CHAPTER : 3

ADSORPTION OF POLYMERS AT SOLID-LIQUID INTERFACE

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This chapter deals with adsorption of PBR, GR and InR from its various solutions on inorganic adsorbents, in Sections 3.2, 3.3 and 3.4 respectively. The Section 3.1 discusses the experimental procedure adopted in determining the adsorption isotherm of all the above mentioned polymers. The adsorption has been studied at different temperatures. Adsorbents used were silica gel and alumina. The solvents used were toluene [T], cyclohexane [C], chlorobenzene [CB], and various binary mixtures of T & C and T & CB. The adsorption study was done from various pure and mixed solvent systems on those adsorbents. The Section 3.5 highlights polymer-surfactant interaction.

3.1 EXPERIMENTAL

The solutions of PBR, GR and InR of highest concentration were prepared by dissolving the weighed amount of the respective polymer in a known volume of solvent. The other solutions of desired concentrations were prepared from it by dilution. Exactly weighed amount of adsorbent [silica gel with 13% $CaSO_4$ or acidic alumina] was placed with known volume of experimental solutions, in a series of jacketed glass bottles. These bottles were then placed on a shaker for continuous shaking. Thermostated water [± 0.1°C] was pumped through these jacketed bottles till the equilibrium adsorption condition was reached. The amount of polymer in the solution during adsorption was estimated at various time intervals to ensure the attainment of equilibrium condition i.e. till two consecutive readings were within 2% of each other. The same procedure was adopted at all temperatures. The time required to attain the equilibrium condition varied from system to system and was generally more than 24 hours but less than 48 hours. In some preliminary runs, we determined the adsorption values at intervals of 3, 5 and 7 days to check on the probable quasiequilibrium state of the system. We feel that such a problem did not exist in this study.

The concentration of the polymer in solution was determined by both UV spectroscopy and gravimetry. UV method was adopted for cyclohexane and chlorobenzene solvent systems. For PBR in cyclohexane, λmax was found to be 240 nm. For GR in cyclohexane, λmax was 275 nm. InR was insoluble in cyclohexane but soluble in chlorobenzene. Hence adsorption of InR on adsorbents was done from chlorobenzene. Concentration was determined by UV spectroscopy where λmax was found to be at 286.5 nm. Calibration curves were obtained earlier for each system and the concentration after adsorption was computed from the same.

For all other solvent systems i.e. pure toluene and all the mixed solvent systems, equilibrium concentration was obtained gravimetrically. In the gravimetric procedure /122,365/ dry small weighed beakers were taken. 2 ml of the polymer solution was pipetted out in each beaker and placed under a low vacuum at 50°C till complete dryness. The beakers were then weighed to determine the amount of the residual polymer present. The procedure was repeated until two consecutive weighings at a difference of 2h. on 3rd day gave the same result. Each reading was duplicated simultaneously to check on the reproducibility of the result. The concentration range chosen varied for the three rubbers. For PBR, the concentration range studied was from 0.05% [w/v] to 1.2% [w/v] in pure solvent systems. Different mixtures of two liquids : cyclohexane and toluene were prepared in ratios of 80:20, 50:50 and 20:80 by volume. This was considered as the stock solvent and the highest concentration of the polymer solution was made by dissolving weighed amount of PBR or GR in the required solvent. The solutions of lower concentrations were then made by diluting with the solvent. The equilibrium bulk concentration was estimated gravimetrically. UV spectroscopy could not be used because of high cut off [λmax = 280 nm] of toluene. The concentration range of PBR, in mixed solvent systems was from 0.05% [w/v] to 1.0% [w/v]. The maximum error in gravimetric estimation was ± 2.0%. The concentration range of GR was from 0.05% [w/v] to 0.8% [w/v], for both pure and mixed solvent systems.

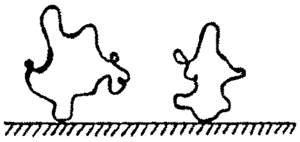
Different mixtures of two liquids : chlorobenzene and toluene were also prepared in ratios of 80:20, 50:50 and 20:80 by volume. This was then considered as the stock solvent and the highest concentration of InR solution was made by dissolving weighed amount of InR in the required solvent. The solutions of lower concentrations were then made by diluting with the stock solvent. Adsorption of InR was also studied from pure solvent systems i.e. chlorobenzene and toluene. Equilibrium bulk concentration of InR in chlorobenzene was obtained by UV spectroscopy method. For toluene and mixed solvent systems, residual polymer concentration was estimated gravimetrically. The concentration range chosen for InR was from 0.05% [w/v] to 0.8% [w/v], for all the solvent systems. The concentration range studied varied from system to system because of the attainment of plateau region in the isotherm and the high viscosity of polymer solutions.

Characteristics of adsorbents [silica gel and alumina] have been discussed earlier in Section 2.2 [B].

RESULTS AND DISCUSSION

3.2 Adsorption of PBR

The adsorption of PBR was studied from cyclohexane and toluene, on silica gel at four different temperatures of 25, 30, 35 and 40°C. In Figs.3.2.1 and 3.2.2 the amount of PBR adsorbed per gram of silica gel from cyclohexane and toluene respectively [x/m], are plotted against the equilibrium concentration of PBR [C_{PBR}]. The amount of adsorption is more from cyclohexane than from toluene and decreases with increase in temperature. The isotherms which are relatively more sharp than rounded, show both maxima and minima and at higher concentrations they finally level off. Similar isotherms were observed earlier /366/. It was suggested /124,218/ that as the polymer gets adsorbed on the surface of the adsorbent, a second phenomenon of the spreading of polymer on the surface of the adsorbent starts. Conceptual representations of the adsorption of macromolecules are shown below /367/



(A)

(B)

At lower initial concentration, the adsorbed layer thickness is large and also the adsorbed polymer mass is large, though distributed randomly, resulting in the lower concentration of the polymer in the adsorbed layer. It can be seen that at low initial concentration, the macromolecules are first adsorbed "three dimensionally" [A] and then spread more and more "two dimensionally" over the surface with time [B]. At higher initial concentrations, the polymer molecules compete more and more for the substrate surface, adsorbing three dimensionally. This results in greater layer thickness and higher polymer concentration in the adsorbed layer. The layer thickness increases with the square root of the molar mass at higher initial concentrations /367/. This spreading starts much before the equilibrium is reached and therefore will determine the amount of PBR adsorbed. The rate of adsorption is expected to be proportional to the concentration of the polymer in solution and the rate of spreading to the concentration of the adsorbed polymer on the surface. Hence, more the spreading of the polymer on the surface, less is the possibility of the polymer to be adsorbed. The nature of the observed isotherm is therefore due to these two antagonistic effects, besides others.

In Fig.3.2.3 the SEM photographs of silica gel before and after adsorption are shown. The adsorbent was removed from the jacketed

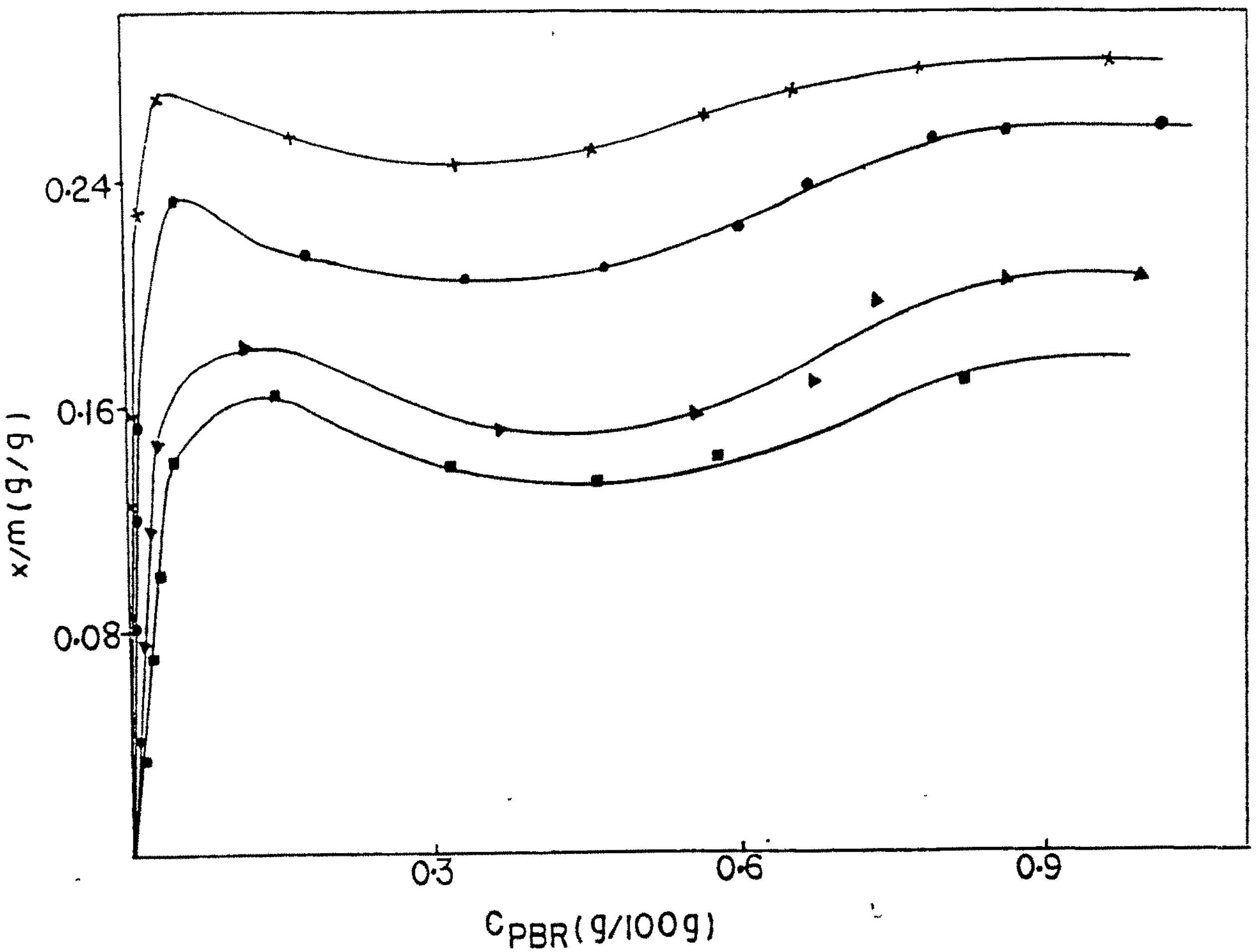


Fig.3.2.1 Plot of specific adsorption against the equilibrium concentration of PBR from cyclohexane on silica gel
× 25°C ● 30°C ▲ 35°C ■ 40°C

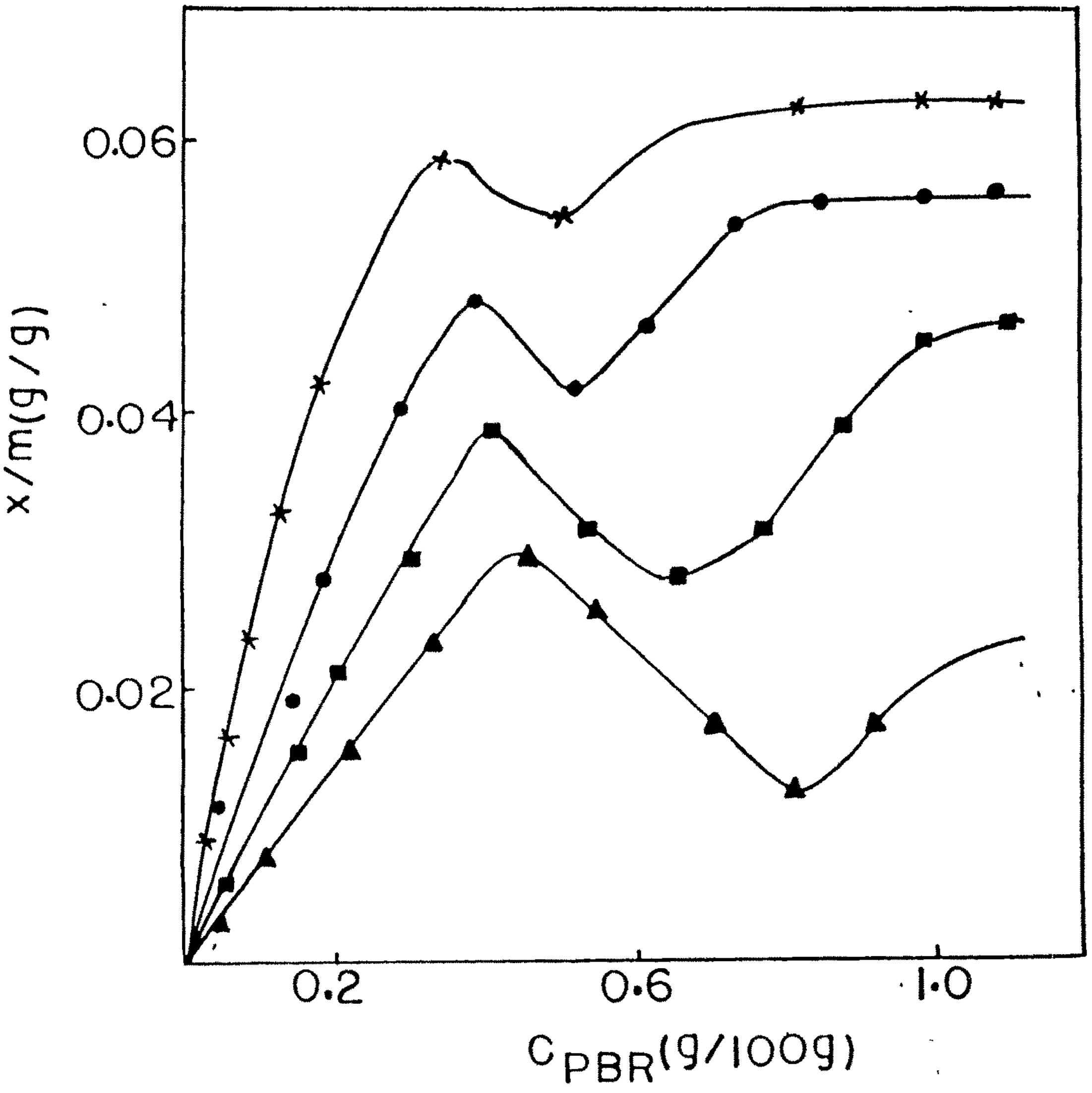


Fig.3.2.2 Plot of specific adsorption against the equilibrium concentration of PBR from toluene on silica gel

X 25°C ● 30°C ■ 35°C ▲ 40°C

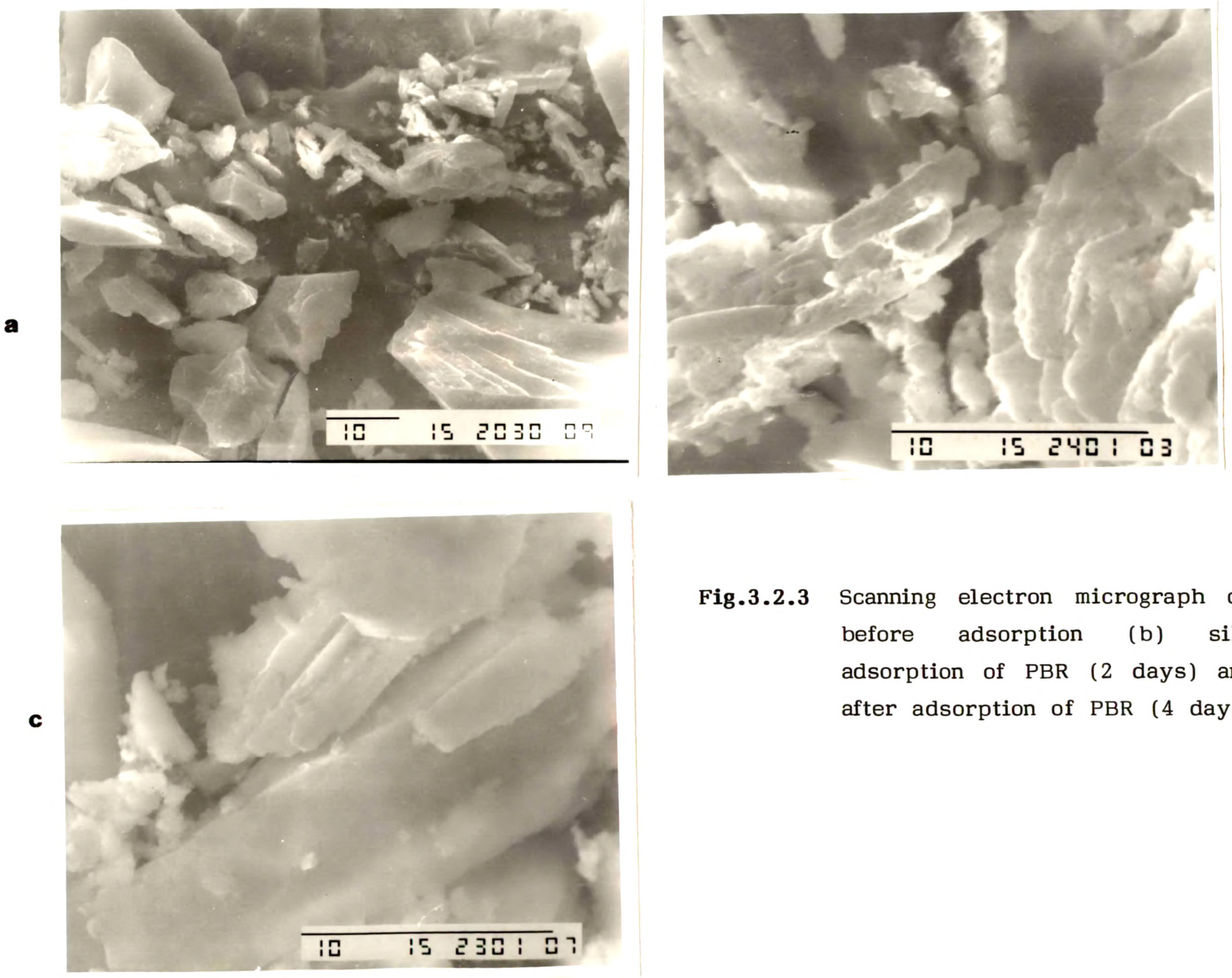


Fig.3.2.3 Scanning electron micrograph of (a) silica gel before adsorption (b) silica gel after adsorption of PBR (2 days) and (c) silica gel after adsorption of PBR (4 days)

bottle 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 two days. It can be easily concluded from the photographs that the system did change with time. One can see more polymer sheath on the surface and decrease in the rough edges of the inorganic material with time. This we think is a good proof of polymer spreading as well as of multilayer formation. This has been observed earlier for polystyrene /368/.

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 /198/. At the outset, the lower molecular weight species get adsorbed because it could diffuse relatively easily to the surface of adsorbent. But with time the higher molecular weight species replace the lower ones because of preferential adsorption. If the polymer 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 the bulk phase /119/. 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 /369/. However, if the adsorption bond is very strong, such a displacement may not occur and the smaller molecules will also remain adsorbed. The adsorption of larger and smaller molecules, is thus dependent on the porosity of the adsorbent and the nature of the adsorbent surface.

