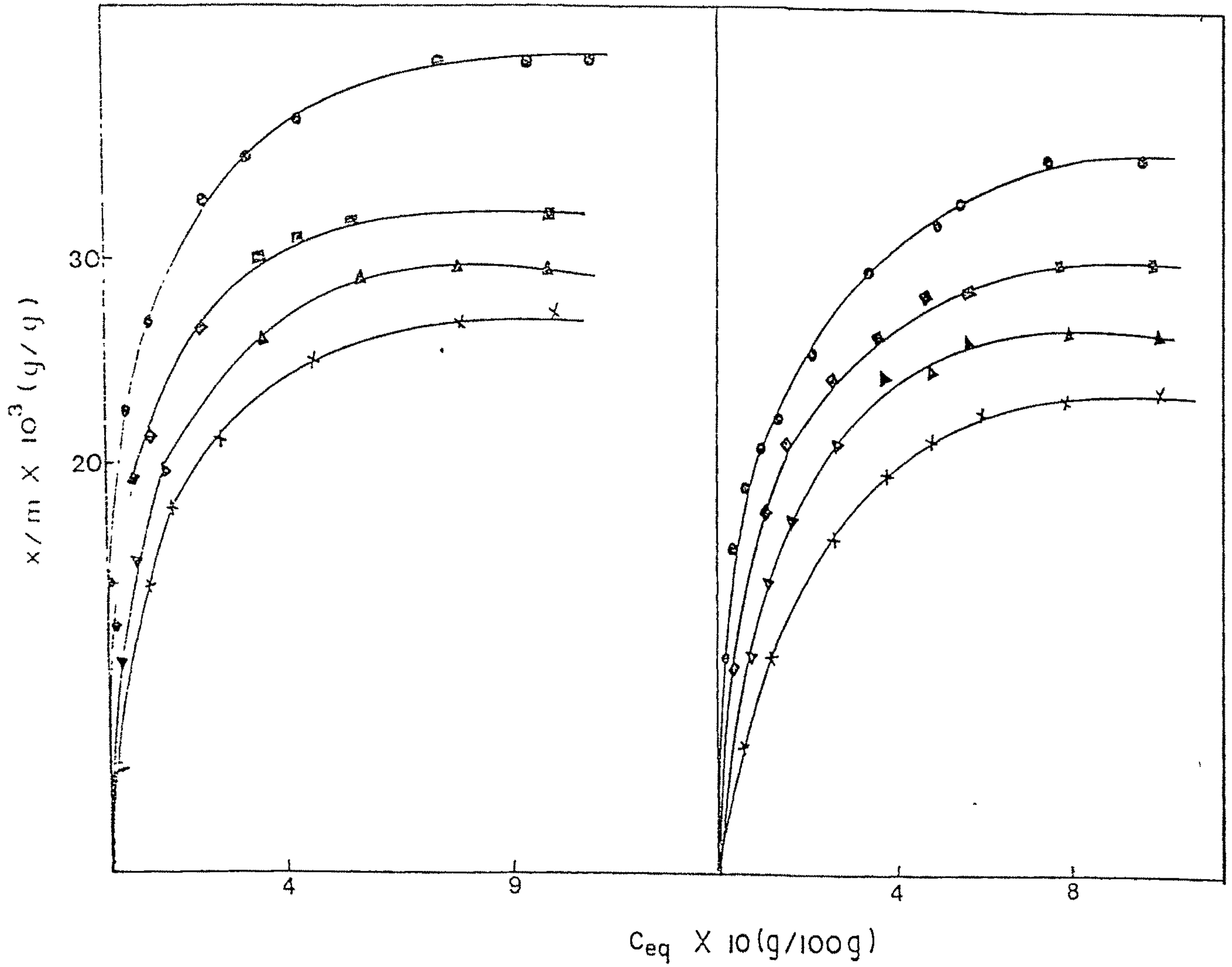


Fig.3.49 Plot of specific adsorption against equilibrium concentration of $ANMA_{11}$ on alumina.

⊖30°C ⊠ 35°C ▲ 40°C X 45°C

Fig.3.50 Plot of specific adsorption agsinst equilibrium concentration of ANMA $_{12}$ on alumina.

⊖30°C ⊠ 35°C ▲ 40°C X 45°C

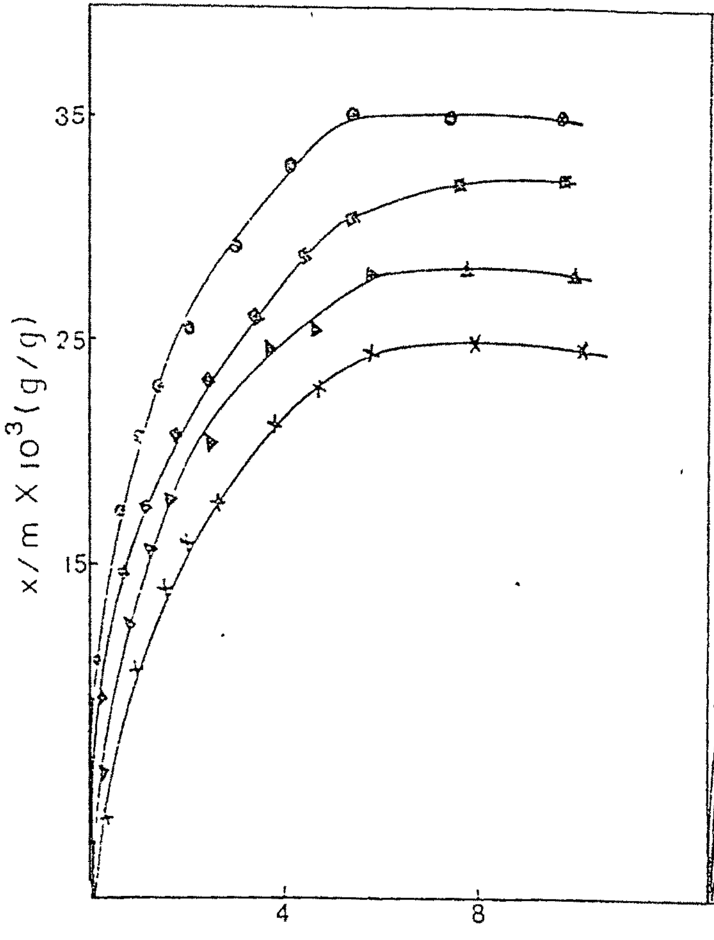


Fig.3.51 Plot of specific adsorption against equilibrium concentration of $ANEA_{11}$ on alumina.