The PBR used was polydisperse with MWD being 2.52 [Chapter 2]. This indicates that it does have various molecular weight species. At lower original concentrations, both the species are adsorbed. But at higher concentrations, lower molecular weight species are desorbed and replaced by the higher molecular weight species. Therefore, more amount of PBR gets desorbed, compared to the amount getting adsorbed, resulting in the above mentioned nature of the isotherms. Moreover, around the concentration at which the dip is observed, probably no further adsorption of polymer happens on the surface. But at a little higher concentration, polymer-polymer interaction becomes important enough, resulting in a higher adsorption, hence the prominency of the dip. All these factors taken together are responsible for the nature of the isotherms observed in Figs.3.2.1 and 3.2.2.

From viscosity study of PBR in toluene and cyclohexane, the shape factor was calculated [Chapter 2]. It was found to be 2.5 in both the cases thereby suggesting that the polybutadiene macromolecules acquire spherical conformation in these solvents. It is difficult to visualise the conformational nature of the polymer at solid-liquid interface. Being a linear molecule, we expected it to show the train, loop and tail conformation, as was first suggested by Jenkel and Rumbach /218/ leading to a change in IR frequency of the adsorbed polymer. However, we did not observe any such change. Hence it is suggested that the conformation of the polymer on the surface is same as that in solution /138/.

The adsorption can be written in the following way :

$$\text{A [solid]} + \text{PBR [in solution]} \rightleftharpoons \text{APBR [solid]} \qquad \text{..... [1]}$$

where A is the adsorbent. The equilibrium constant is therefore :

$$K = 1/a_{PBR}\ \text{[solution]} \simeq 1/C_{PBR}\ \text{[solution]} \qquad \text{..... [2]}$$

which is true for average surface coverage /224/.

Therefore the free energy of adsorption is

$$\Delta G_{ads} = -\, RT \ln K = RT \ln C_{PBR} \qquad \text{..... [3]}$$

where R & T have their usual significance and C_{PBR} is the equilibrium concentration of the polymer in g/100g of solution. To obtain free energy of adsorption at infinite dilution ΔG^{o}_{ads}, the ΔG_{ads} values at the low concentration region, at a given temperature, were plotted against the original concentration of the polymer solution. The straight line plot obtained was extrapolated linearly by regression analysis to C = 0, to yield ΔG^{o}_{ads}. The reference state is defined as a hypothetical solution of unit concentration possessing the properties of an infinitely dilute polymer solution. The ΔG^{o}_{ads}-T plot showed linearity, the slope and the intercept being ΔS^{o}_{ads} and

ΔH^{o}_{ads} respectively. The thermodynamic values obtained for different systems are compiled in Table 3.2.1. It is obvious from the data that the adsorption from the solvents mentioned, is exothermic with negative entropy change. Both the enthalpy and entropy change values of the adsorption process in the silica gel-cyclohexane system are highly negative in comparison to those of other systems. The adsorption process from a solution as in these cases, are complicated due to the presence of many different phenomena. A plot of ΔH^{o}_{ads} and ΔS^{o}_{ads} values show a complete linearity signifying compensation effect in these systems.

We have already mentioned the possibility of spreading of adsorbed polymer on the adsorbent surface. The adsorption of PBR on the adsorbents will also be effected by [1] polymer-solvent, [2] solvent-adsorbent, [3] polymer adsorbent, [4] polymer-polymer, and [5] solvent-solvent interactions. We are not in a position to compute the interaction parameter of the polymer-solvent systems. However, from the intrinsic viscosity of the solution, we can qualitatively characterize the two solvents as good or bad /124, 370/. Schulz /371/ compared the different methods for evaluating the quality of the solution and showed that intrinsic viscosity $[\eta]$ can be used as a criterion for solvent power. In dilute solutions of polymers in poor solvents, the macromolecules are coiled more if their size is smaller, and are usually adsorbed more than from good solvents because of the relatively weaker interaction with the solvent. Koral et al. /124/ have observed that the amount of adsorbed polymer is inversely proportional to the $[\eta]$, that is, the adsorption is greater from a

TABLE : 3.2.1

FREE ENERGY ΔG^{o}_{ads}, ENTHALPY ΔH^{o}_{ads} AND ENTROPY ΔS^{o}_{ads} OF PBR ADSORPTION ON SILICA GEL AT INFINITE DILUTION FROM DIFFERENT SOLVENTS

[CONCENTRATION IS EXPRESSED IN g/100g OF SOLUTION]

Solvent System C : T	$-\Delta G^{o}_{ads}$ [kJ mol^{-1}]				$-\Delta H^{o}_{ads}$ [kJ mol^{-1}]	$-\Delta S^{o}_{ads}$ [J mol^{-1}K^{-1}]
	25°C	30°C	35°C	40°C		
100 : 00	18.83	16.48	14.14	11.79	158.5	468.4
80 : 20	11.29	10.01	9.55	8.27	68.0	190.7
50 : 50	7.77	7.66	7.56	7.43	14.6	23.0
20 : 80	7.19	7.03	6.96	6.87	13.2	20.6
00 : 100	9.73	9.36	9.03	8.66	31.8	74.0

poor solvent. Similar results have been observed for adsorption of poly[vinyl acetate] on carbon /372/. Poly[vinyl acetate] does not adsorb from a good solvent i.e. the solution having the highest intrinsic viscosity. Polystyrene on activated carbon, silica and alumina is also better sorbed from the poorer solvent /218/. Sometimes reversal in the adsorption pattern is also observed. The copolymer of isobutylene and isoprene is adsorbed on carbon black much better from benzene solutions [good solvent] than from cyclohexanone solution [poor solvent] /122/.

The intrinsic viscosity of PBR in toluene and cyclohexane have been determined [Chapter 2]. It is found to be 2.38 and 2.48, at 30°C, in cyclohexane and toluene respectively. This signifies that toluene is a good solvent, hence there should be less adsorption from this solvent system, which is experimentally observed and seen from ΔG^{o}_{ads} values in Table 3.2.1.

The solubility parameter is another criterion used to evaluate the solvent power /373/. If there is large difference in the magnitude of solubility parameter, δ , between that of polymer and solvent, the solvent is poor. Mizuhara et al. /14,373/ compared the values of the adsorption and solubility parameter, and found a linear relationship. Sometimes, however, the pattern is reversed and the polymers are more strongly adsorbed from good solvents. Thus, poly[dimethyl siloxane] on carbon and pigments is adsorbed more from carbon tetrachloride than from xylene /374/. However, the intrinsic viscosity of the polymer is higher in carbon tetrachloride than in xylene, while the solubility parameter of poly[dimethyl siloxane] is closer to that of carbon tetrachloride than to that of xylene.

The solubility parameters of PBR, cyclohexane and toluene were calculated to be 8.13, 8.2 and 8.9 respectively, indicating that cyclohexane should be a better solvent for PBR /375,376/. Solubility parameter was computed using the relation :

$$\delta = d \quad \Sigma G/M \qquad \ldots\ldots [4]$$

The molar attraction constant G is additive over the formula and ΣG is the sum for all atoms and groupings in the molecule. d and M stand for the density of the polymer and molecular weight of repeat unit respectively. The result from the solubility parameter concept is contrary to our expectation from intrinsic viscosity data, where toluene was found to be a better solvent. This type of conflicting observation was also reported earlier /124/.

McConnel /366/ studied the adsorption of ethylene oxide copolymers on solid surfaces from different solvents and the affinity of these solvents to various adsorbents. No distinct correlation was observed between the solvent power and the adsorption of polymers from the respective solvents. Luce and Robertson /377/ found that the adsorption of poly[vinyl acetate] on cellulose does depend on the nature of the solvent, though no clear sequence was found for all the solvents studied. The above results show that when the effect of the solvent on the adsorption of a polymer is considered, the interactions of both the polymer and the solvent with the surface of the adsorbent are as important as the polymer-solvent interaction. A strong solvent-surface interaction will decrease the adsorption of the polymer, and prevents the passage of the macromolecules from the solution phase onto the adsorbent. By comparing the parameters characterizing the power of the solvent and its affinity to adsorbent surface, it is thus possible to give some explanation of the dependence of the polymer adsorption on the nature of the solvent. The characteristics of adsorbent surfaces are therefore important.

It is known that the aromatics are easily adsorbed on silica gel surface /65/. It is also known that the surface 'OH' groups on which the adsorption occurs are not all equivalent /65/. The solvent strength values [E°] for both the solvents and adsorbents are known /144/. Preliminary calorimetric data also support this view /378/. Hence, qualitatively, we expect that toluene will be adsorbed more on the surface, thereby PBR will be adsorbed less from toluene solutions, than from cyclohexane solutions. The experimental observation, prediction from the solvent strength parameter values, from eleutropic series, and the intrinsic viscosity data as discussed earlier, all support the above contention, although the solubility parameter data belie this. All these different phenomena, including polymer spreading on the surface of the adsorbent, contribute to the overall thermodynamic quantities obtained.

In Figs.3.2.4 and 3.2.5 the amount of PBR adsorbed per gram of silica gel is plotted against the equilibrium concentration of PBR at

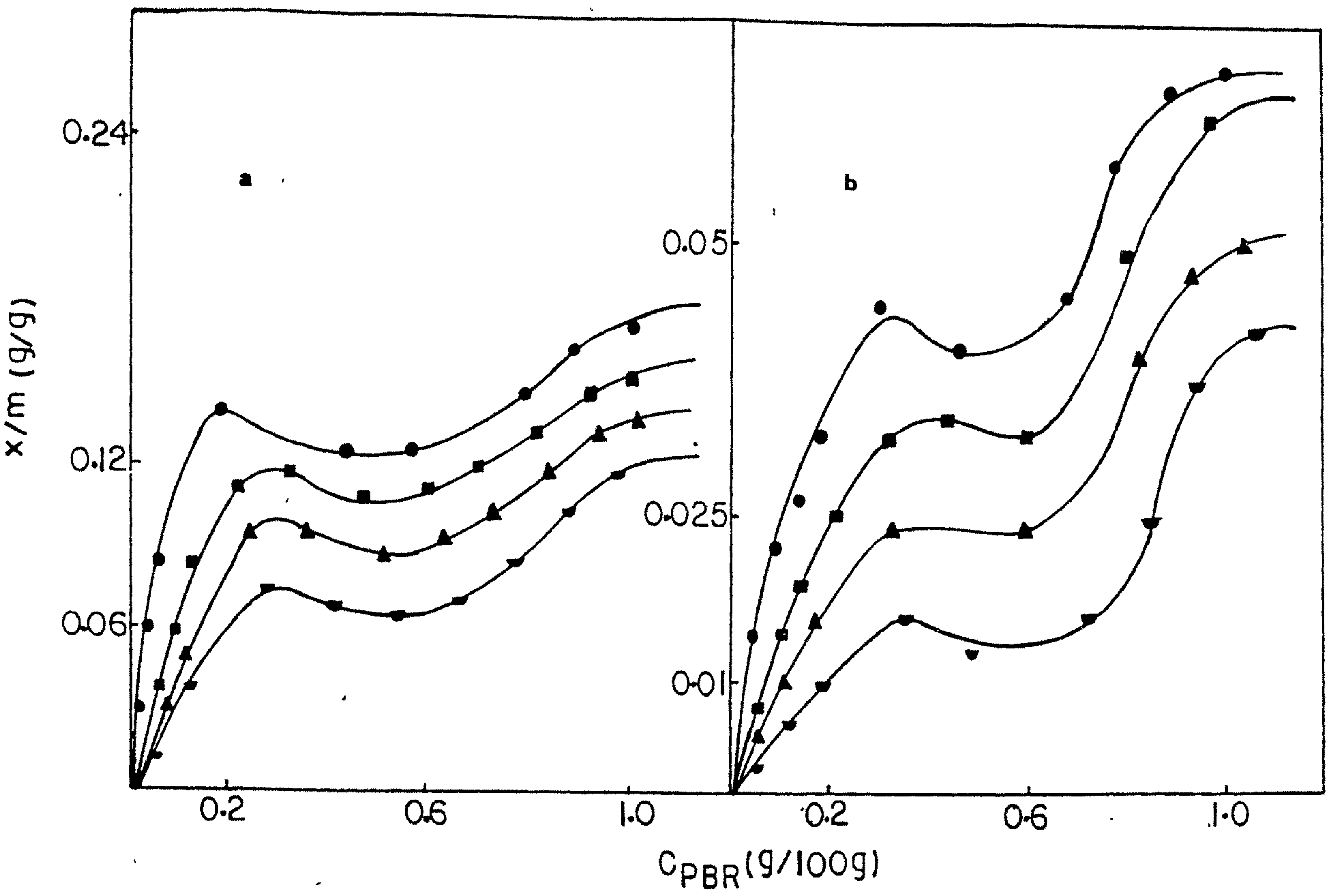


Fig.3.2.4 Plot of specific adsorption against the equilibrium concentration of PBR from (a) 80C:20T and (b) 50C:50T on silica gel

● 25°C ■ 30°C ▲ 35°C ▼ 40°C

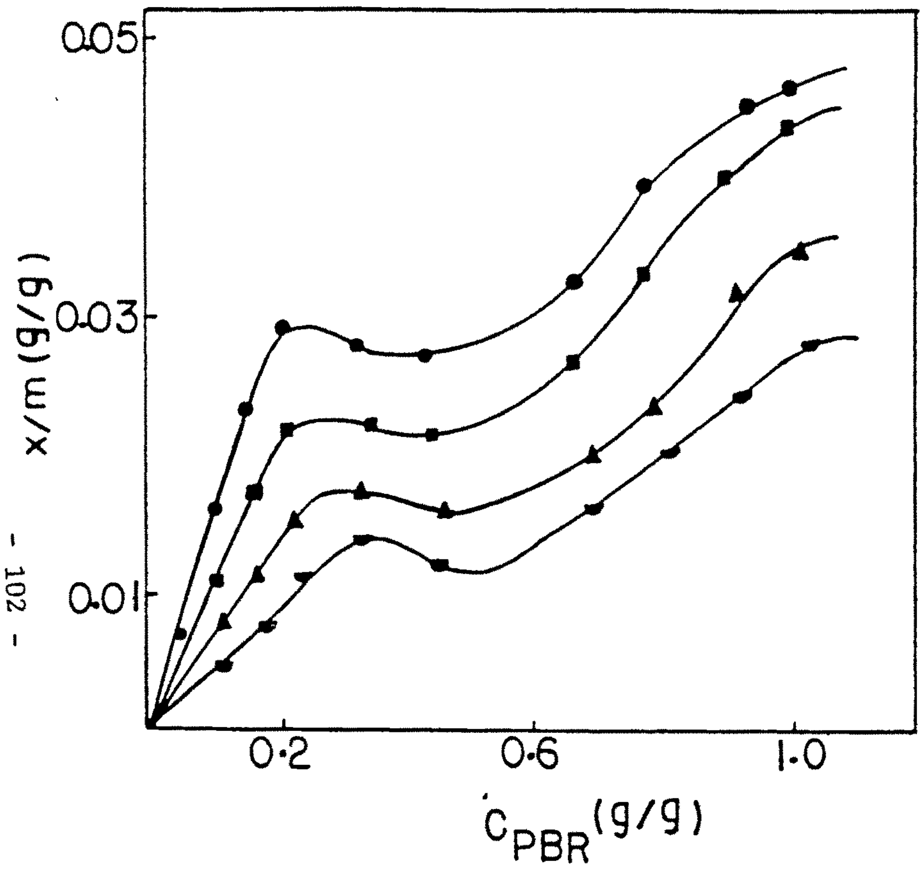


Fig.3.2.5 Plot of specific adsorption against the equilibrium concentration of PBR from 20C:80T on silica gel
● 25°C ■ 30°C ▲ 35°C ▼ 40°C

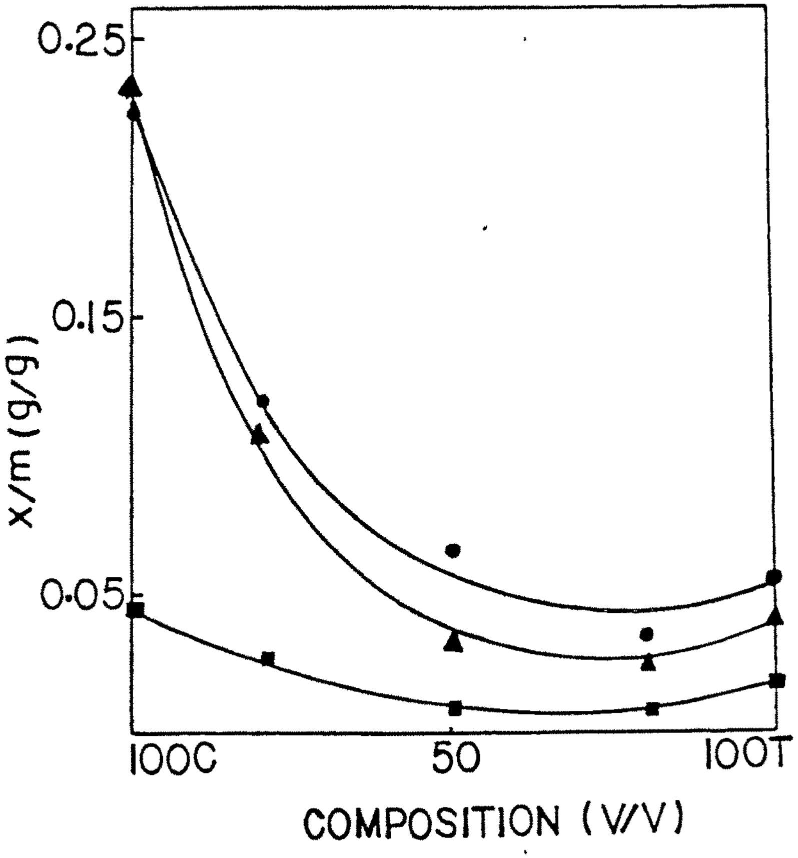


Fig.3.2.6 Plot of specific adsorption against the percentage composition of solvent mixtures at 30°C and different original concentrations
● 0.7% ▲ 0.3% ■ 0.05%

different temperatures and from various solvent mixtures. Nature of the isotherms are similar to those observed earlier for pure solvent systems and was also reported by other workers /220/.

The dip observed in all the isotherms, i.e. the slight desorption of the adsorbed polymer is for the same reason as that for pure solvent systems. In other words, the combined effect of polydispersity of the polymer, spreading of the adsorbed polymer molecules on the surface of the adsorbent and considerable polymer-polymer interaction resulted in the prominency of the dip in all the adsorption isotherms. The Figs. 3.2.4 and 3.2.5 also show that the amount of the polymer adsorbed decreases with increase in temperature. This is a very common observation, reported previously by many workers /122,137,217/, and was obtained in pure solvent systems as mentioned earlier.

The adsorption data obtained for mixed solvents is similar to that obtained for pure solvents i.e. cyclohexane and toluene. The absolute magnitudes are, ofcourse, different. Fig.3.2.6 shows that the amount of polymer adsorbed per gram of silica gel decreases with increase in toluene content. On plotting the specific adsorption against percentage composition of the mixed solvents at any given original concentration, a minima is observed. This type of behaviour was also obtained for alumina as the adsorbent /379/.

As seen from the voluminosity and shape factor [Chapter 2], PBR molecules acquire spherical conformation in both pure solvents.

Therefore, we believe that the conformation of PBR in mixed solvent systems is also spherical [Sec. 3.3 discusses this aspect]. In general, when the polymer chains adsorb on the silanol groups via an interaction such as hydrogen bonding, the frequency of the silanol groups should shift lower i.e. the frequency shift in the vibrations of silanol groups is due to perturbed silanol groups /205/. In our study, this particular shift of silanol vibration frequency was not apparent in IR spectra of silica gel on which the polymer was adsorbed. Secondly, because of the diffused adsorption band due to silanol groups around 3700 cm^{-1}, extra peak due to -CH stretching of adsorbed PBR could not be distinguished [Fig.3.2.7]. We therefore assume that there is no change in conformation of polymer molecules after getting adsorbed from different solvent mixtures.

The thermodynamic quantities for all the systems are presented in Table 3.2.1. All ΔS^{o}_{ads} and ΔH^{o}_{ads} values, as for the pure solvent systems, are found to be negative. This shows that the adsorption of PBR from mixed solvent systems is also exothermic and polymer molecules after adsorption become less randomised than in the bulk. From Table 3.2.1, it can be easily surmised that the adsorption process is spontaneous, though that from the mixed systems is relatively less. In Fig.3.2.8 the variations of ΔG^{o}_{ads} as a function of solvent composition at different temperatures are shown. It definitely establishes the fact that the solvent power of cyclohexane is a relatively large function of temperature and becomes better solvent for PBR with rise in temperature. The effect of temperature on toluene solvent power is not that prominent. As long as solvent

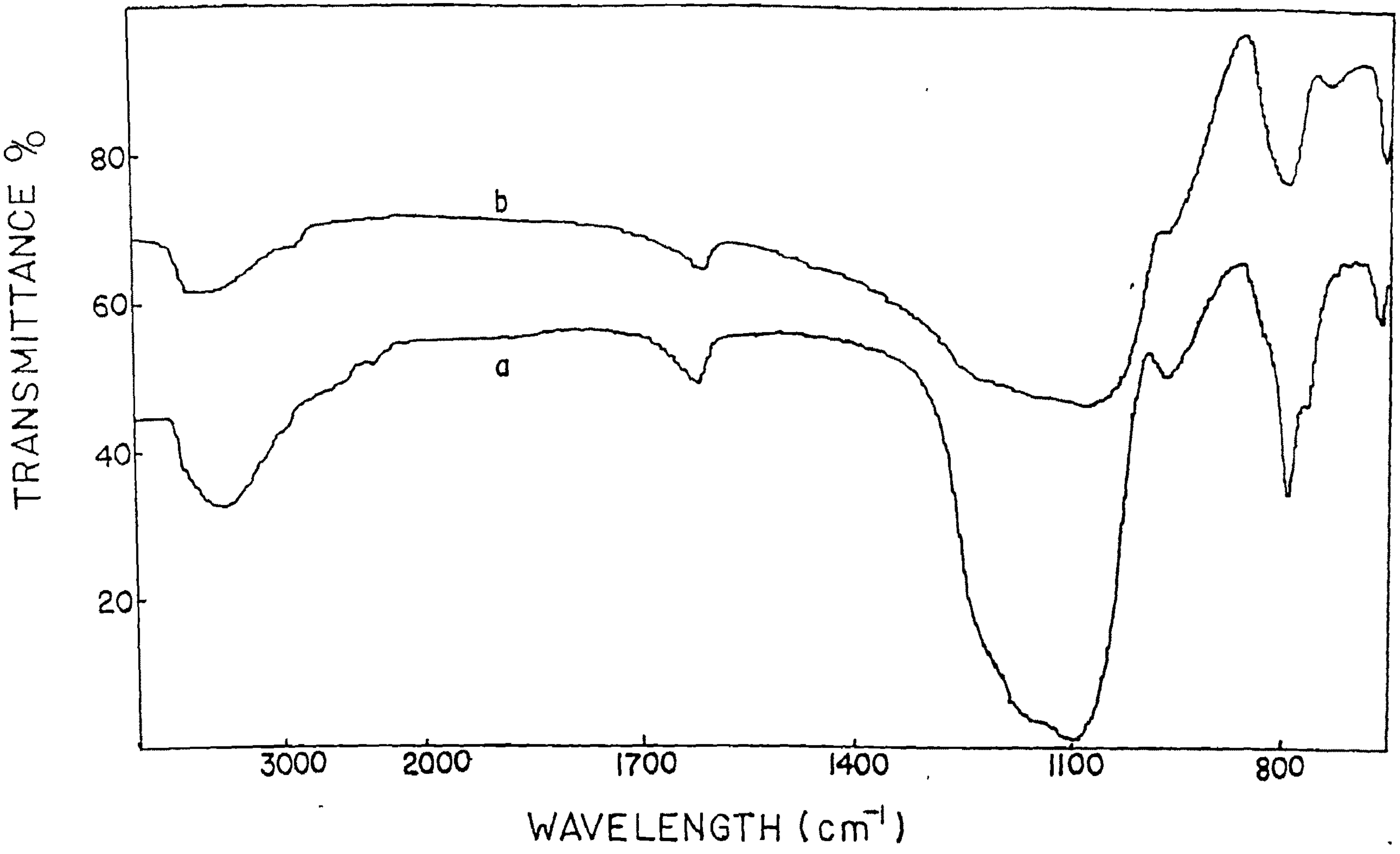


Fig.3.2.7 IR Spectra of silica gel pellet with KBr (a) before adsorption and (b) after adsorption

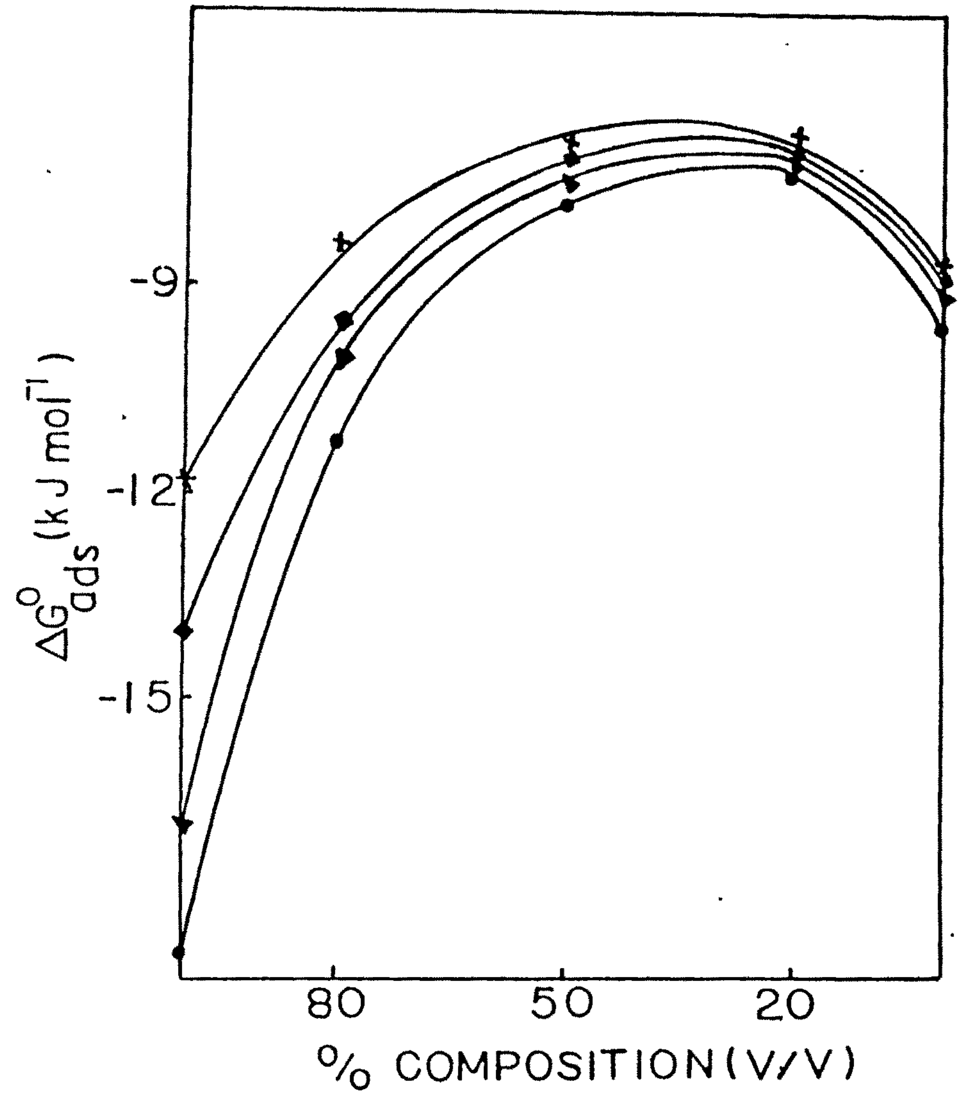


Fig.3.2.8 Plot of free energy of adsorption at infinite dilution G_{ads} against percentage composition of solvent mixture at different temperatures

● 25°C ▲ 30°C ■ 35°C × 40°C

composition contains more than 50% toluene, the solvent power remains reasonably constant.

The variations in the thermodynamic quantities $\triangle H^{o}_{ads}$ and $\triangle S^{o}_{ads}$ with the percentage composition of the mixed solvents are shown in Fig.3.2.9. This nature can be explained on basis of heat of mixing of cyclohexane and toluene. It is known that the heat of mixing of cyclohexane and toluene is a positive quantity i.e. it is an endothermic process /169/. Thus, if two liquids are miscible and if that process is endothermic, then that mixed solvent system for polybutadiene is a better solvent than the pure ones. This results in a lower adsorption from that mixed solvent system. This is in agreement with earlier observation, that a polymer though not soluble in pure liquids may become soluble in a mixture of the two liquids, due to their unfavourable enthalpy of mixing /164,169/. Due to unfavourable heat of mixing, the liquids may not have a randomly mixed three dimensional matrix. By its presence, the polymer might bring the two liquids near each other by being a part of both. In other words though the polymer may not be highly soluble individually, becomes so for a mixed solvent. Hence, it will not get adsorbed on an adsorbent preferentially. But with the solvent mixtures having negative heat of mixing the solvent system is randomly mixed. A polymer molecule will find it difficult to get into this matrix and thereby the system will remain a poor solvent for the polymer. The polymer, therefore, will like to get adsorbed on an adsorbent.

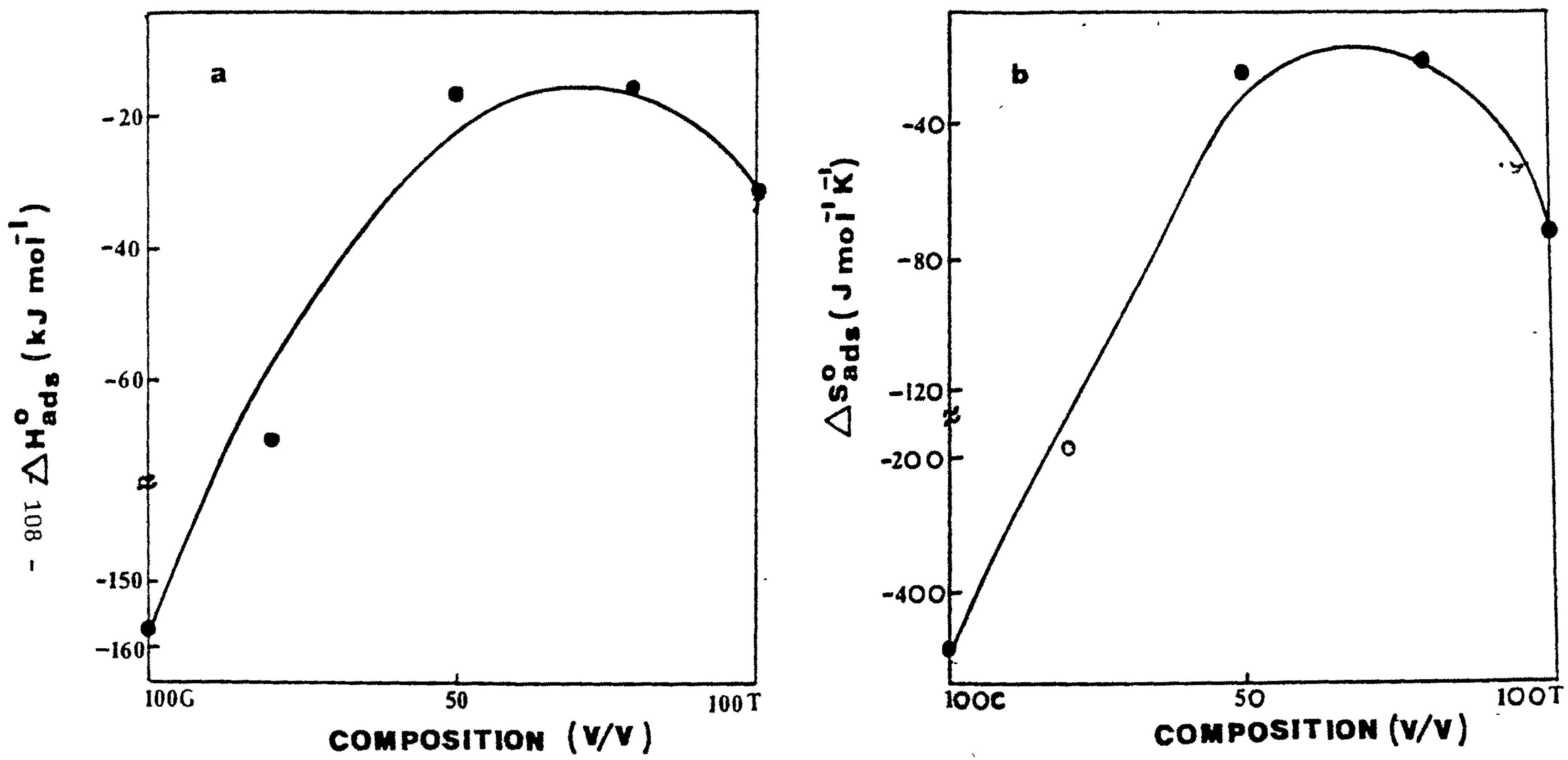


Fig.3.2.9 Plot of (a) enthalpy ΔH^{o}_{ads} and (b) entropy ΔS^{o}_{ads} of adsorption at infinite dilution against the percentage composition of solvent mixtures

As in pure solvent systems, in the mixed solvents also the solubility parameter is one of the criteria for determining the solvent power. The solubility parameter values of the various mixtures of liquids are calculated with the help of Scatchard equation /380/. i.e.

$$E^{1/2}\ [n_C V_C + n_T V_T]^{1/2} = n_C\ [E_C V_C]^{1/2} + n_T\ [E_T V_T]^{1/2} \qquad \ldots\ldots [5]$$

where n_C, V_C and n_T, V_T are moles and molar volumes of cyclohexane and toluene respectively, E_C, E_T and E are cohesive energy densities of cyclohexane, toluene and the mixture respectively. The solubility parameter values for the various mixtures of liquids are presented in Table 3.2.2.

TABLE : 3.2.2

CALCULATED SOLUBILITY PARAMETER VALUES FOR BINARY SOLVENT MIXTURES

Solvent ratio [v/v] C : T	No. of moles of cyclohexane n_C	No. of moles of toluene n_T	Solubility parameter δ
80 : 20	0.737	0.187	8.02
50 : 50	0.461	0.467	8.24
20 : 80	0.180	0.750	8.45

The values indicate that 80:20 of C:T and 50:50 of C:T should be good solvents for PBR, resulting in lower adsorption from these solvent mixtures. This is contradictory to our 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 solvents, relative solvent strength of the binary mixtures [E_{CT}] were computed as follows :

$$E_{CT} = E_C + [E_T - E_C]\,[E_{CT} - E_C]/[E_T - E_C] \qquad \ldots\ldots [6]$$

E_{CT} obtained for various solvent mixtures is shown in Fig.3.2.10. 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^o for pure solvent i.e. toluene [second component] calculated with the help of the above equation differs slightly from that in the eleutropic series /144/. 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 plot in Fig.3.2.6. Thus, the solvent strength values explain the overall observations, even though the solubility parameter values are in contradiction. This type of discrepancy has nevertheless been observed before /14/.

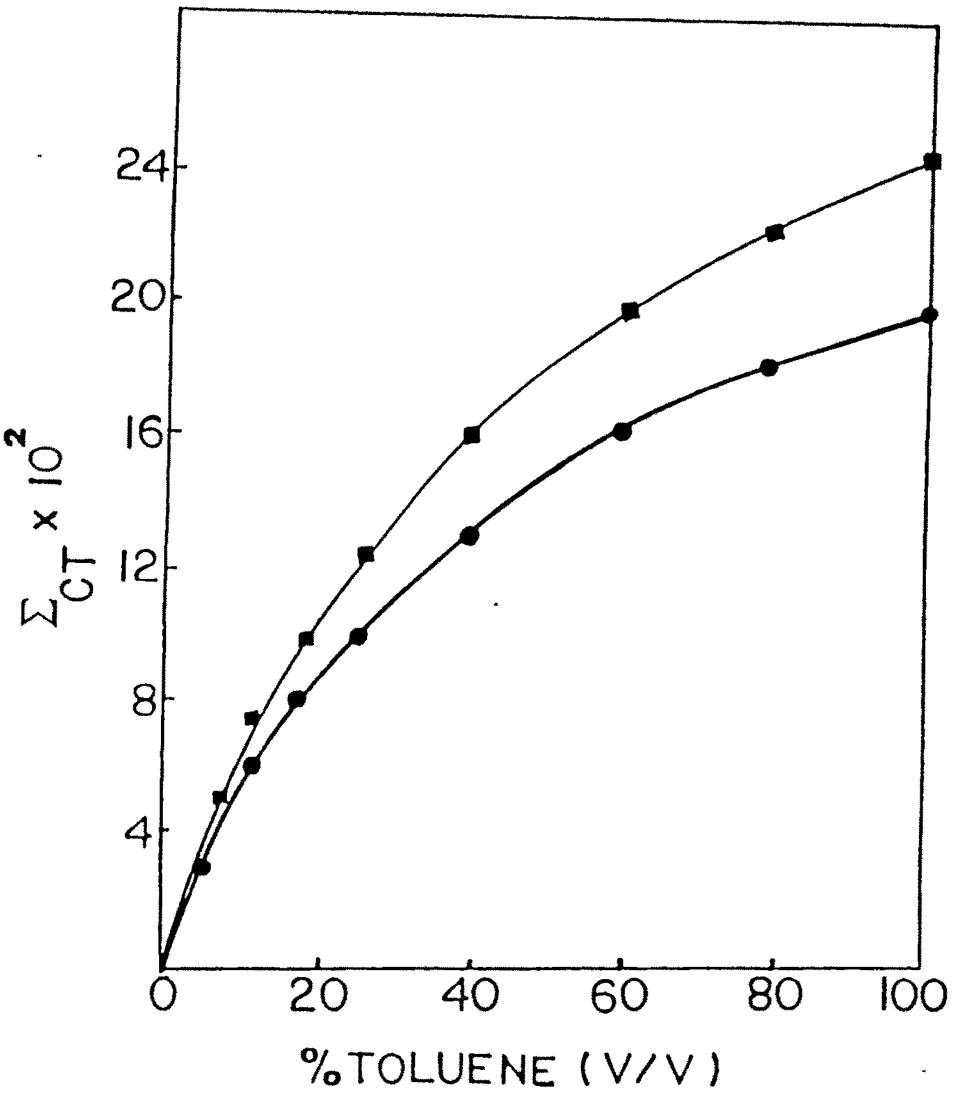


Fig.3.2.10 Plot of relative solvent strength parameter of the binary mixture against the percentage composition of toluene in solvent mixture
■ alumina ● silica gel

Thermodynamic quantities can also be calculated for various extent 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 [silica gel] was calculated using the relation /224/

$$A = [(C_o - C_{PBR}) \;.\; V \;.\; 100]/m \qquad ..... [7]$$

where C_o = initial concentration of PBR in g/l,

C_{PBR} = equilibrium concentration of PBR in g/l,

V = volume of solution of PBR taken for the adsorption study [0.015 l],

m = weight of the test sample of absolutely dry silica gel in g.