⊙ 30°C ▨ 35°C ▲ 40°C X 45°C

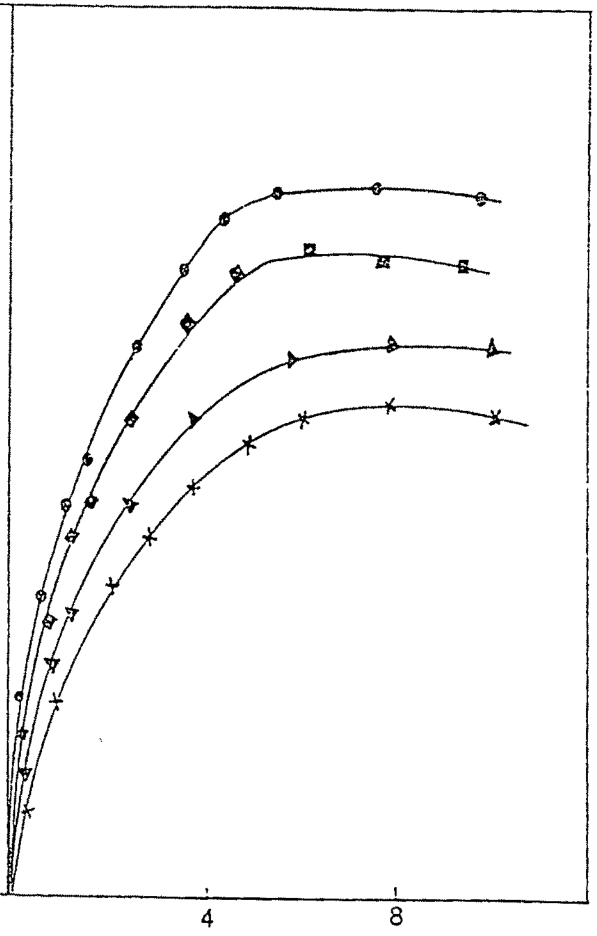


Fig.3.52 Plot of specific adsorption against equilibrium concentration of $ANEA_{12}$ on alumina.

⊙ 30°C ▨ 35°C ▲ 40°C X 45°C

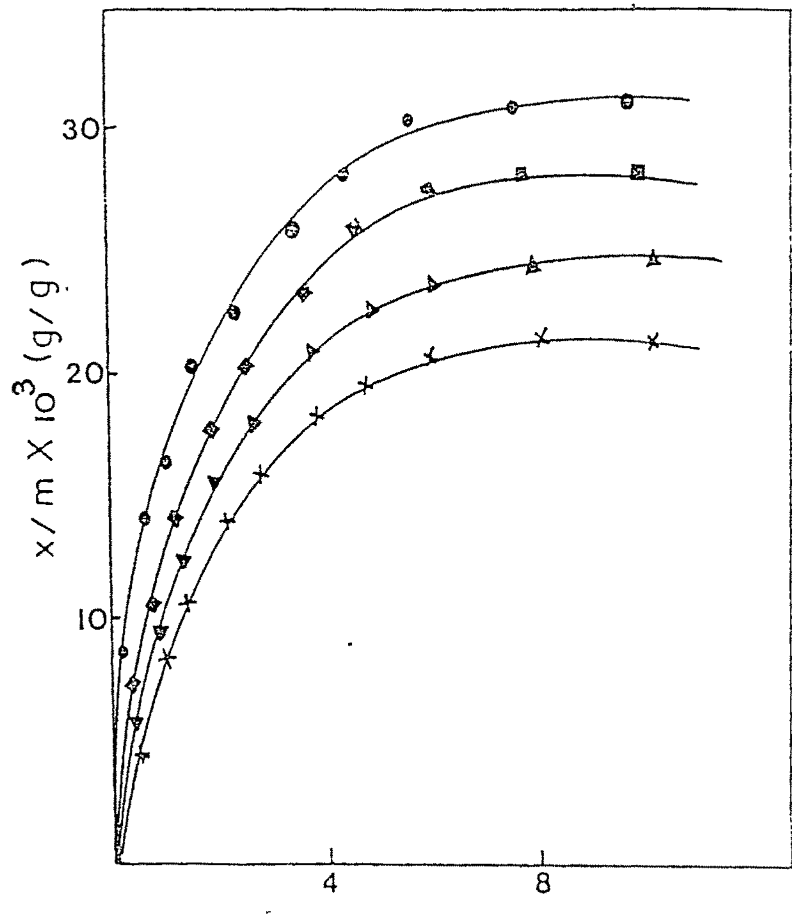


Fig.3.53 Plot of specific adsorption against equilibrium concentration of $ANBA_{11}$ on alumina.

● 30°C ▣ 35°C ▲ 40°C X 45°C

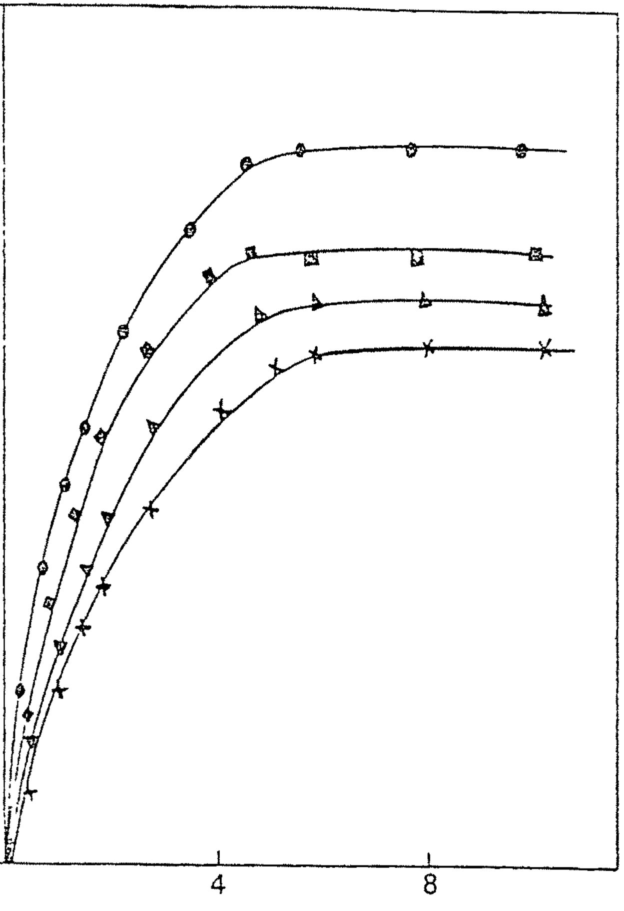
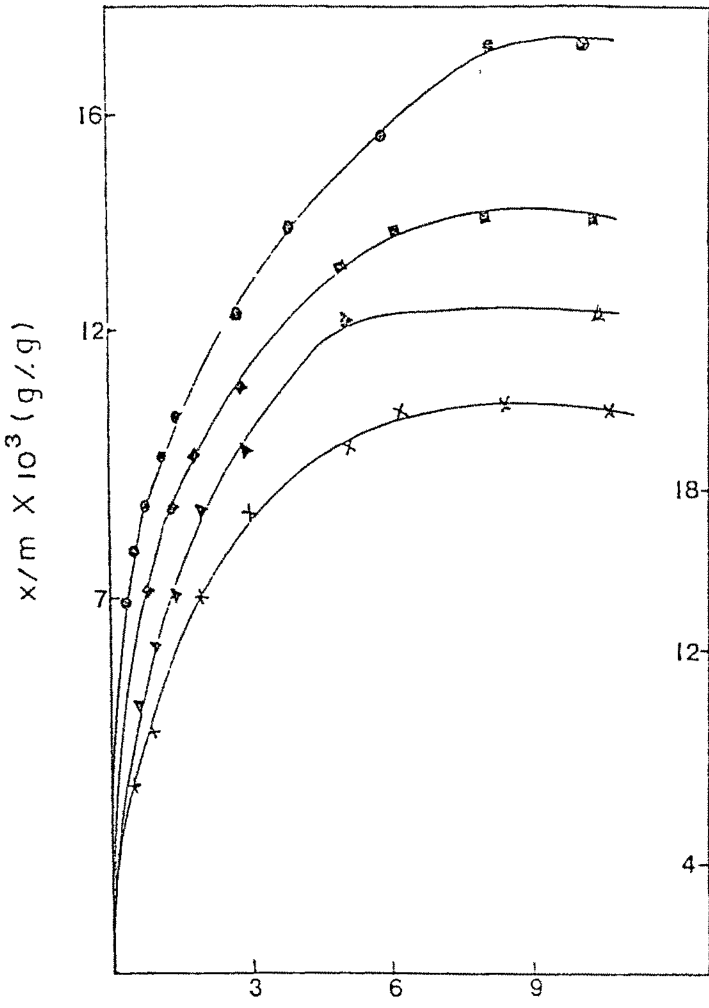


Fig.3.54 Plot of specific adsorption against equilibrium concentration of $ANBA_{12}$ on alumina.

● 30°C ▣ 35°C ▲ 40°C X 45°C



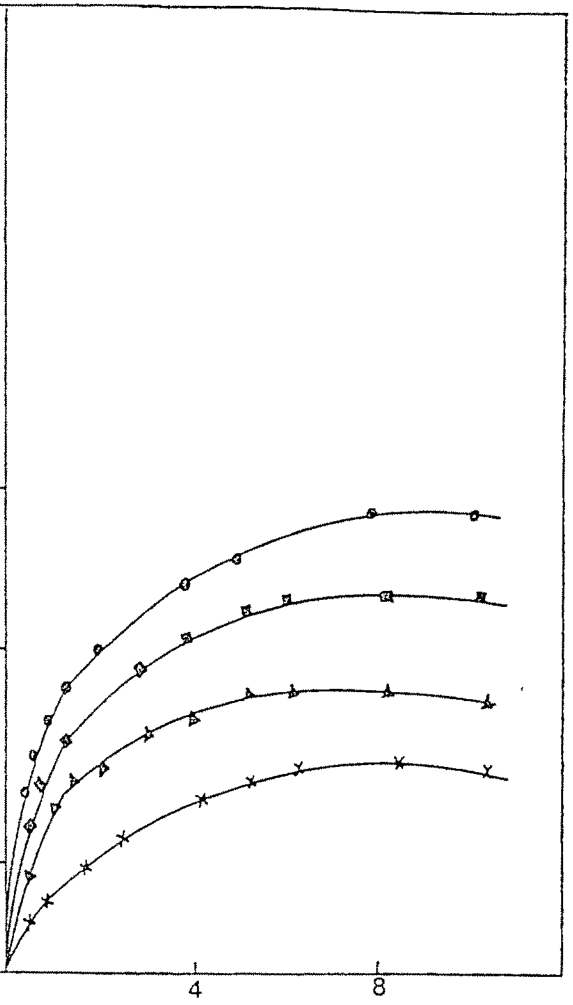


Fig.3.55 Plot of specific adsorption against equilibrium concentration of $ANMA_{11}$ $CaCO_3$.

● 30°C ▨ 35°C ▲ 40°C X 45°c

Fig.3.56 Plot of specific adsorption against equilibrium concentration of $ANMA_{12}$ on $CaCO_3$

○ 30°C ▨ 35°C ▲ 40°C X 45°C

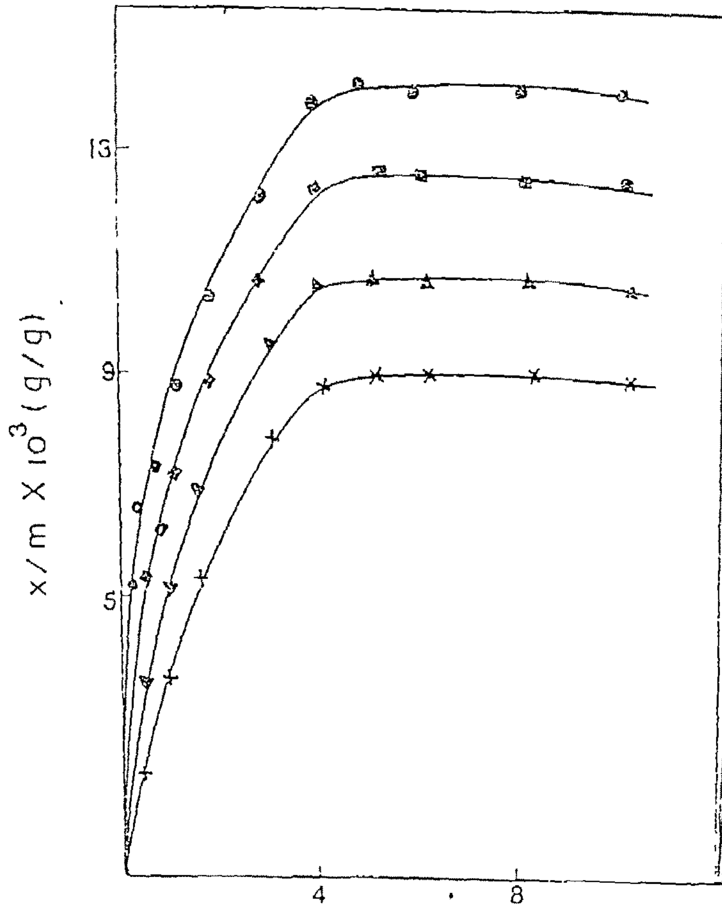


Fig.3.57 Plot of specific adsorption against equilibrium concentration of $ANEA_{11}$ on $CaCO_3$.

● 30°C ▨ 35°C ▲ 40°C X 45°C

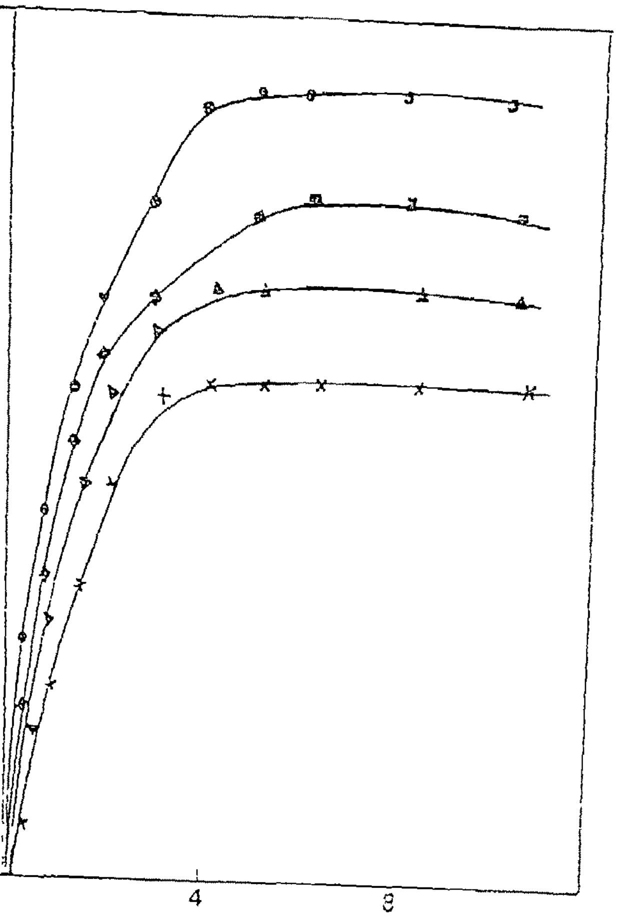


Fig.3.58 Plot of specific adsroption ~~against~~ equilibrium concentration of $ANEA_{12}$ on $CaCO_3$.