The equilibrium constants [K_A] were calculated for different amounts of adsorbed PBR according to the expression :

$$K_A = 1/C_{PBR} \qquad ..... [8]$$

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

$$\log K_A = \Delta S_A/2.3R - \Delta H_A/2.3RT \qquad ..... [9]$$

The isosteric heat [ΔH_A] was thus calculated from the slope of the linear dependence of log K_A against 1/T, obtained for different values of A. The values obtained for various systems are compiled in

Tables 3.2.3 and 3.2.4. The negative values obtained show that the adsorption of PBR, from all the solvent systems is exothermic i.e. heat is released during adsorption, which varies with the amount of polymer adsorbed. The isosteric heat decreased linearly with increase in the amount of polymer adsorbed, A, according to the relation :

$$[\ -\triangle H_A\ ] = [\ -\triangle H_0\ ] - CA \qquad \ldots\ldots [10]$$

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 characterises the energetic heterogeneity of the adsorbent [silica gel]. Linear plots obtained on plotting $\triangle H_A$ vs. A are shown in Figs.3.2.11 and 3.2.12. $\triangle H_0$ values hence obtained are compiled in Tables 3.2.3 and 3.2.4.

As known from the theory of adsorption /224/, when the isosteric heat decreases with increase in the amount of the substance adsorbed, the surface of the adsorbent is treated as uniformly heterogeneous. From Tables 3.2.3 and 3.2.4 we find that such decrease in $\triangle H_A$ are observed in these systems. This indicates that silica gel used is uniformly heterogeneous. A reason for this inverse relation between $\triangle H_A$ and amount of adsorption could also be found in the change in the conformation of macromolecules of the adsorbed polymer. In such cases, the adsorption equilibrium is defined by the logarithmic isotherm of Tjumkin /381/.

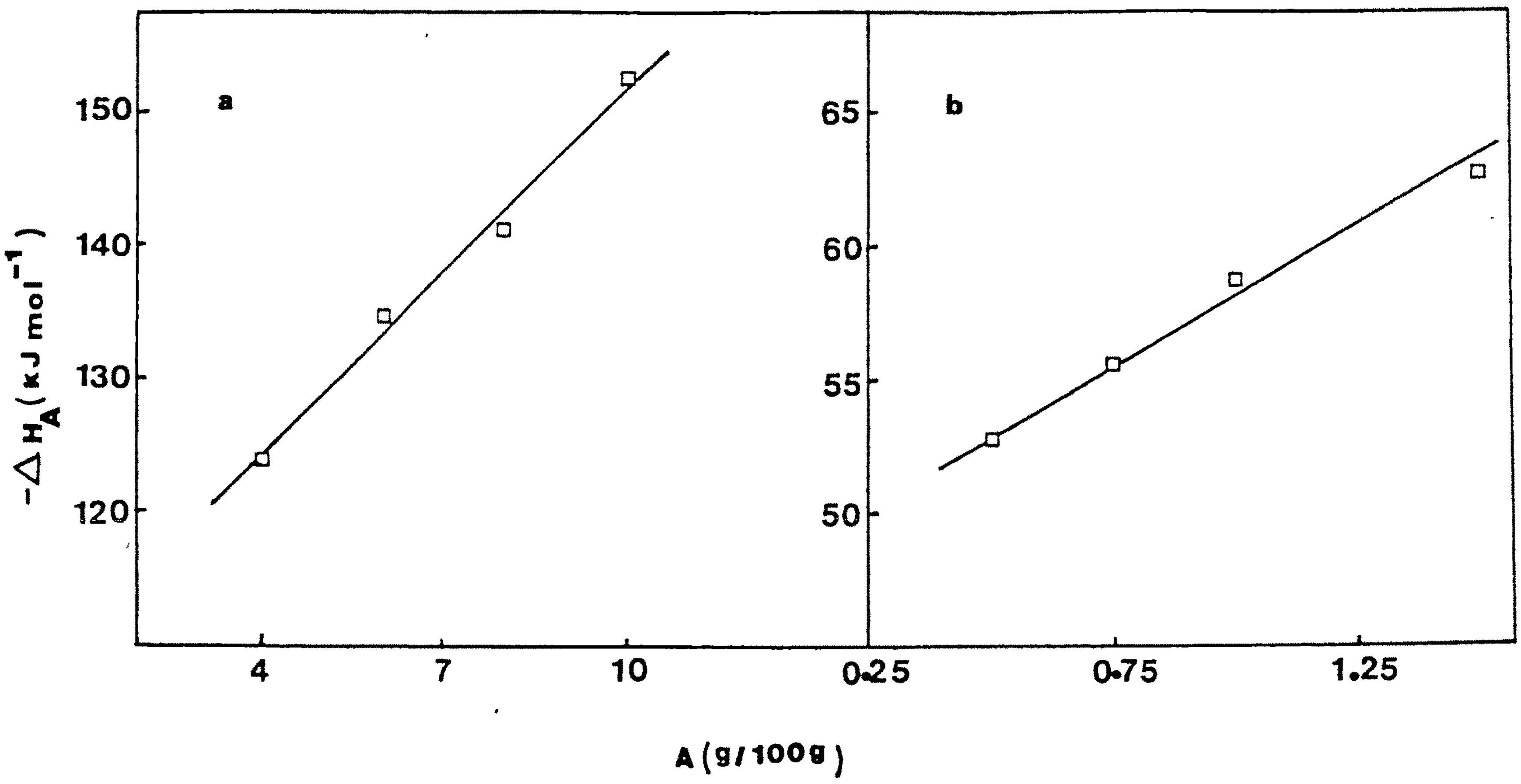


Fig.3.2.11 Change in ΔH_A with the amount of PBR adsorbed, A, from (a) cyclohexane and (b) toluene

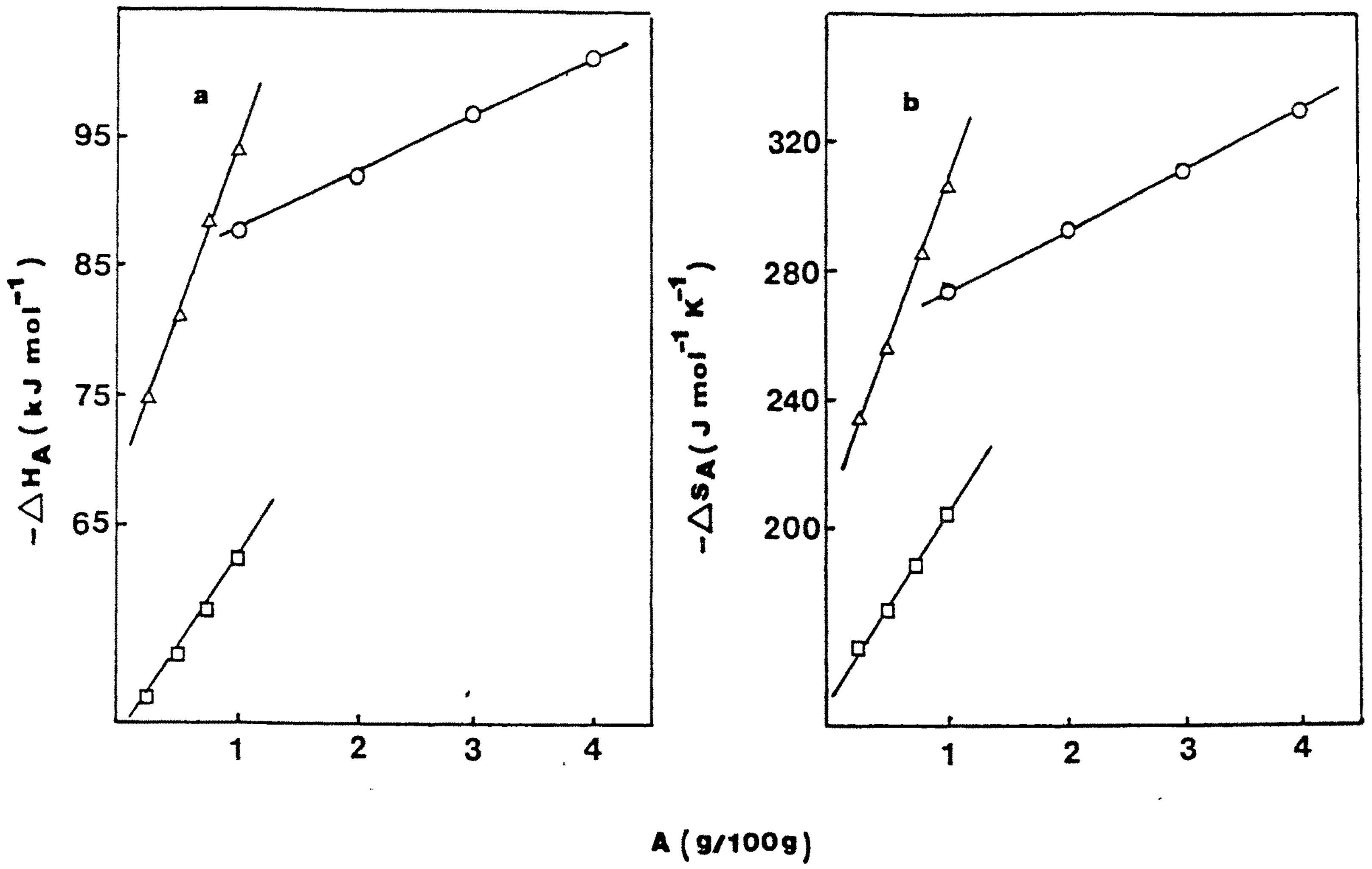


Fig.3.2.12 Change in (a) ΔH_A and (b) ΔS_A with A from various solvent mixtures

○ 80C:20T △ 50C:50T □ 20C:80T

TABLE : 3.2.3

THERMODYNAMIC PARAMETERS OF PBR ON SILICA GEL FROM PURE SOLVENTS

Solvent System	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$ [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$[303K] [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
Cyclohexane [C]	4.00	124.2	379.2	9.1	106.0	316.2	10.1	1.9
	6.00	134.5	416.1	8.4				
	8.00	141.2	440.4	7.8				
	10.00	152.6	479.0	7.5				
Toluene [T]	0.50	52.6	165.2	2.5	48.2	147.1	3.6	5.4
	0.75	55.6	178.0	1.7				
	1.00	58.8	190.3	1.1				
	1.50	62.4	205.8	0.1				

TABLE : 3.2.4

THERMODYNAMIC PARAMETERS OF PBR ON SILICAGEL FROM MIXED SOLVENTS

Solvent System C : T	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$ [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$[303K] [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
80 : 20	1.00	87.8	273.7	4.9	83.2	255.5	5.8	2.2
	2.00	92.2	292.5	3.6				
	3.00	96.8	310.9	2.6				
	4.00	101.5	328.9	1.8				
50 : 50	0.25	75.1	234.0	4.2	68.3	209.0	5.1	1.6
	0.50	80.8	256.9	3.0				
	0.75	88.8	286.3	2.1				
	1.00	94.2	306.9	1.2				
20 : 80	0.25	52.0	160.4	3.4	48.3	145.1	4.3	6.9
	0.50	55.0	174.7	2.1				
	0.75	57.9	188.0	0.9				
	1.00	62.5	205.2	0.3				

$$A = \ln [C_{PBR} \cdot K_o]/f \qquad \ldots\ldots [11]$$

where f = coefficient of heterogeneity, and

K_o = equilibrium constant of adsorption at infinite dilution.

The above equation can be rewritten as :

$$A = 2.3 \log K_o/f + 2.3 \log C_{PBR}/f \qquad \ldots\ldots [12]$$

Linearity was observed on plotting A against log C_{PBR}. The coefficient 'f' is determined from the slope and K_o from the intercept of the above plots. The temperature dependence of the coefficient 'f' is expressed by the equation :

$$f = C/RT - f_o \qquad \ldots\ldots [13]$$

It can be seen from Table 3.2.5 that as temperature rises, the heterogeneity of the adsorbent increases, for all systems.

TABLE : 3.2.5

'f' VALUES FOR DIFFERENT SYSTEMS

Solvent System C : T	25°C	30°C	35°C	40°C
100 : 00	0.09	0.11	0.15	0.17
80 : 20	0.38	0.42	0.44	0.47
50 : 50	1.39	1.59	1.74	1.89
20 : 80	1.60	1.69	1.77	1.86
00 : 100	0.93	1.00	1.06	1.14

The temperature dependence is shown in Fig.3.2.13. The coefficient C is determined from the slope of the linear plots in Fig.3.2.13. The value of C so obtained coincides with that obtained from Equation 10. Both the values are listed in Table 3.2.6. The intercept of the plots in Fig.3.2.13 yields f_o, which is related to the entropy change. The f_o in Equation 14 is related to 'm' by /382/

$$m = f_o \cdot R \qquad \ldots\ldots [14]$$

Entropy change [$\triangle S_A$] was calculated from the intercept of the plot of log K_A vs. 1/T, using equation [9]. The dependence of entropy change on A is expressed by the equation :

$$\triangle S_A = \triangle S_o - mA \qquad \ldots\ldots [15]$$

The linear plots obtained on plotting $\triangle S_A$ vs A are shown in Figs. 3.2.12 and 3.2.14. The values of 'm' so obtained coincide with those obtained from Equation 14. The values are tabulated in Table 3.2.6.

The nature of the dependence in Figs. 3.2.12 and 3.2.14 shows that as A increases, the degree of freedom of polymer molecules on the surface of the adsorbent decreases, the result of which is that their mobility is restricted. It is possible that the conformational changes of the polymer molecules are responsible for that effect. As we discussed earlier [Sec. 3.2] we could not determine any IR frequency change of "SiOH" after adsorption, indicating no change in conformation of polymer. We also did mention that Kawaguchi et al.

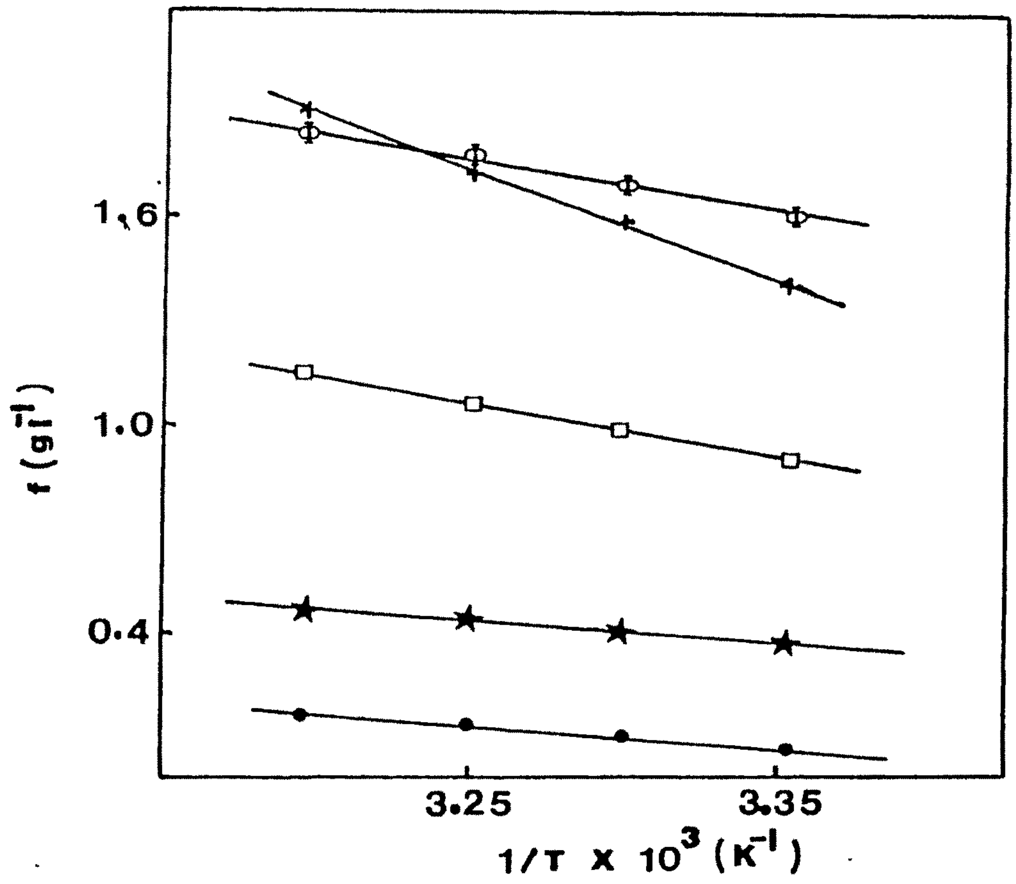


Fig.3.2.13 Temperature dependence of 'f' for different systems

● 100C:00T ✱ 80C:20T ✕ 50C:50T Φ 20C:80T □ 00C:100T

TABLE : 3.2.6

COMPARISON OF PARAMETERS OBTAINED FROM DIFFERENT EQUATIONS

Solvent System C : T	- C [kJ mol^{-1}] [From Eq.10]	- C [kJ mol^{-1}] [From Eq.13]	- m [J $mol^{-1}K^{-1}$] [From Eq.15]	- m [J $mol^{-1}K^{-1}$] [From Eq.14]
100 : 00	4.6	4.5	16.1	15.8
80 : 20	4.6	4.4	18.4	18.0
50 : 50	26.2	25.5	99.3	97.3
20 : 80	13.7	13.1	59.0	57.4
00 : 100	9.7	11.2	40.2	45.3