● 30°C ▨ 35°C ▲ 40°C X 45°C

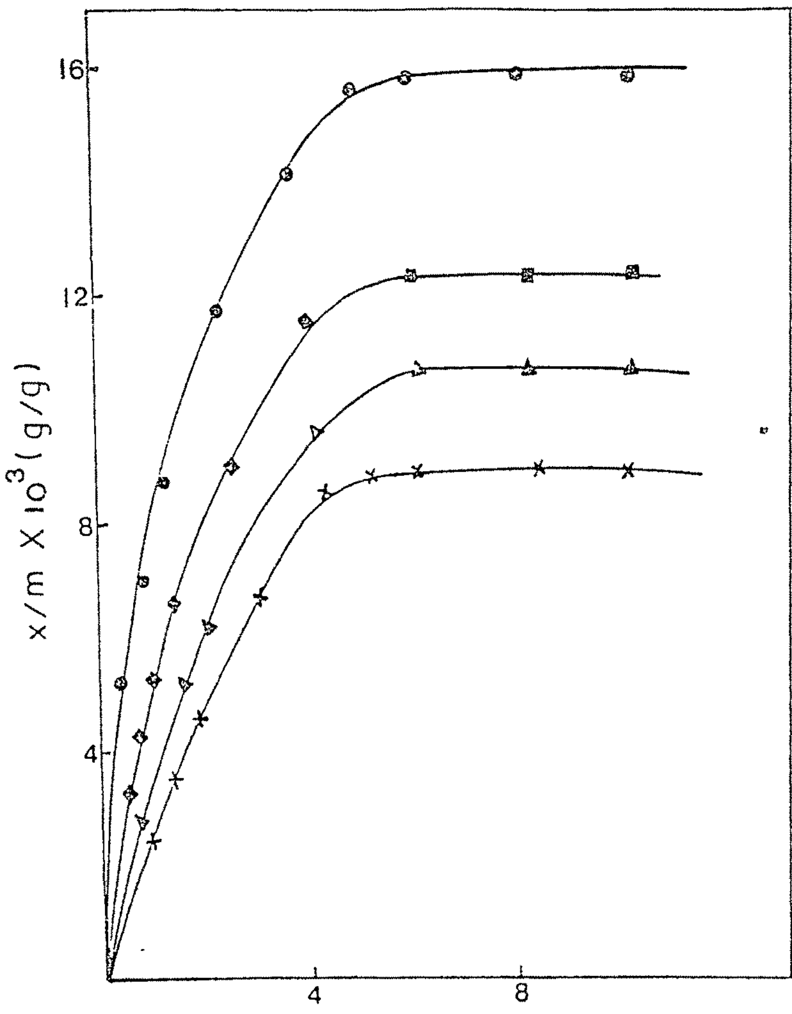


Fig.3.59 Plot of specific adsorption against equilibrium concentration of $ANBA_{11}$ on $CaCO_3$.
● 30°C ▨ 35°C ▲ 40°C X 45°C

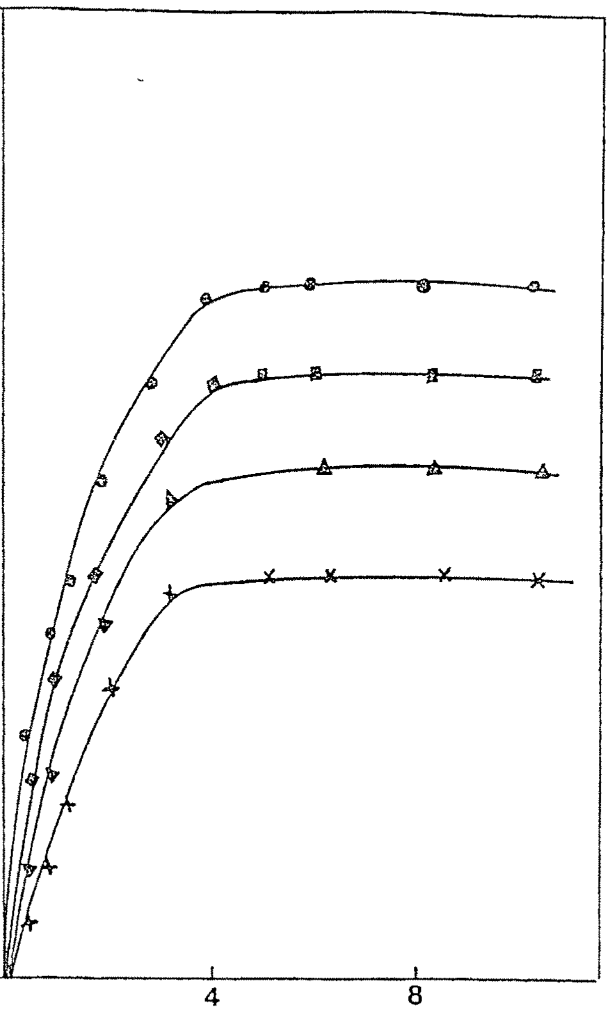


Fig.3.60 Plot of specific adsorption against equilibrium concentration of $ANBA_{12}$ on $CaCO_3$

● 30°C ▨ 35°C ▲ 40°C X 45°C

acrylate. Hence the presence of acrylonitrile in the copolymers reduces the importance of polymer - adsorbent interaction vis a vis polymer - polymer interaction as can be deduced from PAN isothems (fig. 3.35 - 3.37). The isotherms of PAN - silica gel systems were of the Langmuir type, devoid of any semi plateau region. The adsorption sites of alumina and $CaCO_3$ are Al^{3+} /112/ and CO_3^{2-} /327/ respectively. The polymer - adsorbent interactions are weaker in these cases. Desorption studies with DMSO showed more desorption from $CaCO_3$ and the least from silica gel.

The amount of polymer adsorbed is also a factor of the surface area of the adsorbents /24/, and the adsorbed amount showed a corresponding increase with the surface area. The surface area and the specific adsorption of copolymer on the three adsorbents follows the order

Silica gel $>$ alumina $>$ $CaCO_3$

On the basis of adsorption per unit area follows the reverse order is followed as discussed in section 3.3.2.

It was also observed that as the acrylate concentration in the copolymers increases, the adsorption decreases (Fig. 3.43 to 3.60). This was more prominent in case of lower alkyl acrylates. Adsorption of the corresponding homopolymers as discussed in the earlier sections (3.3.2 and 3.3.3) revealed that the polyacrylate adsorption was much less compared to that of polyacrylonitrile and specific adsorption decreased in the series poly(methyl acrylate), poly(ethyl acrylate) and poly(butyl acrylate). Specific adsorption of the copolymers lie in between the poly acrylate and poly acrylonitrile, but nearer to that of polyacrylates.