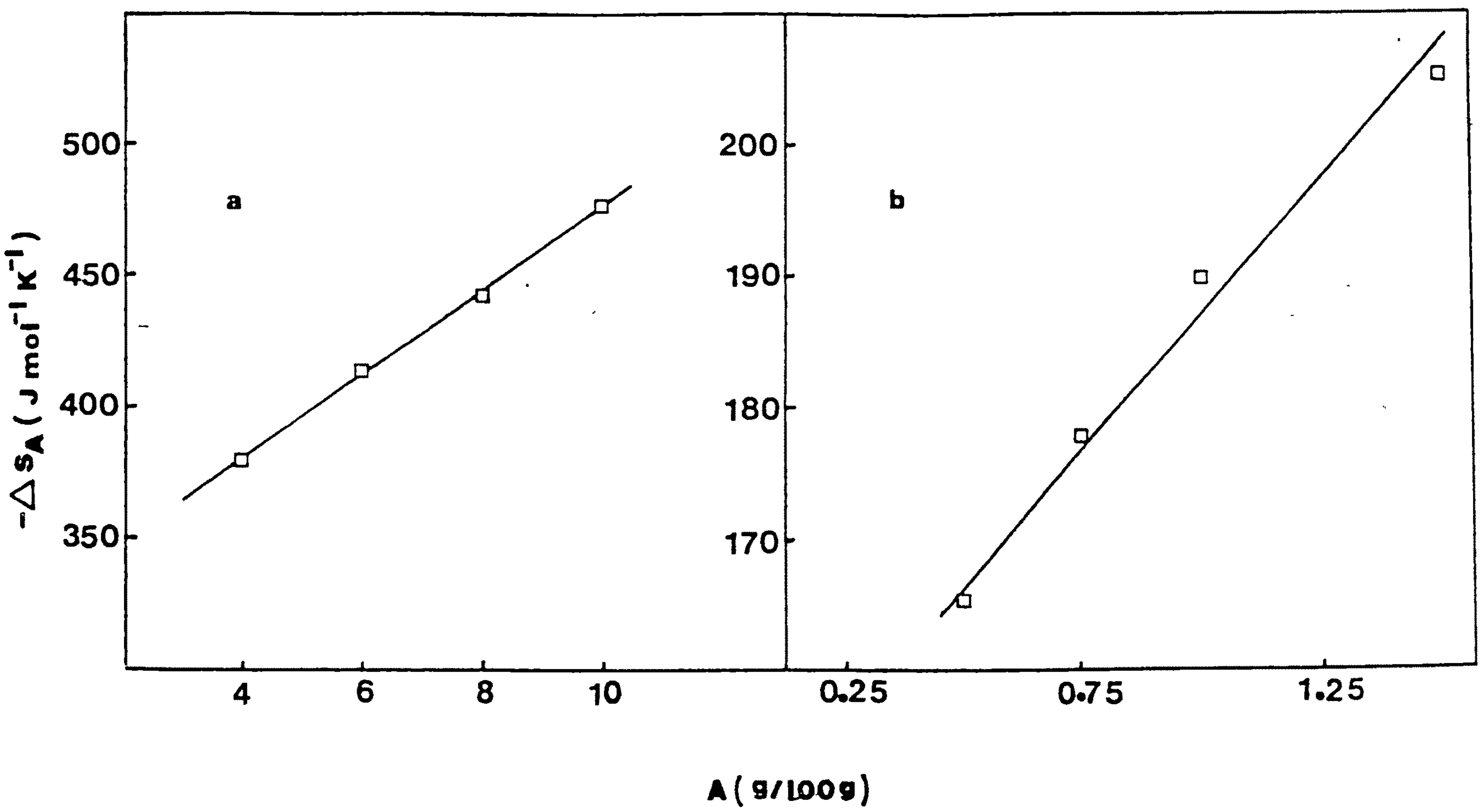


Fig.3.2.14 Change in ΔS_A with the amount of PBR adsorbed, A, from (a) cyclohexane and (b) toluene

/205/ did get such a change. Hence, we deduce that this dependence of $\triangle S_A$ on adsorption may be due to some other reason in this case. Ofcourse at this moment we appreciate the fact that [i] "SiOH" band may be diffused and [ii] amount adsorbed was too low to be detected. According to the theory of the process of adsorption taking place on uniform heterogeneous surfaces, the equilibrium constant depends upon the amount adsorbed as follows :

$$K_A = K_o e^{-fA} \qquad \text{..... [16a]}$$

$$\ln K_A = \ln K_o - fA \qquad \text{..... [16b]}$$

The dependence of log K_A on A [as per eqn. 16(b)] at different temperatures is shown in Fig.3.2.15 [a representative plot]. On solving equationS 10 and 15, the following dependence is observed :

$$\triangle S_A = \triangle S_o - m \triangle H_o/C + m \triangle H_A/C \qquad \text{..... [17]}$$

According to the above relation, $\triangle S_A$ linearly changes with $\triangle H_A$, hence proving the existence of compensation effect. This can be seen from Tables 3.2.3 and 3.2.4. This also indicates that the process under study takes place with the simultaneous change in the entropy and energy factors. The two factors have determining effect on the affinity of the polymer towards the adsorbents, a measure of which is the change in free energy, given by the relation :

$$\triangle G_A = \triangle H_A = T \triangle S_A \qquad \text{..... [18]}$$

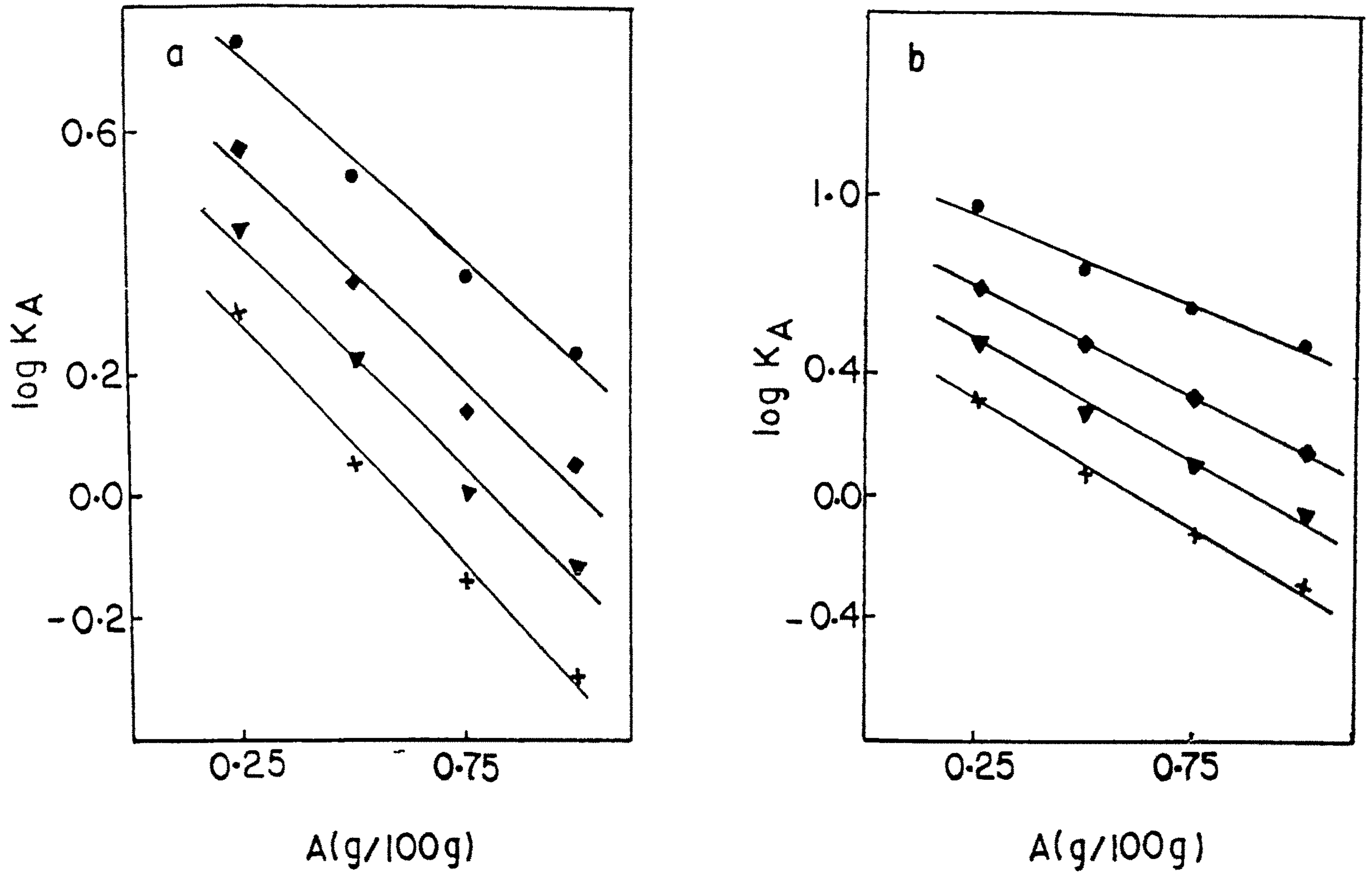


Fig.3.2.15 Change in log K_A with A for different solvent mixtures
a) 80C:20T b) 50C:50T
● 25°C ■ 30°C ▲ 35°C ✕ 40°C

The values of $\triangle G_A$ obtained for different systems at different amounts of PBR adsorbed are compiled in Tables 3.2.3 and 3.2.4. The $\triangle G_A$ values were plotted against A, the intercept yielding $\triangle G_o$. The values have been listed in Tables 3.2.3 and 3.2.4.

3.3 ADSORPTION OF GR

The adsorption isotherms of GR given in Fig.3.3.1, are at various temperatures from cyclohexane solutions on alumina and silica gel. The isotherms obtained are of high affinity type. The amount of adsorption increases steeply with increase in equilibrium concentration of GR and then levels off to a plateau. The steep rise is, of course, not as steep as expected from theories for high molecular weight polymers /256/. The isotherms correspond to typical Langmuir plots, though it will not be prudent to assume a monolayer formation for polymer adsorption. Adsorption isotherms for both the adsorbents from toluene are shown in Fig.3.3.2. In all the systems, the amount of adsorption decreased with increase in temperature indicating exothermic adsorption process. A comparison of Figs. 3.3.1 and 3.3.2 shows that adsorption of GR from cyclohexane is higher than that from toluene, on both the adsorbents. The intrinsic viscosity of GR in toluene [1.73 at 25°C] is more than that in cyclohexane [1.55 at 25°C] [Chapter 2]. This indicates that toluene is a better solvent than cyclohexane for GR, hence lower adsorption from the former.

The solvent-adsorbent interaction can also be responsible for the above observation. The aromatics get easily adsorbed on the alumina

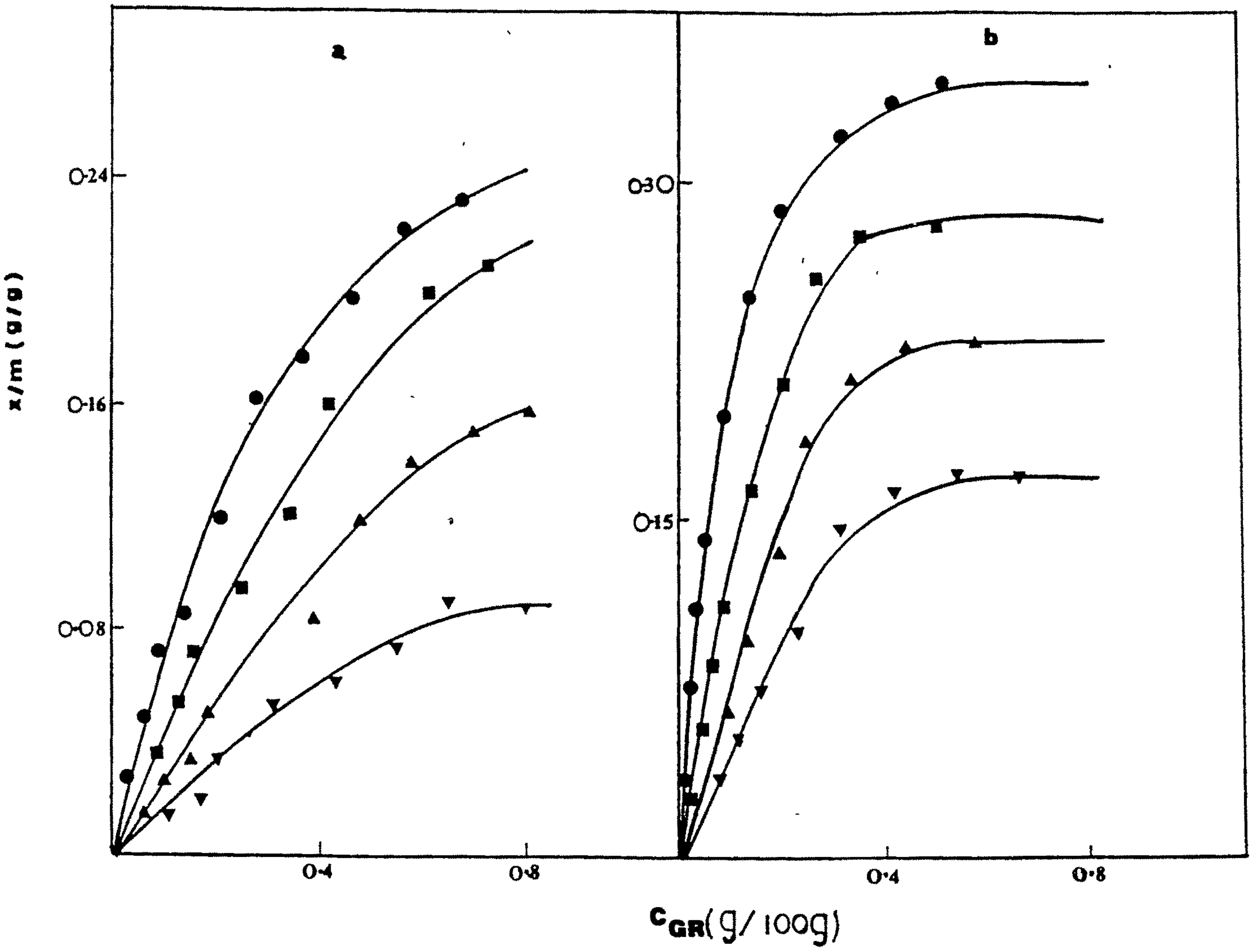


Fig.3.3.1 Plot of specific adsorption against equilibrium concentration of GR in cyclohexane at various temperatures : (a) alumina and (b) silica gel
● 25°C ■ 30°C ▲ 35°C ▼ 40°C

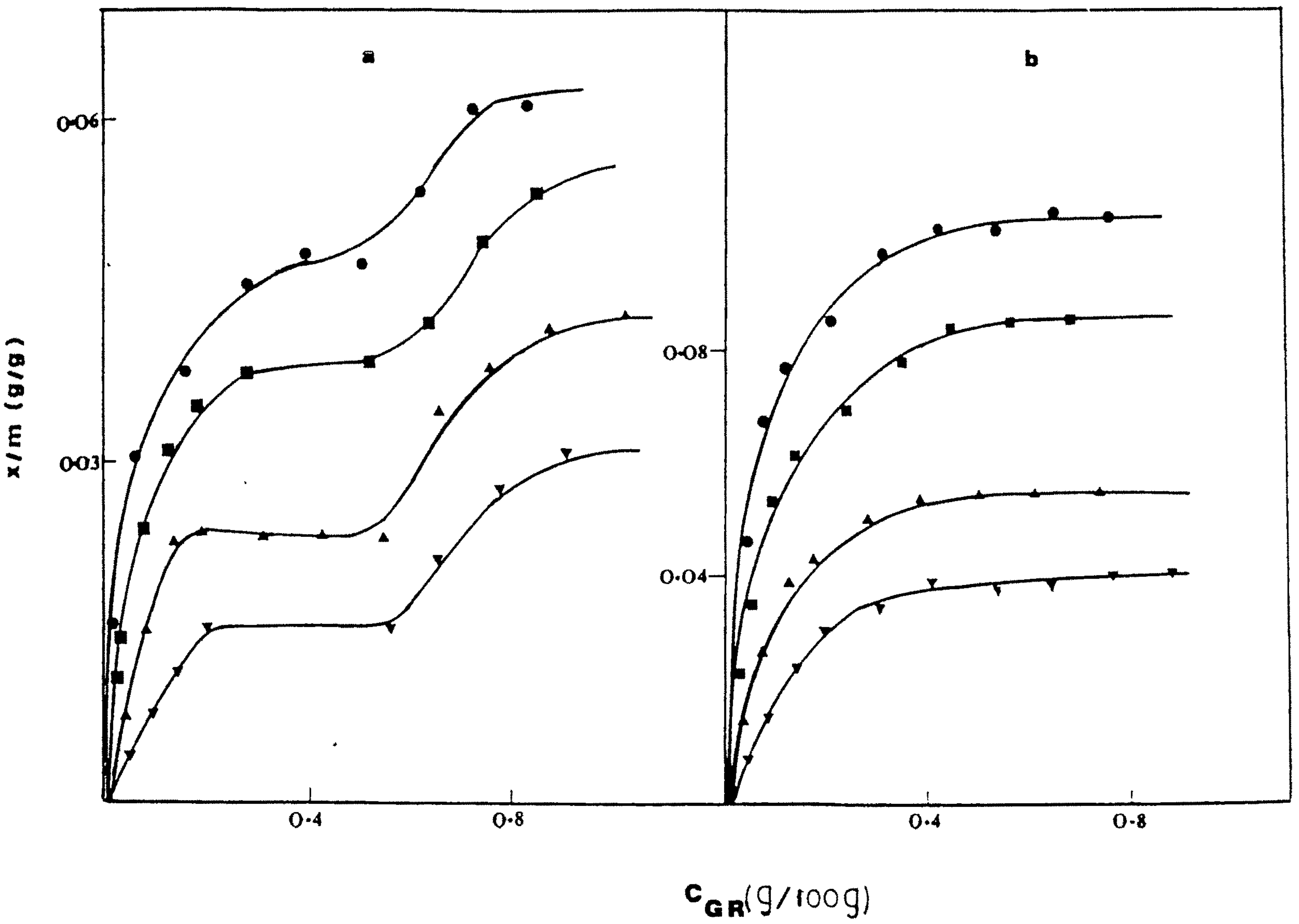


Fig.3.3.2 Plot of specific adsorption against equilibrium concentration of GR in toluene at various temperatures : (a) alumina and (b) silica gel
● 25°C ■ 30°C ▲ 35°C ▼ 40°C

surface, due to the adsorption occuring on the Al^{3+} site. Hence, qualitatively more toluene gets adsorbed on the surface, and less amount of natural rubber [GR] in comparison to cyclohexane. This is also true for silica gel, where the adsorption takes place on the surface 'OH' groups. The amount of adsorption is therefore an outcome of different interactions i.e. [a] polymer-solvent, [b] adsorbent-solvent, [c] polymer-adsorbent, [d] polymer-polymer and [e] solvent-solvent. First two interactions, as seen above, can together explain higher adsorption from cyclohexane than from toluene. The polymer-adsorbent interaction, which unfortunately we are unable to quantify, is also responsible for the overall system behaviour.

Fig.3.3.2[a] shows slightly different nature in comparison to others. There is a slight dip at the lower temperature [25 and 30°C] isotherms around the equilibrium concentration of 0.5%. At the higher temperatures [35 and 40°C] the dip is replaced by a dominant plateau region. At the lower concentration, polymers are adsorbed three dimensionally and begin to spread laterally. We guess that, at this 0.5% concentration, no further polymer adsorption occurs from the solution. But at higher concentrations, polymer-polymer interaction becomes important enough to result in higher adsorption. Secondly, such behaviour may also be observed due to polydispersity of the polymer sample. At lower concentration, samples of low and high molecular weights get adsorbed, but at higher concentration, the lower molecular weight polymer samples get desorbed from the adsorbent and are replaced by the higher molecular weight polymer.

This is because high molecular weight polymers are preferentially adsorbed /105/. Around 0.5% equilibrium concentration, more lower molecular weight polymers get desorbed than the adsorption of higher molecular weight ones, because of the realtively large number of possible contact points. Hence, an overall desorption is observed, resulting in a small dip. At still higher concentrations, all higher molecular weight species are adsorbed, hence higher adsorption. A pertinent question that can be asked at this stage is the fact as to why such a dip is observed on alumina but not on silica gel. It is known /383/ that double bond of GR interacts with the 'OH' group of silica gel. This interaction is probably stronger than double bond-Al^{3+} interaction. Hence, the desorption doesn't occur from silica gel surface but happens from the alumina surface. The dip is not seen from the poorer solvent cyclohexane, but is observed from the better solvent, toluene. Then at higher temperature plateaus are observed. This is probably because of no change in conformation of GR with temperature, which might be possible at lower temperatures. Again multilayer formation on the adsorbent surface cannot be totally discounted. These points are discussed in detail in Section 3.4 for InR.

In order to know the effect of one solvent in presence of another, on the overall adsorption process, a mixed solvent system was studied. The solvent system studied was 50:50 of C:T [v/v]. The adsorption isotherms at various temperatures for this mixed solvent system, on both the adsorbents, are shown in Fig.3.3.3. The isotherms for these systems do not show the dip, as was seen in pure toluene-alumina-GR system. This indicates that in this particular mixture, cyclohexane

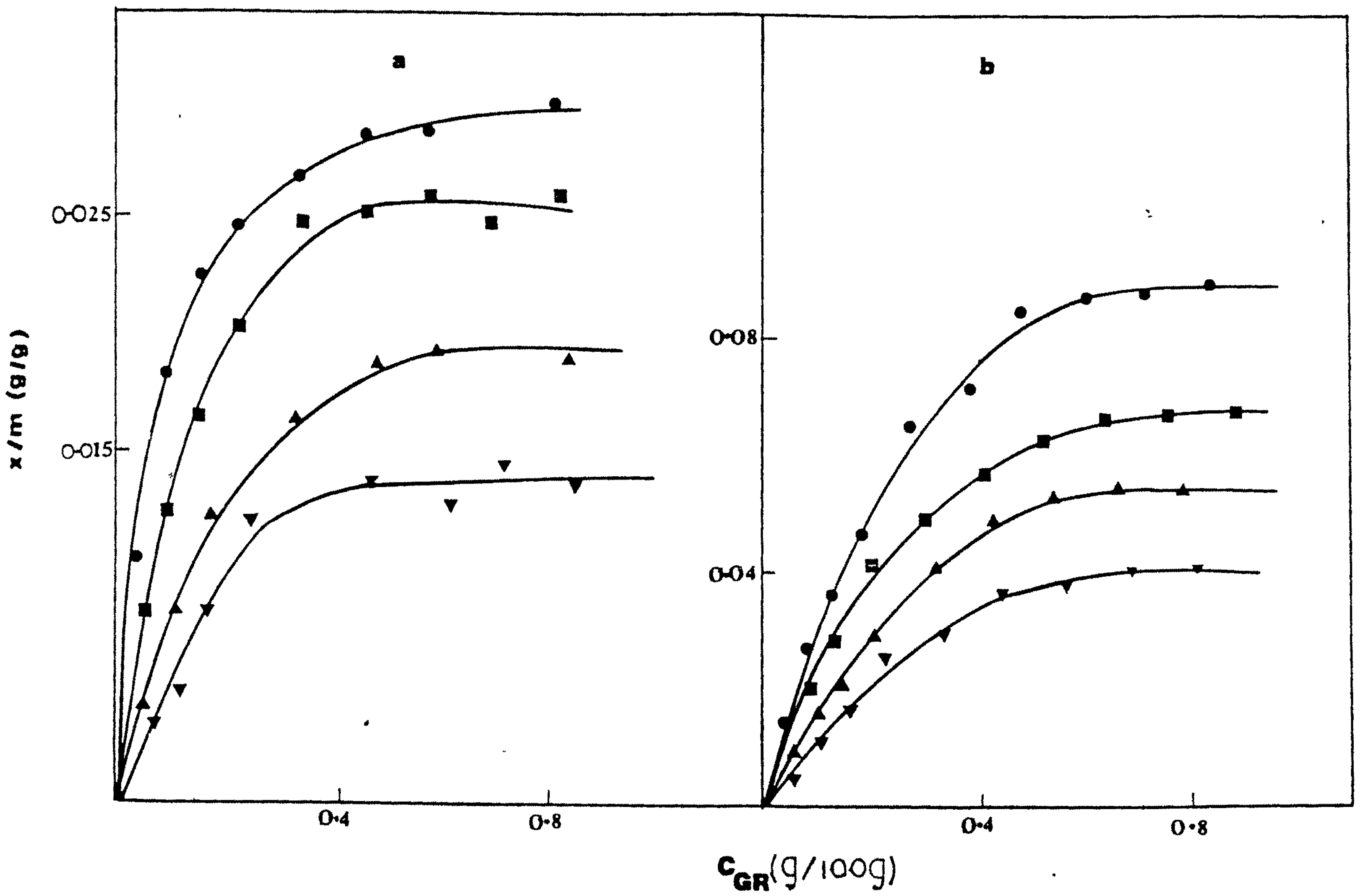


Fig.3.3.3 Plot of specific adsorption against equilibrium concentration of GR in 50C:50T [v/v] at various temperatures : (a) alumina and (b) silica gel
● 25°C ■ 30°C ▲ 35°C ▼ 40°C

has a dominating influence on the overall solvent property. The nature of the adsorption isotherms remains similar in both mixed and cyclohexane systems. The amount of GR adsorbed per gram of the adsorbent, is less from mixed solvent system than from pure solvent systems, for both the adsorbents. This is due to the relatively higher solvent power of the mixed cyclohexane-toluene solvent than the pure cyclohexane or pure toluene.

The intrinsic viscosity of GR in mixed cyclohexane-toluene solvent was determined at various temperatures and the values are listed in Table 3.3.1.

TABLE : 3.3.1

VARIATION IN INTRINSIC VISCOSITY WITH TEMPERATURE FOR DIFFERENT SOLVENT SYSTEMS

Solvent System	Intrinsic viscosity [η] [dl/g]			
	30°C	35°C	40°C	45°C
Toluene [T]	1.70	1.62	1.58	1.54
50 : 50 [v/v] C : T	1.83	1.77	1.70	1.64
Cyclohexane [C]	1.52	1.50	1.47	-

It is seen that at all temperatures, intrinsic viscosity of GR is more in the mixed solvent, compared to that in pure solvents at respective temperatures. This suggests that mixed solvent is a better solvent than either of the pure solvents for GR, hence least adsorption from the mixed solvent system /371/.

Free energy of adsorption was calculated using the equation

$$\Delta G_{ads} = RT \ln C_{GR} \qquad \ldots\ldots [1]$$

where C_{GR} is the equilibrium concentration in g/100g of the polymer in solution [This relation has already been deduced in Chapter 3.2]. ΔG^{o}_{ads}, ΔS^{o}_{ads} and ΔH^{o}_{ads} were calculated, as was done for PBR [Chapter 3.2]. All values are compiled in Table 3.3.2. All ΔG^{o}_{ads}, ΔH^{o}_{ads} and ΔS^{o}_{ads} values are negative. As ΔG^{o}_{ads} is negative for all systems, we can surmise that adsorption process is a spontaneous one. In other words, the polymer prefers the solid surface than the solution phase. The negative ΔH^{o}_{ads} and ΔS^{o}_{ads} values indicate that the adsorption process is exothermic and polymer molecules after adsorption, become less randomised than at the beginning. Though the adsorption process is exothermic, it is relatively less so and less randomised when mixed solvent is used. This is because, the mixed solvent system is better solvent than pure ones, for GR.

This can also be seen by considering the heat of mixing of cyclohexane and toluene. It is known /164/ that mixing of cyclohexane and toluene is an endothermic process. Thus one can come to the

TABLE : 3.3.2

THE FREE ENERGY [ΔG°_{ads}], ENTHALPY [ΔH°_{ads}] and ENTROPY [ΔS°_{ads}] OF ADSORPTION OF GR AT INFINITE DILUTION FROM DIFFERENT SOLVENTS [CONCENTRATION IS IN g/100 g OF SOLUTION]

Solvent system C:T [v/v]	$-\Delta G^{\circ}_{ads}$ [kJ mol^{-1}]				$-\Delta H^{\circ}_{ads}$ [kJ mol^{-1}]	$-\Delta S^{\circ}_{ads}$ [J $mol^{-1}K^{-1}$]
	25°C	30°C	35°C	40°C		
	Silica gel					
100 : 00	11.86	11.41	10.91	10.45	40.2	95.1
50 : 50	8.15	8.09	8.05	7.93	12.4	14.0
00 : 100	9.30	8.95	8.67	8.21	31.4	74.0
	Alumina					
100 : 00	9.05	8.3	8.01	7.46	39.3	101.7
50 : 50	7.57	7.45	7.35	7.24	14.1	21.9
00 : 100	8.68	8.41	8.01	7.67	30.8	74.0

conclusion that if two liquids are completely miscible and if that process is endothermic, then that mixed solvent system, atleast for natural polyisoprene, will be a better solvent, resulting in a lower adsorption from that mixed system /169/. Thus, a polymer though not soluble in two pure liquids, becomes soluble in a mixture of the two liquids, which results from the unfavourable enthalpy of mixing of two liquids. From the magnitudes and signs of both $\triangle H^{o}_{ads}$ and $\triangle S^{o}_{ads}$, it can be easily said that the adsorption at infinite dilution is determined by enthalpic forces.

The isosteric heat [$\triangle H_A$] was computed for various systems. The amount [A] of GR adsorbed per 100 g of adsorbent was calculated from the formula /224/

$$A \quad = \quad [(C_o - C_{GR}) \cdot V \cdot 100]/m \qquad ..... [2]$$

where C_o and C_{GR} are initial and equilibrium concentrations of GR in solution in g/l,

V = volume of GR solution taken for adsorption study [0.015l],

m = weight of the test sample of absolutely dry adsorbent [alumina or silica gel] in g.

The equilibrium constants [K_A] were calculated for different amounts of adsorbed GR, according to the expression :

$$K_A \quad = \quad 1/C_{GR} \qquad ..... [3]$$

The temperture dependence of the equilibrium constant follows the equation :

$$\log K_A = \triangle S_A/2.3R - \triangle H_A/2.3RT \qquad \ldots\ldots [4]$$

The isosteric heat [$\triangle H_A$] is determined from the slope of the linear dependence log K_A vs. 1/T plot for specific values of A. Different $\triangle H_A$ were obtained for different values of A. The negative values obtained for $\triangle H_A$ [Table 3.3.3 and 3.3.4] show that during the process of adsorption of GR from all the solvent systems, heat is released which varies with the amount of polymer adsorbed. The isosteric heat decreased linearly with increase in A, according to the following relation :

$$-\triangle H_A = -\triangle H_0 - CA \qquad \ldots\ldots [5]$$

where $\triangle H_A$ and $\triangle H_0$ are the heat released during the process of adsorption of A amount of polymer and when $A \rightarrow 0$ respectively. The coefficient C characterises the energetic heterogeneity of the adsorbent. $\triangle H_0$ values so obtained are listed in Tables 3.3.3 and 3.3.4.

The plots obtained are shown in Fig.3.3.4. Entropy change [$\triangle S_A$] has been calculated from the intercept of the plot of log K_A vs. 1/T, as per equation [4]. The dependence of entropy change on A is expressed by equation :

TABLE : 3.3.3

THERMODYNAMIC PARAMETERS OF GR ON SILICA GEL FROM DIFFERENT SOLVENTS SYSTEMS

Solvent System C : T	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$ [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$[303K] [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
100 : 00	1.00	87.1	265.6	6.6	82.1	246.7	7.3	2.6
	2.00	91.8	285.9	5.2				
	3.00	97.0	305.8	4.3				
	4.00	101.9	323.7	3.8				
50 : 50	0.50	54.0	166.7	3.5	50.6	152.8	4.3	3.4
	1.00	57.5	183.7	1.8				
	1.50	61.0	198.7	0.8				
	2.00	64.3	211.4	0.2				
00 : 100	1.00	81.2	253.0	4.5	71.2	215.6	5.8	4.5
	1.50	87.0	276.3	3.3				
	2.00	93.9	301.0	2.7				
	2.50	96.5	311.2	2.2				

TABLE : 3.3.4

THERMODYNAMIC PARAMETERS OF GR ON SILICA GEL FROM DIFFERENT SOLVENTS SYSTEMS

Solvent System C : T	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$ [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$[303K] [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
100 : 00	1.00	75.4	237.4	3.5	68.4	210.1	4.7	3.5
	1.50	79.4	253.2	2.7				
	2.00	82.8	266.3	2.1				
	2.50	86.3	279.7	1.6				
50 : 50	0.25	63.9	199.1	3.6	58.9	179.8	4.4	9.2
	0.50	68.9	220.0	2.2				
	0.75	73.3	238.0	1.2				
	1.00	78.9	258.6	0.5				
00 : 100	0.25	83.6	256.4	5.9	78.8	237.6	6.8	9.5
	0.50	88.7	277.4	4.6				
	0.75	93.5	297.1	3.5				
	1.00	98.4	315.1	2.9				

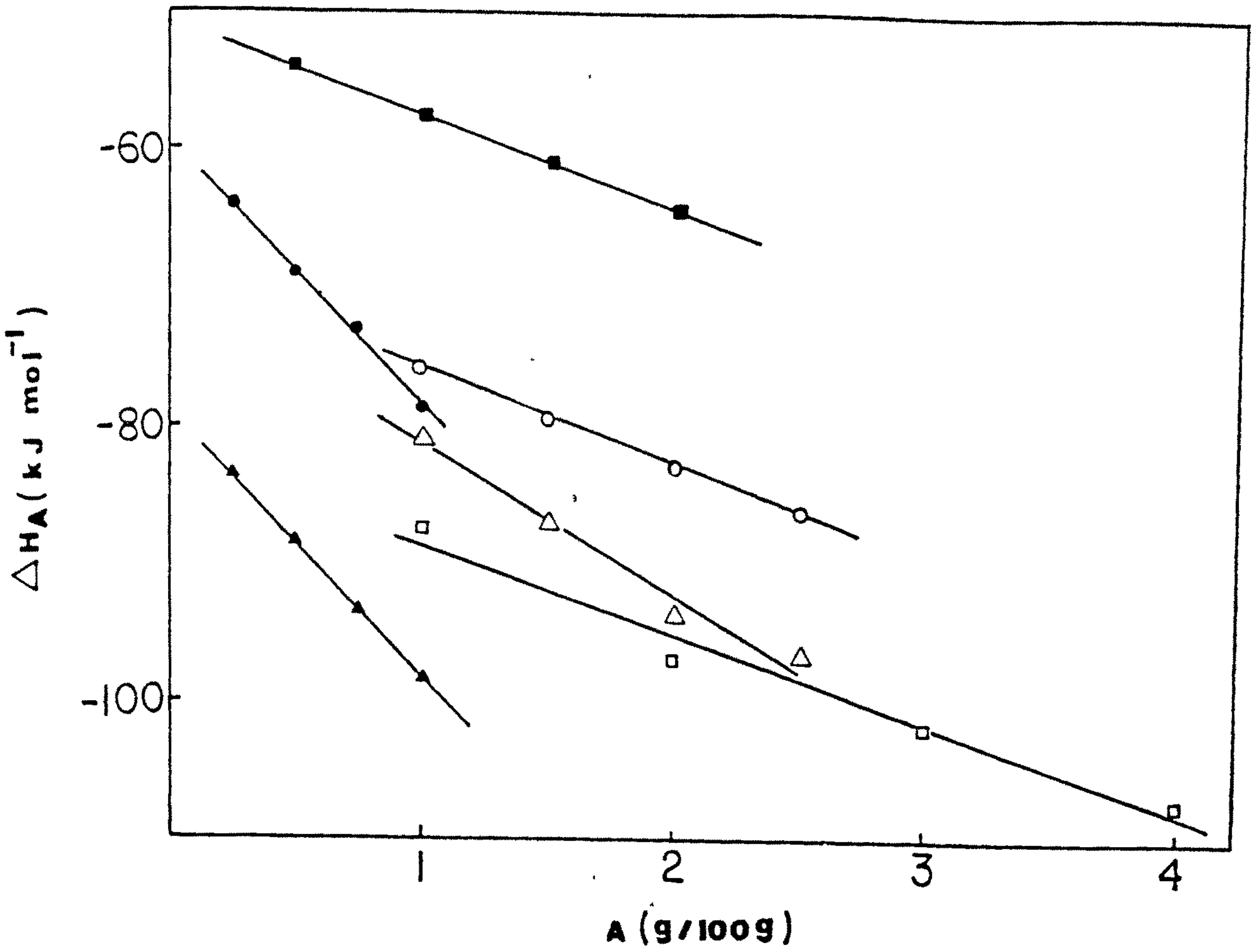


Fig.3.3.4 Change in ΔH_A with the amount of GR adsorbed on alumina from ○ 100C:00T ● 50C:50T ▲ 00C:100T and silica gel from □ 100C:00T ■ 50C:50T △ 00C:100T

$$\triangle S_A = \triangle S_o - mA \qquad \text{..... [6]}$$

The plots obtained for different systems are shown in Fig.3.3.5.