The thermodynamic quantities computed at infinite dilution are given in Tables 3.14 to 3.16 for the three adsorbent systems silica gel, alumina and $CaCO_3$ respectively. It can be seen that the free energy values were negative in all the systems indicating spontaneous adsorption. The negative free energy of adsorption at infinite dilution decreases with (i) rise in temperature (ii) the higher concentration of acrylates and (iii) when higher alkyl acrylates are used. These indicate that the adsorption process was relatively less spontaneous as the temperature increases and also as the acrylate concentration and size increase.

Among these three adsorbents, the values were more negative in silica gel systems. The effect of temperature on free energy values of $CaCO_3$ system was nominal, as indicated by the lower rate of change of free energy with respect to temperature. That is the entropy change is not large (Table 3.16). Enthalpy values also show relatively low exothermicity, compared to the values of silica gel and alumina. These indicate that the $CaCO_3$ - copolymer interactions are also weaker than the silica gel - copolymer and alumina - copolymer interactions. The negative entropy change with silica gel as well as

TABLE : 3.14

FREE ENERGY ΔG^{o}_{ads}, THE ENTHALPY ΔH^{o}_{ads} AND THE ENTROPY ΔS^{o}_{ads} AT INFINITE DILUTION FOR COPOLYMER - SILICA GEL SYSTEMS

(Concentration is expressed in g/100g solution)

Copolymer	$-\Delta G^{o}_{ads}$ (kJ mol^{-1})				$-\Delta H^{o}_{ads}$ (kJ mol^{-1})	$-\Delta S^{o}_{ads}$ (J $mol^{-1}K^{-1}$)
	30°C	35°C	40°C	45°C		
$ANMA_{11}$	14.0	12.8	11.9	10.4	83.7	229.9
$ANMA_{12}$	13.2	12.3	11.6	10.4	68.8	183.5
$ANEA_{11}$	12.6	11.8	11.3	10.2	58.6	151.8
$ANEA_{12}$	12.1	11.4	10.9	10.0	52.9	134.6
$ANBA_{11}$	11.7	11.1	10.6	10.0	44.0	106.8
$ANBA_{12}$	11.3	10.7	10.1	9.8	41.8	101.0

TABLE : 3.15

FREE ENERGY $\triangle G^{o}_{ads}$, THE ENTHALPY $\triangle H^{o}_{ads}$ AND THE ENTROPY $\triangle S^{o}_{ads}$ AT INFINITE DILUTION FOR COPOLYMER - ALUMINA SYSTEMS

(Concentration is expressed in g/100g solution)

Copolymer	$-\triangle G^{o}_{ads}$ (kJ mol^{-1})				$-\triangle H^{o}_{ads}$ (kJ mol^{-1})	$-\triangle S^{o}_{ads}$ (J mol^{-1}K^{-1})
	30°C	35°C	40°C	45°C		
$ANMA_{11}$	12.7	11.5	10.4	9.6	75.5	207.5
$ANMA_{12}$	12.6	11.8	11.2	10.8	47.8	116.5
$ANEA_{11}$	11.5	10.9	10.2	9.9	45.6	112.4
$ANEA_{12}$	10.8	10.4	9.9	9.4	39.2	93.5
$ANBA_{11}$	10.9	10.4	10.0	9.5	36.9	85.9
$ANBA_{12}$	10.4	10.1	9.7	9.5	29.8	63.9

TABLE : 3.16

FREE ENERGY ΔG°_{ads}, THE ENTHALPY ΔH°_{ads} AND THE ENTROPY ΔS°_{ads} AT INFINITE DILUTION FOR COPOLYMER - CALCIUM CARBONATE SYSTEMS

(Concentration is expressed in g/100g solution)

Copolymer	$-\Delta G^{\circ}_{ads}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{ads}$ (kJ mol^{-1})	$-\Delta S^{\circ}_{ads}$ (J $mol^{-1}K^{-1}$)
	30°C	35°C	40°C	45°C		
$ANMA_{11}$	10.3	10.2	10.1	10.0	16.4	20.2
$ANMA_{12}$	10.0	9.9	9.9	9.8	14.9	16.0
$ANEA_{11}$	9.8	9.7	9.7	9.6	14.5	15.5
$ANEA_{12}$	9.6	9.5	9.4	9.3	13.8	14.2
$ANBA_{11}$	9.6	9.5	9.5	9.4	12.4	9.4
$ANBA_{12}$	9.4	9.3	9.3	9.3	11.8	7.9

alumina adsorbent is very high indicating strong interaction between the polymer and adsorbent.

Comparing these thermodynamic values of the copolymers with the corresponding homopolymer values, it can be seen that they are in between the values of polyacrylates and PAN, but more closer to the values of polyacrylates. Nevertheless, PAN values are exceptionally high. Hence it could be surmised that in the copolymer - adsorbent interactions, acrylate group has a predominant effect than the nitrile group.

It is also observed that the $\triangle H^o_{ads}$ and $\triangle S^o_{ads}$ values of $ANMA_{11}$ systems are very much higher than rest of the systems. This is because the steric effect of methyl acrylate is less compared to the ethyl and butyl acrylate side chains, so more of acrylonitrile group get access to the adsorbent surface, increasing the specific adsorption considerably. The isotherms also reveal this fact, showing maximum adsorption of $ANMA_{11}$ on all the three adsorbents than the isotherms of other copolymers. Moreover, the reason for the decreased specific adsorption in copolymers like ANEA and ANBA can be accounted on the basis of covering up of the adsorbent sites by the bulkier ethyl and butyl acrylates as discussed earlier in section 3.3.2.

During the process of polymer adsorption the solvent molecules gets adsorbed initially and are later displaced by the polymer molecules /27/. The former step is associated with an entropy gain and the latter with an entropy loss when polymer molecules begin to adsorb. The net change in entropy is associated with the compensating effect of these processess. The change in entropy is negative in all these copolymers on the three adsorbents. This shows that, though entropy change is a major factor contributing to the process of adsorption, the enthalpic changes are dominant and the process is enthalpy controlled.

The thermodynamic quantities obtained by the surface coverage approach are given in Tables 3.17 to 3.19. The detail procedure is given in section 3.3.1. The isosteric heat values $\triangle H_A$ and entropy $\triangle S_A$ showed linear increase in negative values with the increase in amount of polymer adsorbed (A). Representative plots are shown in figs. 3.61 and 3.62. The energetic heterogeneity coefficient 'C' and entropic heterogeneity factor m were also computed and are presented in Tables 3.20 to 3.22 for all copolymer - adsorbent systems.

The heterogeneity coefficients were calculated for all systems at the four temperatures and are also presented in Tables 3.20 to 3.22. A linear relation exists when f is plotted against 1/T. The intercept gives f_o which is a measure of heterogeneity. The f_o values are compiled in tables 3.20 to 3.22.

The f_o values i.e. heterogeneity increases as the amount adsorbed becomes less and m and C values also show a corresponding increase. Comparing the values of m, C and f_o for the three

TABLE : 3.17

THERMODYNAMIC PARAMETERS OF ADSORPTION BY SURFACE COVERAGE APPROACH FOR COPOLYMER - SILICA GEL SYSTEMS

Copolymer	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K (kJ mol^{-1}
ANMA$_{11}$	0.50	85.8	255.5	8.4	79.8	232.9	9.2
	0.75	90.3	272.6	7.7			
	1.00	95.7	295.4	7.2			
	1.25	102.3	317.2	6.2			
ANMA$_{12}$	0.25	75.1	222.6	7.7	69.1	199.4	8.7
	0.50	81.9	248.5	6.6			
	0.75	87.3	270.2	5.4			
	1.00	93.9	294.9	4.5			
ANEA$_{11}$	0.25	68.7	201.7	7.6	62.3	177.2	8.6
	0.50	76.1	229.5	6.6			
	0.75	82.1	253.3	5.4			
	1.00	88.8	278.5	4.4			

Contd

TABLE 3.17 (Contd.)