The amount adsorbed on the surface according to Tjumkin is /381/

$$A = \ln [C_{GR} \cdot K_o]/f \qquad \text{.... [7]}$$

where : f is the coefficient of heterogeneity and K_o is the equilibrium constant of adsorption at infinite dilution. Above equation can further be expressed as follows :

$$A = 2.3 \log k_o/f + 2.3 \log C_{GR}/f \qquad \text{..... [8]}$$

Linear plots were obtained on plotting A vs. log C_{GR}. The coefficient 'f' is determined from the slope of the straight lines and the equilibrium constant K_o - from the intercept. The temperature dependence of the coefficient f is expressed by the equation :

$$f = C/RT - f_o \qquad \text{..... [9]}$$

The temperature dependence is shown in Fig.3.3.6. It is clear from the straight line that as the temperature rises, the heterogeneity of the adsorbent increases. All the values are compiled in Table 3.3.5. The coefficient C is determined from the slope of the straight line in Fig.3.3.6, and it coincides with the coefficient determined form equation [5]. This can be seen from Table 3.3.6. The intercept of

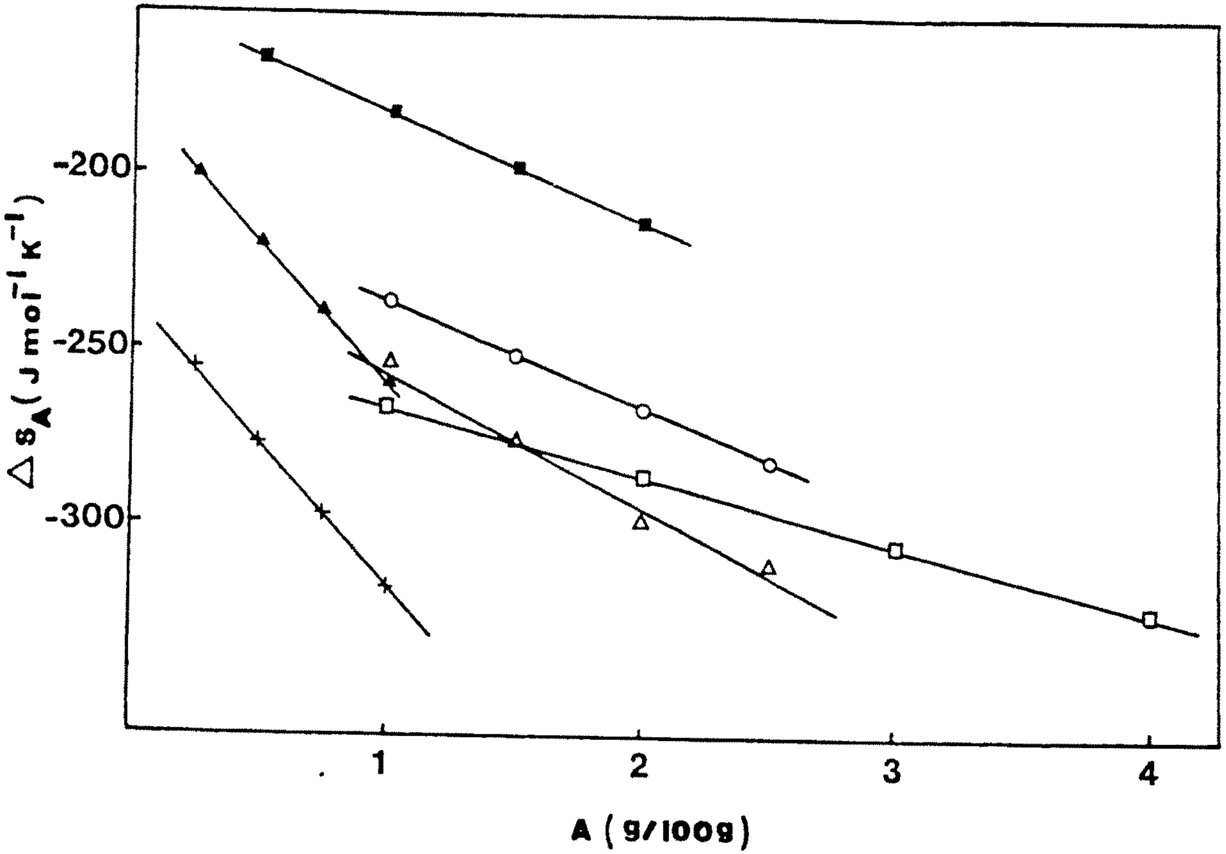


Fig.3.3.5 Change in ΔS_A with the amount of GR adsorbed on alumina from ○ 100C:00T ▲ 50C:50T × 00C:100T and silica gel from □ 100C:00T ■ 50C:50T △ 00C:100T

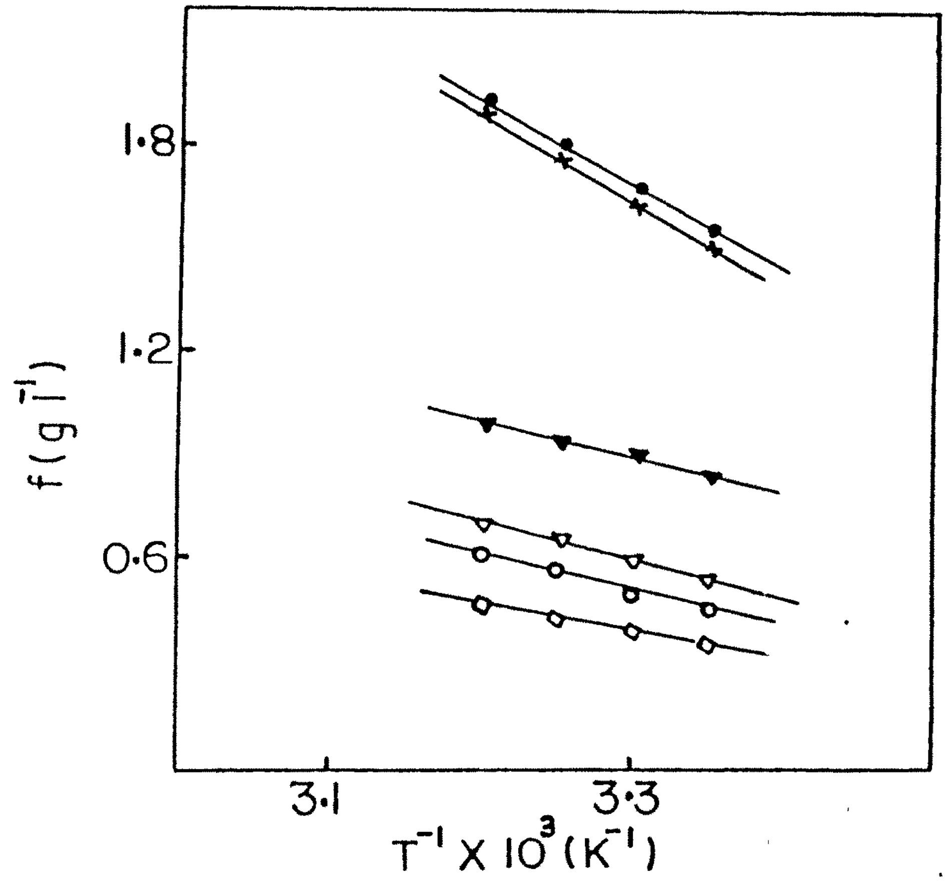


Fig.3.3.6 Temperature dependence of 'f' for adsorption of GR on alumina from

O 100C:00T ● 50C:50T X 00C:100T and

silica gel from ◻ 100C:00T ▲ 50C:50T

△ 00C:100T

TABLE : 3.3.5

'f' VALUES FOR DIFFERENT SYSTEMS

Solvent System C:T	25°C	30°C	35°C	40°C
	Silica gel			
100 : 00	0.36	0.39	0.43	0.47
50 : 50	0.85	0.91	0.94	0.97
00 : 100	0.53	0.60	0.67	0.73
	Alumina			
100 : 00	0.46	0.51	0.55	0.60
50 : 50	1.55	1.67	1.79	1.91
00 : 100	1.52	1.63	1.77	1.90

TABLE : 3.3.6

COMPARISON OF PARAMETERS OBTAINED FROM TWO DIFFERENT EQUATIONS

Solvent System C:T	$-C$[kJ mol^{-1}] [from Eq.5]	$-C$[kJ mol^{-1}] [from Eq.9]	$-m$[J mol^{-1}K^{-1}] [from Eq.6]	$-m$[J mol^{-1}K^{-1}] [from Eq.10]
	Silica gel system			
100 : 00	5.0	5.5	19.4	21.4
50 : 50	6.9	6.2	29.8	28.0
00 : 100	10.6	9.9	39.9	37.8
	Alumina system			
100 : 00	7.2	7.4	28.0	28.8
50 : 50	19.7	19.0	78.7	76.6
00 : 100	19.6	19.8	78.2	79.1

the same straight line has been used to determine the coefficient f_o, which is related to the entropy change during the adsorption process by the following equation /382/.

$$m = f_o . R \qquad ..... [10]$$

The values of m so obtained coincide with those obtained from equation [6].

It follows from the character of the dependence in Fig.3.3.5 that as A increases, the degree of freedom of the polymer molecules on the surface of the adsorbent decreases, the result of which is that their mobility is restricted. It is also possible that the conformational changes of the polymer molecules are responsible for that effect. According to the theory of the processes taking place on uniform heterogeneous surfaces, the equilibrium constant depends on the amount of the polymer adsorbed, A, as follows :

$$K_A = K_o . e^{-fA} \qquad ..... [11]$$

The dependence of log K_A on A at different temperatures shown in Fig. 3.3.7 [a representative plot] was obtained after taking the logarithm of Equation [11].

On solving equation [6] and equation [7], the following dependence is observed.

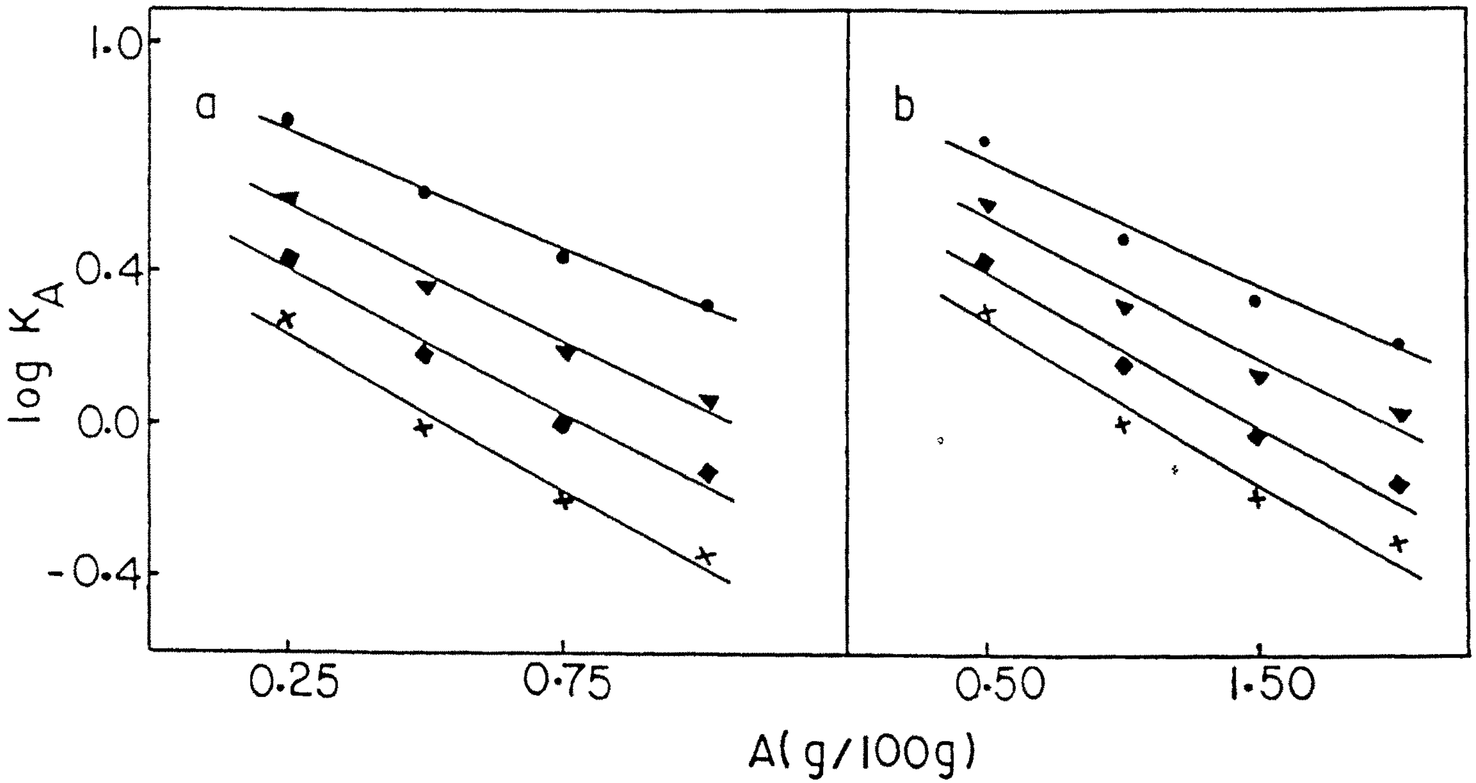


Fig.3.3.7 Change in log K_A with A from 50C:50T on (a) alumina and (b) silica gel
● 25°C ▲ 30°C ■ 35°C × 40°C

$$\Delta S_A = \Delta S_o - m\Delta H_o/C + m\Delta H_A/C \qquad \text{..... [12]}$$

According to this dependence, ΔS_A linearly changes with the isosteric heat, which proves the existence of compensation effect. This dependence can be seen from Tables 3.3.3 and 3.3.4.

The ΔG_A values obtained for various systems are computed in Tables 3.3.3 and 3.3.4. The ΔG_A values obtained were plotted against A, the intercept yielding ΔG_o. The ΔG_o values obtained are also listed in Tables 3.3.3 and 3.3.4.

3.4 ADSORPTION OF InR

The adsorption isotherms obtained for InR from chlorobenzene, on alumina and silica gel, at various temperatures are shown in Fig.3.4.1. The isotherms obtained are of high affinity type. The amount of adsorption increases steeply with increase in equilibrium concentration of InR and then levels off to a plateau. The adsorption decreased with increase in temperature. The adsorption isotherms on both the adsorbents from toluene are shown in Figs.3.4.2 and 3.4.3. Comparison of Figs.3.4.1, 3.4.2 and 3.4.3 shows that adsorption from chlorobenzene is higher than that from toluene [we could not study adsorption isotherm for InR from cyclohexane solution due to its insolubility].

One can qualitatively characterise the two solvents, toluene and chlorobenzene, as good or bad on the basis of intrinsic viscosity

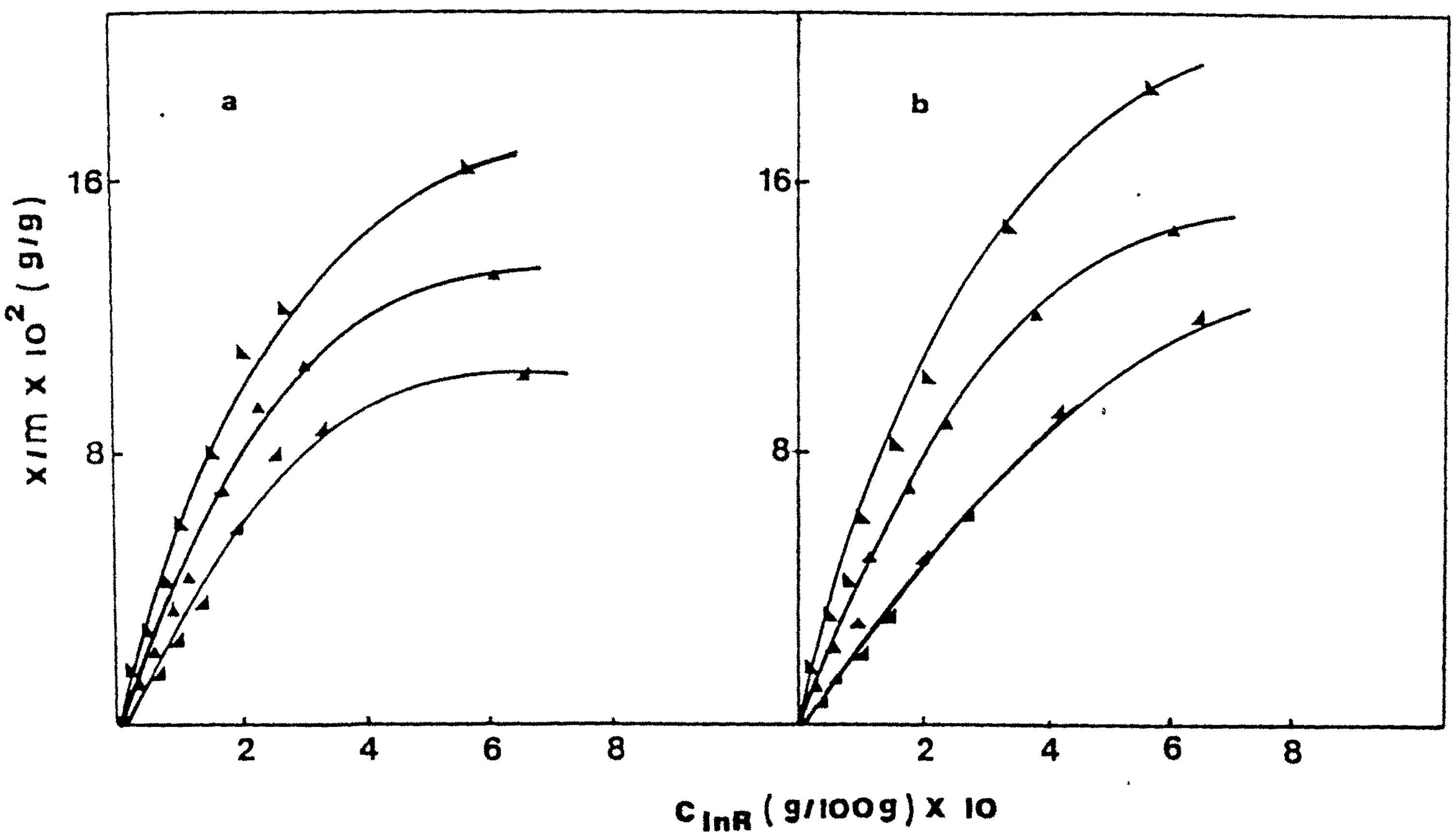


Fig.3.4.1 Plot of specific adsorption against the equilibrium concentration of InR from chlorobenzene at various temperatures
(a) alumina and (b) silica gel