Copolymer	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
ANEA$_{12}$	0.50	72.3	217.1	6.5	57.3	162.8	8.0
	0.75	79.9	244.6	5.8			
	1.00	87.2	271.0	5.1			
	1.20	93.4	293.4	4.5			
ANBA$_{11}$	0.25	63.6	188.6	6.5	54.1	154.6	7.3
	0.50	69.6	210.9	5.7			
	0.75	78.4	242.8	4.8			
	0.95	87.2	273.6	4.3			
ANBA$_{12}$	0.125	53.9	156.0	6.6	49.1	137.9	7.3
	0.250	58.7	176.3	5.3			
	0.375	65.0	198.5	4.9			
	0.500	68.2	212.4	3.8			

TABLE : 3.18

THERMODYNAMIC PARAMETERS OF ADSORPTION BY SURFACE COVERATE APPROACH FOR COPOLYMER - ALUMINA SYSTEMS

Copolymer	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
$ANMA_{11}$	0.50	84.3	253.7	7.4	68.7	197.4	8.9
	0.75	89.1	273.0	6.4			
	1.00	97.5	302.8	5.8			
	1.25	105.8	332.4	5.1			
$ANMA_{12}$	0.50	72.3	217.1	6.5	57.6	163.9	7.9
	0.75	79.9	244.6	5.8			
	1.00	85.4	264.9	5.1			
	1.20	93.4	293.4	4.5			
$ANEA_{11}$	0.50	72.3	217.1	6.5	54.3	153.5	7.8
	0.75	77.2	235.7	5.8			
	1.00	87.0	270.0	5.2			
	1.20	95.2	298.6	4.7			

...Contd....

TABLE : 3.18 (Contd.)

Copolymer	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
$ANEA_{12}$	0.25	63.6	188.6	6.5	53.5	152.6	7.3
	0.50	71.2	216.2	5.7			
	0.75	80.8	250.7	4.8			
	0.90	87.9	275.9	4.3			
$ANBA_{11}$	0.25	59.5	174.4	6.7	48.6	135.7	7.5
	0.50	69.0	210.0	5.4			
	0.75	79.2	246.3	4.6			
	0.90	86.9	273.1	4.2			
$ANBA_{12}$	0.25	55.4	165.5	5.3	43.5	124.0	5.9
	0.35	59.0	178.9	4.8			
	0.50	68.5	211.5	4.4			
	0.75	78.4	246.1	3.8			

TABLE : 3.19

THERMODYNAMIC PARAMETERS OF ADSORPTION BY SURFACE COVERAGE APPROACH FOR COPOLYMER - $CaCO_3$ SYSTEMS

Copolymer	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J $mol^{-1}K^{-1}$)	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J $mol^{-1}K^{-1}$)	$-\Delta G_o$(303°K) (kJ mol^{-1})
$ANMA_{11}$	0.20	48.9	136.8	7.7	22.2	43.9	8.9
	0.30	64.5	190.8	6.7			
	0.40	75.1	228.4	5.9			
	0.50	90.6	282.0	5.2			
$ANMA_{12}$	0.20	48.9	136.8	7.7	18.6	29.7	9.6
	0.30	59.5	174.4	6.7			
	0.40	75.5	231.3	5.4			
	0.50	91.4	286.9	4.5			
$ANEA_{11}$	0.20	49.6	144.0	6.0	15.7	27.4	7.4
	0.30	67.4	204.7	5.4			
	0.35	73.9	227.9	4.8			
	0.40	84.2	262.6	4.6			

...Contd....

TABLE : 3.19 (Contd.)

Copolymer	A (g/100 g)	$-\Delta H_A$ (kJ mol^{-1})	$-\Delta S_A$ (J mol^{-1}K^{-1})	$-\Delta G_A$(303°K) (kJ mol^{-1})	$-\Delta H_o$ (kJ mol^{-1})	$-\Delta S_o$ (J mol^{-1}K^{-1})	$-\Delta G_o$(303°K) (kJ mol^{-1})
$ANEA_{12}$	0.20	38.1	108.1	5.3	12.0	17.3	6.8
	0.30	46.5	137.3	4.9			
	0.40	56.5	171.5	4.6			
	0.50	63.8	197.7	3.9			
$ANBA_{11}$	0.10	30.8	80.2	6.5	11.2	11.4	7.7
	0.20	49.2	149.1	4.0			
	0.25	58.7	182.1	3.5			
	0.30	69.5	218.1	3.4			
$ANBA_{12}$	0.10	28.7	78.9	4.8	8.5	8.9	5.8
	0.15	41.8	124.5	4.1			
	0.20	52.2	160.5	3.6			
	0.25	60.8	190.4	3.1			

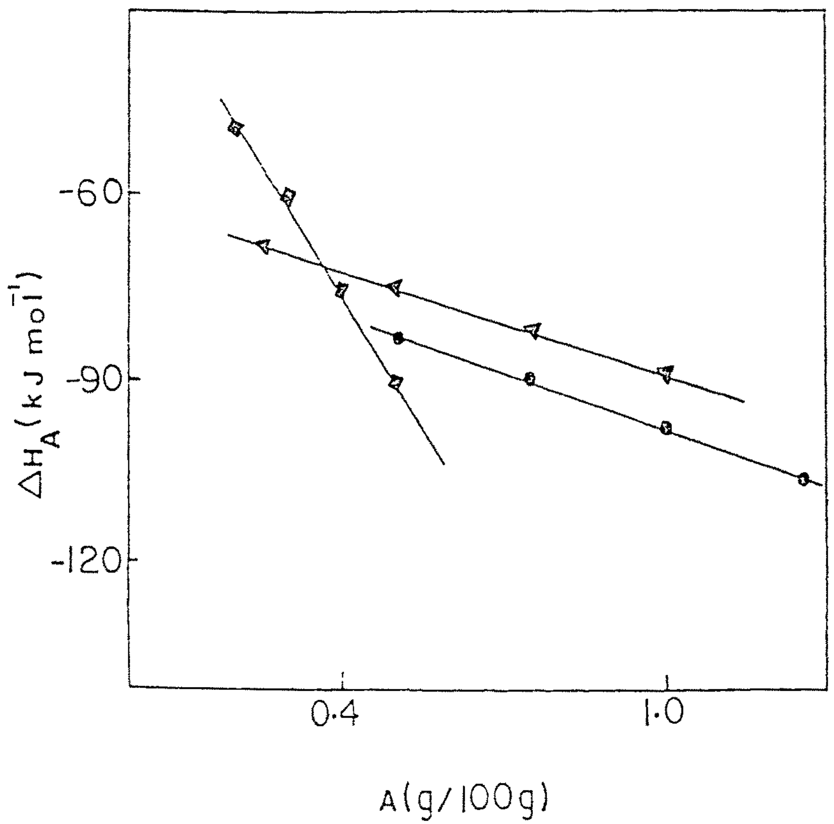


Fig.3.61 Change in ΔH_A against amount of copolymer adsorbed A for some systems.

▲ ANEA$_{11}$ - silica gel ● ANMA$_{11}$ - alumina ■ ANMA$_{12}$ CaCO$_3$

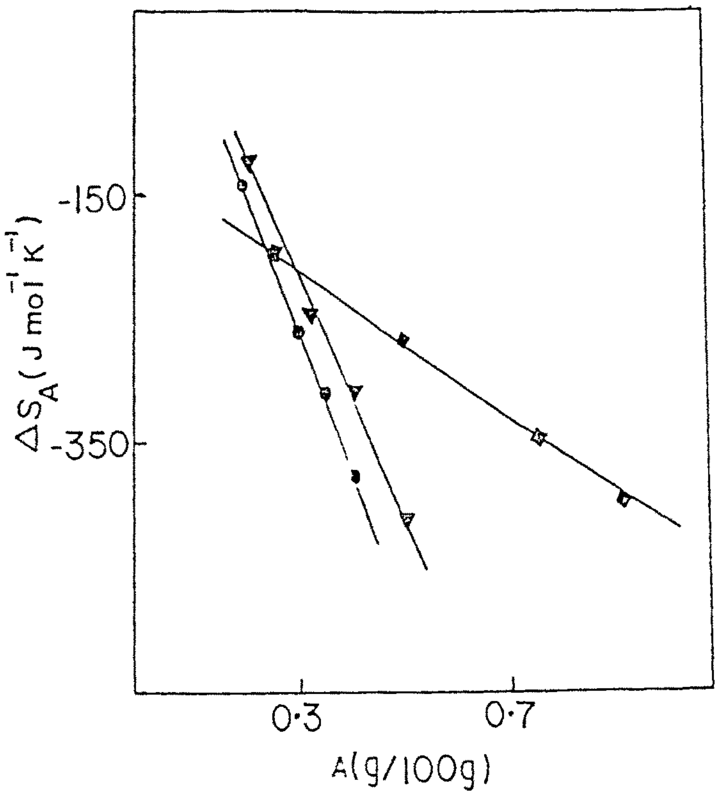


Fig.3.62 Change in ΔS_A against amount of copolymer adsrobed A for some systems.

● ANEA$_{11}$-CaCO$_3$ ▲ ANMA$_{12}$-CaCO$_3$

■ ANBA$_{11}$ - silica gel.

TABLE : 3.20

SURFACE CHARACTERISTIC PARAMETSRS OF ADSORPTION FOR COPOLYMER - SILICA GEL SYSTEMS BY SURFACE COVERAGE APPROACH

Polymer	f (gl^{-1})				$-f_o$ (gl^{-1})	$-m$ ($J\ mol^{-1}K^{-1}$)	$-C$ ($kJ\ mol^{-1}$)
	30°C	35°C	40°C	45°C			
$ANMA_{11}$	0.91	1.02	1.18	1.34	10.1	84	22.4
$ANMA_{12}$	1.72	1.85	1.97	2.18	11.2	94	24.7
$ANEA_{11}$	1.71	1.85	2.02	2.23	12.7	106	26.5
$ANEA_{12}$	1.18	1.37	1.52	1.70	13.2	110	30.0
$ANBA_{11}$	1.28	1.46	1.72	1.88	14.4	120	33.7
$ANBA_{12}$	2.86	3.10	3.38	3.59	18.6	155	39.4

TABLE : 3.21

SURFACE CHARACTERISTIC PARAMETERS OF ADSORPTION FOR COPOLYMER - ALUMINA SYSTEMS BY SURFACE COVERAGE APPROACH

Polymer	f (gl^{-1})				$-f_o$ (gl^{-1})	$-m$ ($J\ mol^{-1}K^{-1}$)	$-C$ ($kJ\ mol^{-1}$)
	30°C	35°C	40°C	45°C			
$ANMA_{11}$	1.24	1.44	1.65	1.75	12.3	103	29.2
$ANMA_{12}$	1.18	1.37	1.52	1.76	13.2	110	29.1
$ANEA_{11}$	0.98	1.23	1.47	1.60	14.4	120	33.2
$ANEA_{12}$	1.34	1.56	1.84	2.05	16.6	139	37.2
$ANBA_{11}$	1.54	1.88	2.02	2.34	17.7	148	41.7
$ANBA_{12}$	1.15	1.49	1.74	2.04	19.7	165	47.2

TABLE : 3.22

SURFACE CHARACTERISTIC PARAMETERS OF ADSORPTION FOR COPOLYMER - $CaCO_3$ SYSTEMS BY SURFACE COVERAGE APPROACH

Polymer	f (gl^{-1})				$-f_o$ (gl^{-1})	$-m$ ($J\ mol^{-1}K^{-1}$)	$-C$ ($kJ\ mol^{-1}$)
	30°C	35°C	40°C	45°C			
$ANMA_{11}$	3.09	3.72	4.67	5.56	56.1	469	136.0
$ANMA_{12}$	4.29	5.07	5.86	6.97	60.3	504	143.5
$ANEA_{11}$	2.84	3.63	4.85	5.93	69.4	580	169.9
$ANEA_{12}$	3.87	4.74	5.80	7.10	72.0	602	174.2
$ANBA_{11}$	4.16	5.14	6.54	7.60	78.6	657	192.1
$ANBA_{12}$	4.65	5.56	7.03	8.62	89.4	747	213.4

adsorbents it can be seen that the values are exceptionally high for the copolymer - $CaCO_3$ systems. This is attributed to the high heterogeneity of $CaCO_3$ and hence, the capacity to adsorb will be least on this adsorbent.

When the copolymers adsorb onto the surface of the adsorbents, the system becomes more homogeneous. As more amount of polymer gets adsorbed, as in the case of silica gel systems, the system becomes less heterogeneous. The lower f_o values obtained for these systems support this view.

The linear relationship of $\triangle H_A$ and $\triangle S_A$ indicates that the compensation effect exists in these systems also. The change in free energy values were also calculated for all the systems. The $\triangle G_A$ values at a given temperature (303 °K) are tabulated in Tables 3.17 to 3.19 for all copolymer - adsorbent systems.

The $\triangle G_A$ - A plot is linear and the intercept gives $\triangle G_o$, the free energy of adsorption at zero coverage. These values are given in Tables 3.17 to 3.19. This isosteric infinitely dilute free energy of adsorption '$\triangle G_o$' does not seem to follow any regularity with the composition of the acrylonitrile - acrylate copolymers on the adsorbents silica gel, alumina and $CaCO_3$. For ANBA copolymers $\triangle G_o$ is independent of the concentration of butyl acrylate on the silica gel adsorbent, whereas on alumina and $CaCO_3$ considerable changes are observed. In these copolymers the presence of higher alkyl acrylates decreases $\triangle G_o$ values for all the three absorbent systems. Hence the free energy of adsorption is a function of the concentration and type of acrylate present in the copolymers. This is in agreement with the observations of the earlier thermodynamic approach the extrapolation method.

The $\triangle H^o_{ads}$ obtained by the extrapolation method for all the systems i.e. homopolymers and copolymers, were plotted against the similarly obtained $\triangle S^o_{ads}$. The linear plot obtained is shown in fig. 3.63. The slope of the plot is 324 °K where K is a temperature unit. Similarly, the isosteric $\triangle H_o$ values for all the systems studied were also plotted against the corresponding $\triangle S_o$ values. This linear plot is shown in fig. 3.64 and the slope yielded a temperature value of 323 °K.

The plots of $\triangle H$ vs $\triangle S$ are linear. Therefore one can write /361/.

$$\triangle H = K_1 + K_2 \triangle S \qquad \ldots\ldots\ 3.23$$

Where K_1 and K_2 are two constants. From thermodynamics we know that

$$\triangle G = \triangle H - T \triangle S \qquad \ldots\ldots\ 3.24$$

By substituting equation 3.23. gives

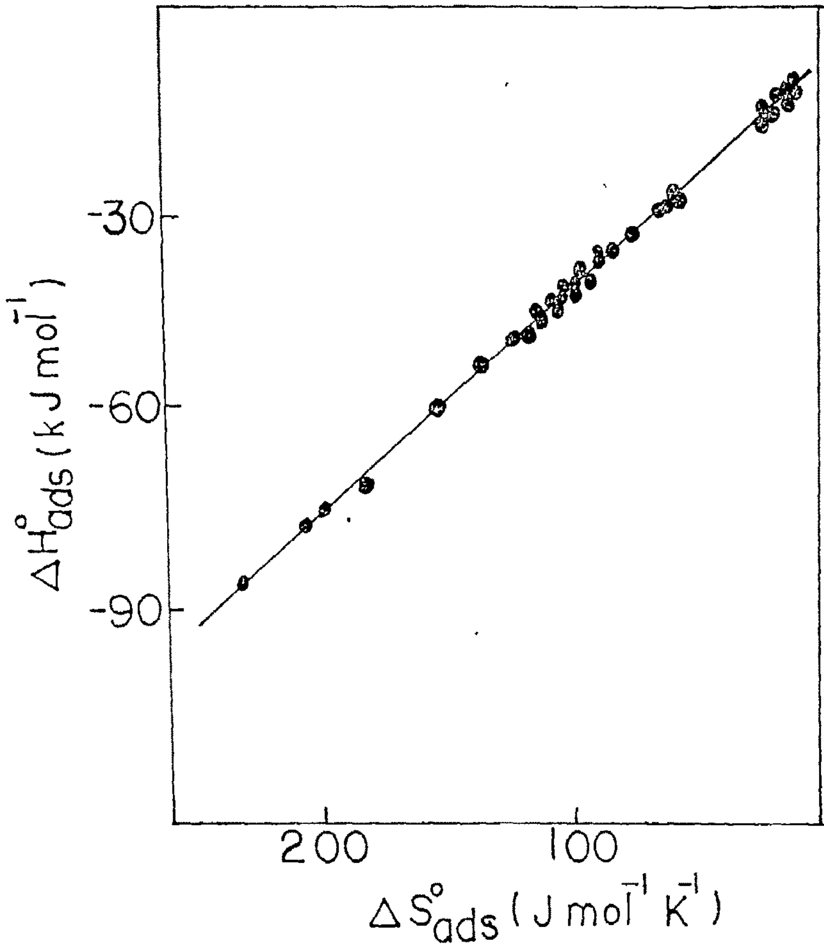


Fig.3.63 Plot of ΔH^{o}_{ads} against ΔS^{o}_{ads} for all the homopolymers and copolymer systems obtained by infinite dilution method.

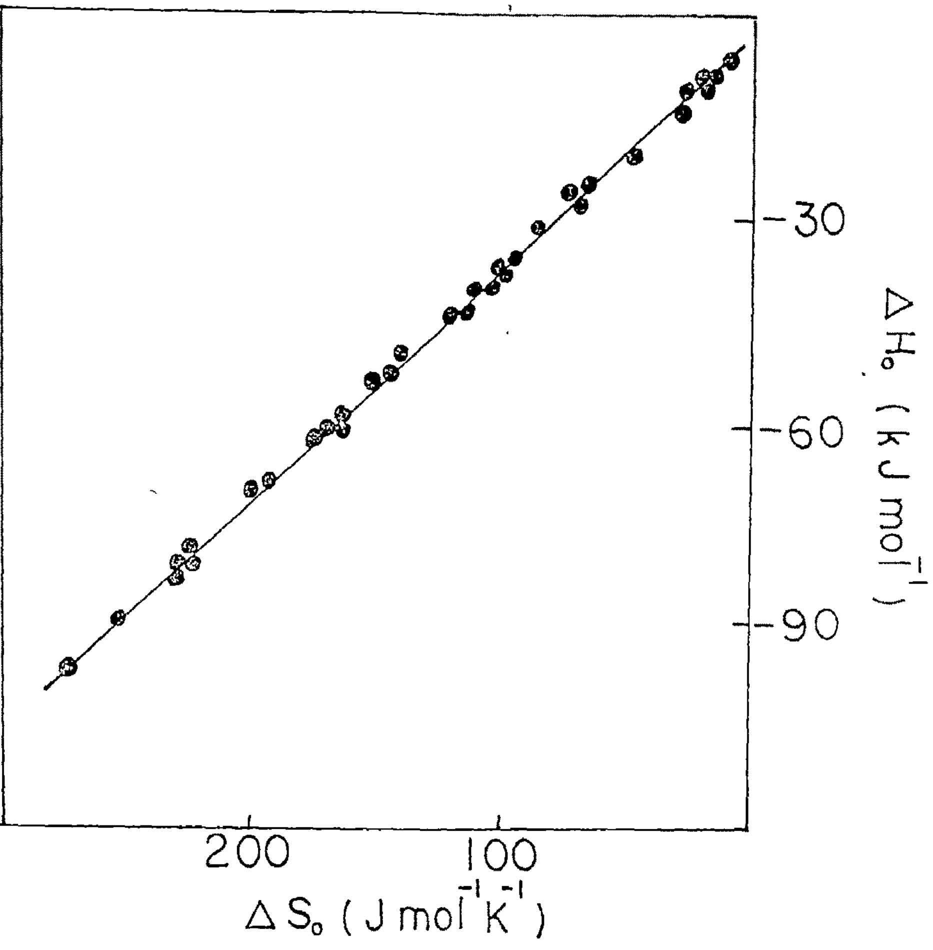


Fig.3.64 Plot of ΔH_{o} against ΔS_{o} for all the homopolymer and copolymer systems obtained by surface coverage approach.

$$\triangle G = K_1 + K_2 \triangle S - T \triangle S$$

$$= K_2 + (K_2 - T) \triangle S \qquad \ldots\ldots\ 3.25$$

That is K_2 has a unit of temperature °K and at $K_2 = T$, the $\triangle G$ is totally independent of entropic forces and becomes a constant.

From two different thermodynamic approaches i.e. extrapolation to infinite dilution and surface coverage approach gives almost the same temperature value of 324° and 323°K, at which $\triangle G$ becomes indendent of entropic forces for all homopolymers and copolymers. Therefore this temperature 323.5 °K is characteristic of the adsorption of these polymers on the adsorbents alumina, silica gel and $CaCO_3$ used for the present investigation.

This was also seen earlier /334/ for 1,4 polyisoprenes (both cis and trans) and 1,4 polybutadiene adsorption on these adsorbents from various solvents that this temperature was 320 °K.