◣ 30°C ▲ 35°C ◢ 40°C

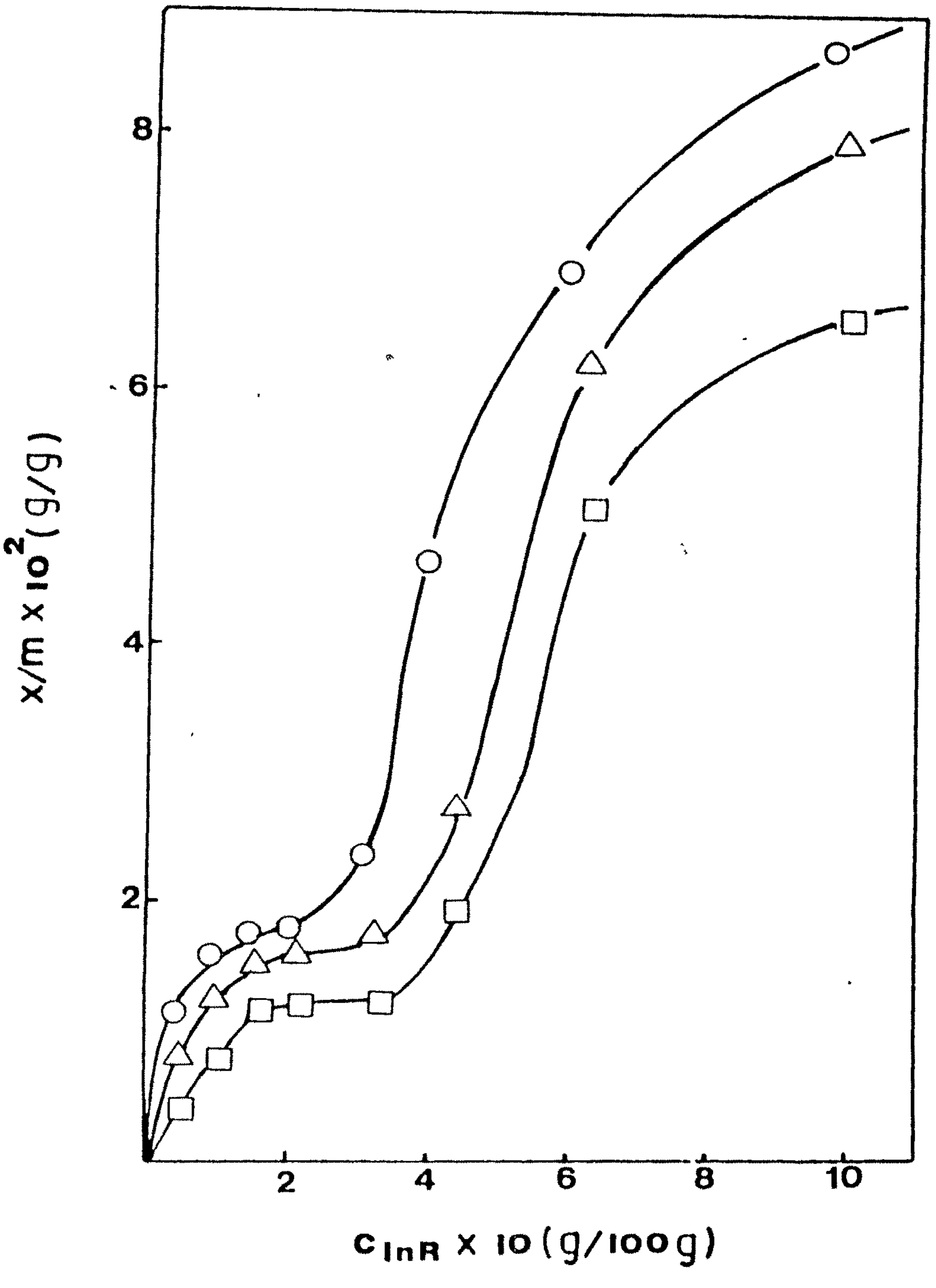


Fig.3.4.2 Plot of specific adsorption against the equilibrium concentration of InR from toluene at various temperatures, on alumina

○ 30°C △ 35°C □ 40°C

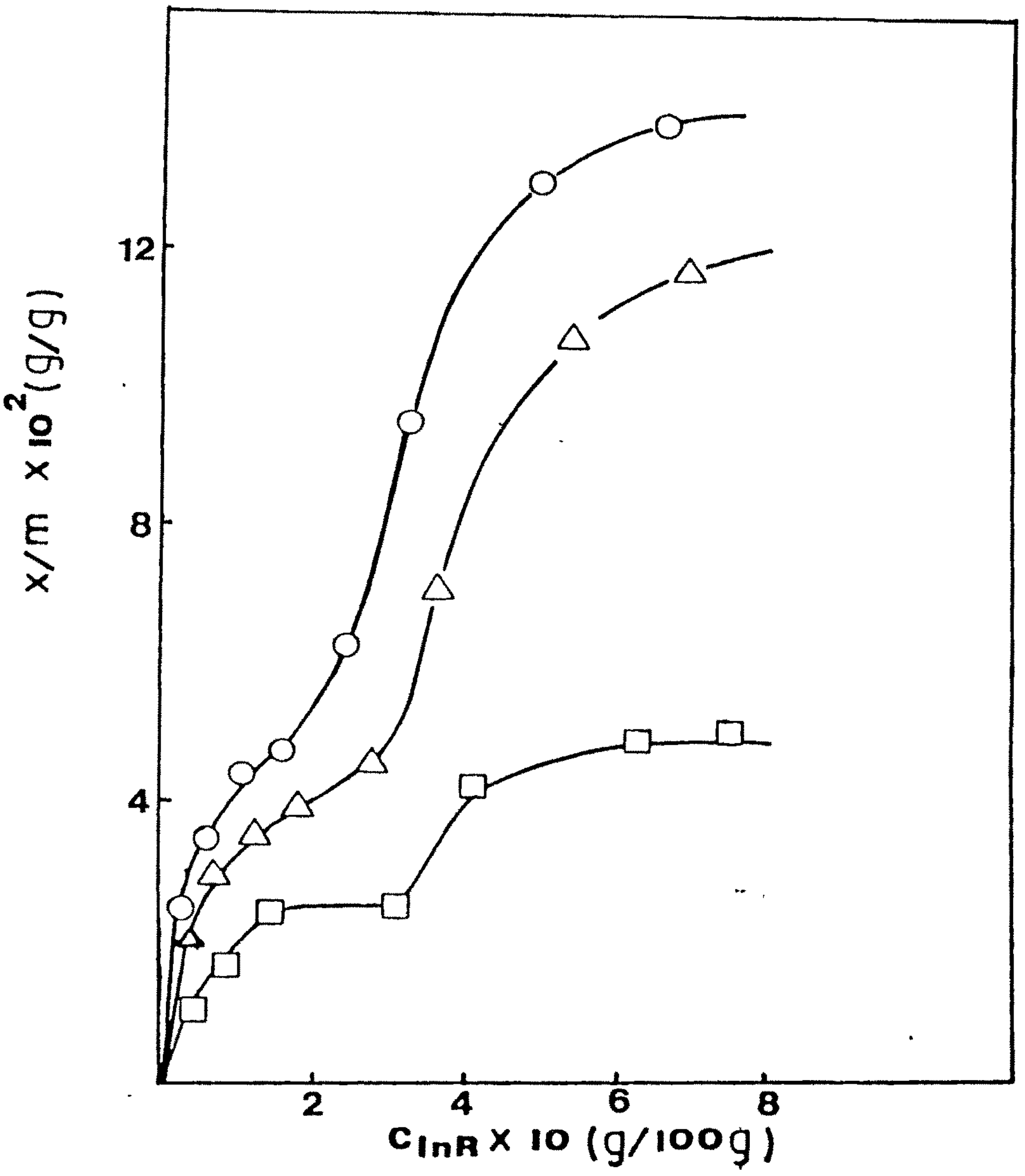


Fig.3.4.3 Plot of specific adsorption against the equilibrium concentration of InR from toluene at various temperatures, on silica gel

○ 30°C △ 35°C □ 40°C

values of the polymer in those solvents. The intrinsic viscosity of InR in toluene [4.29 at 25°C] is more than that in chlorobenzene [4.26 at 25°C] [Chapter 2]. This indicates that toluene is a better solvent and hence lower adsorption from it. The difference in the amount of InR adsorbed on silica gel and alumina, from the same solvent, either toluene or chlorobenzene, can be accounted on basis of polymer-adsorbent interaction. The isotherms shown in Figs.3.4.2 and 3.4.3 differ in nature from those in Fig.3.4.1.

From Figs.3.4.2 and 3.4.3 we can say that the isotherms for adsorption of InR from toluene on both the adsorbents, are somewhat of ladder type, unlike the more commonly observed high affinity type. The amount of InR adsorbed from toluene initially increases as equilibrium concentration increases and then levels off to a semiplateau, then increases very steeply at higher concentrations before finally levelling off. As toluene is a good solvent, desorption of solvent molecules from the adsorbent surface by the polymer molecules will be difficult, thereby resulting in lesser adsorption, observed at lower equilibrium concentrations. Further adsorption at higher equilibrium concentrations could be due to polymer-polymer interactions, resulting in a multilayer formation.

Extensive studies have been done on interaction between adsorbed polymer layers /384/. The forces of interaction are dependent on the nature of the solvent. Chlorobenzene being a poor solvent, displacement of the solvent molecules by polymer molecules becomes relatively easier. Thereby more active sites are available on the adsorbent surface. Thus, all the adsorbed polymer molecules are accomodated in a monolayer, resulting in the high affinity type of isotherms. Moreover chlorobenzene may form a layer on top of the adsorbed polymer and being a poor solvent hinders the polymer-polymer interaction. Whereas, toluene being a good solvent may help second polymer species to approach the first adsorbed one, resulting in the multilayer formation.

The ladder type, or the S-type of isotherms have been observed for adsorption of proteins /385-387/. This nature could be due to stepwise conformational alteration of protein during adsorption process /388/ or due to strong lateral attractive forces existing between adsorbed protein molecules at the interfacial phase /389/ or interfacial coagulation /390/ by forming multilayers of proteins. Similar isotherms have also been observed for adsorption of surfactants /391,392/.

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 monolayer coverage /393/. On the other hand, multilayer adsorption is ubiquitous. The physical reason being that an intervening multilayer region can lower the free energy of the interface between the adsorbed layer and the free solution /394/. 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. However, from the considerations of system free energy, mainly of mixing, the number of nonadsorbed macromolecules from the bulk which occupy the domains created by the loops and tails, is much higher than their concentration in the equilibrium bulk solution. In such cases the molecules will have to be treated as a part of the surface phase and their presence would constitute a true macromolecular multilayer formation /395/.

To our knowledge, the first experimental demonstration of adsorbed polymer multilayers was given by Johnson et al. /393/, though their possibility was anticipated nearly twenty years ago by calculations of Silberberg /395/. The possibility of multilayers was also considered by Terashima /396/. The conclusion of multilayer adsorption was also drawn from the enhanced [but still microscopic] adsorption observed as nonsolvent was added to PS solutions /397/.

The solvent nature is a very important factor in polymer adsorption and attempts to correlate solvent nature with adsorbed amount have been numerous /398-400/. However, it is very difficult to observe a correlation between adsorption and characteristic solvent parameters /401,402/. The adsorption isotherms for adsorption of InR from various mixed solvent systems are shown in Figs.3.4.4-3.4.6. All the isotherms are of high affinity type. The adsorption of InR is much lower from mixed solvent systems than from either of the pure solvents.

Free energy of adsorption was calculated using the relation

$$\Delta G_{ads} = RT \ln C_{InR} \quad [\text{Chapter } 2]$$

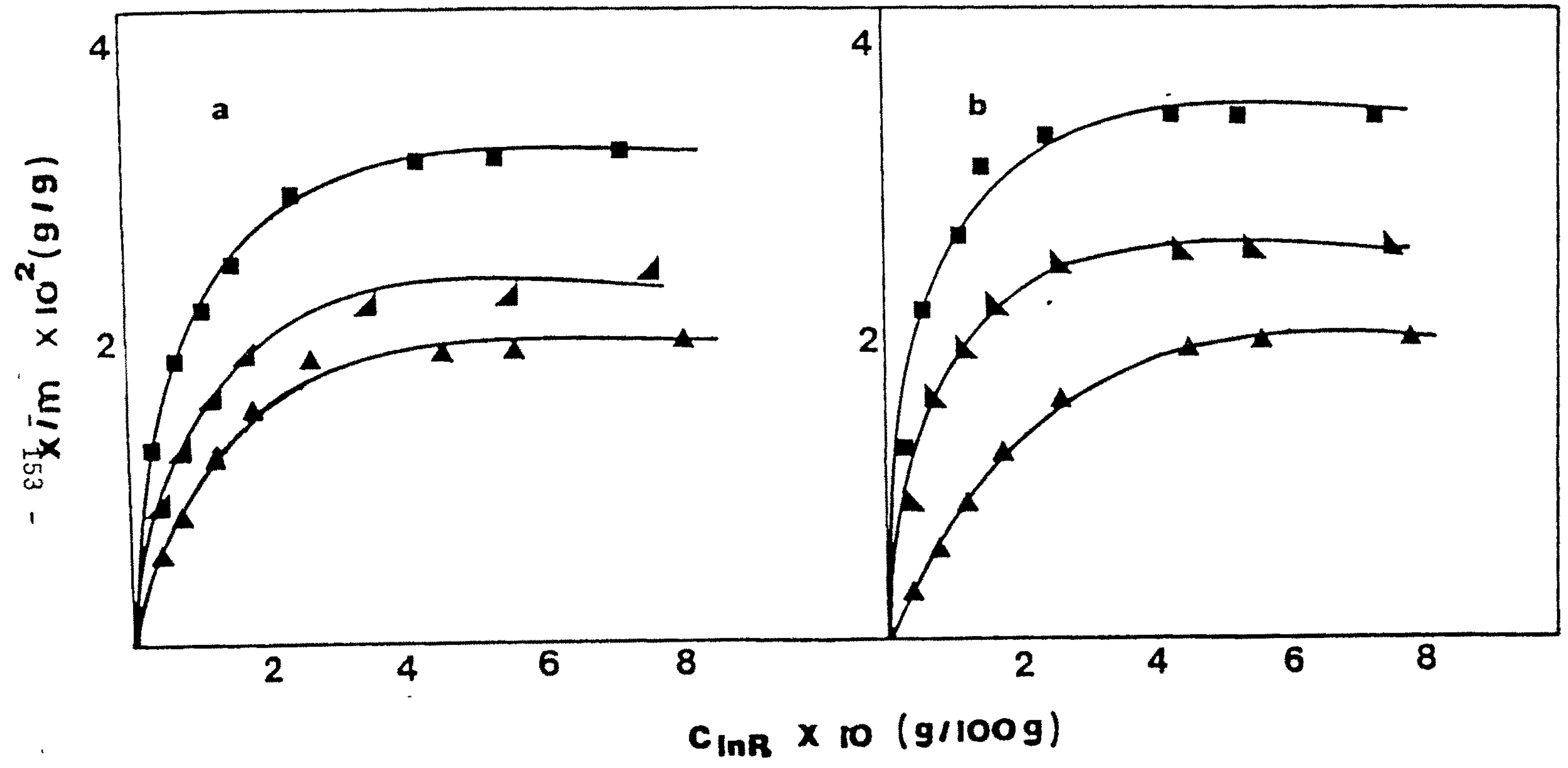


Fig.3.4.4 Plot of specific adsorption against the equilibrium concentration of InR from 80CB : 20T at various temperatures : (a) alumina and (b) silica gel

■ 30°C ◢ 35°C ▲ 40°C

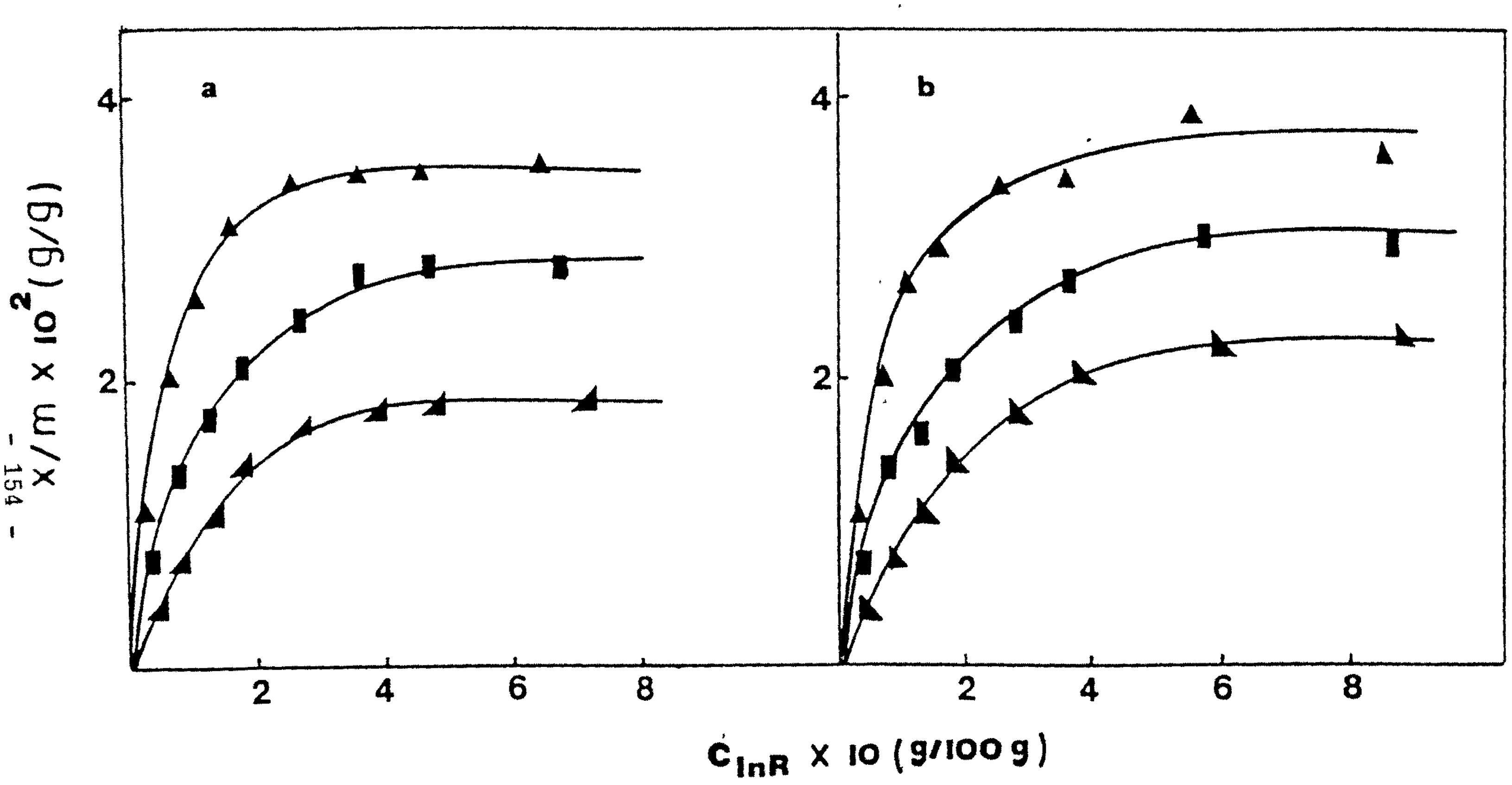


Fig.3.4.5 Plot of specific adospriton against the equilibrium concentration of InR from 50CB:50T at various temperatures : (a) alumina and (b) silica gel

▲ 30°C ▮ 35°C ◢ 40°C

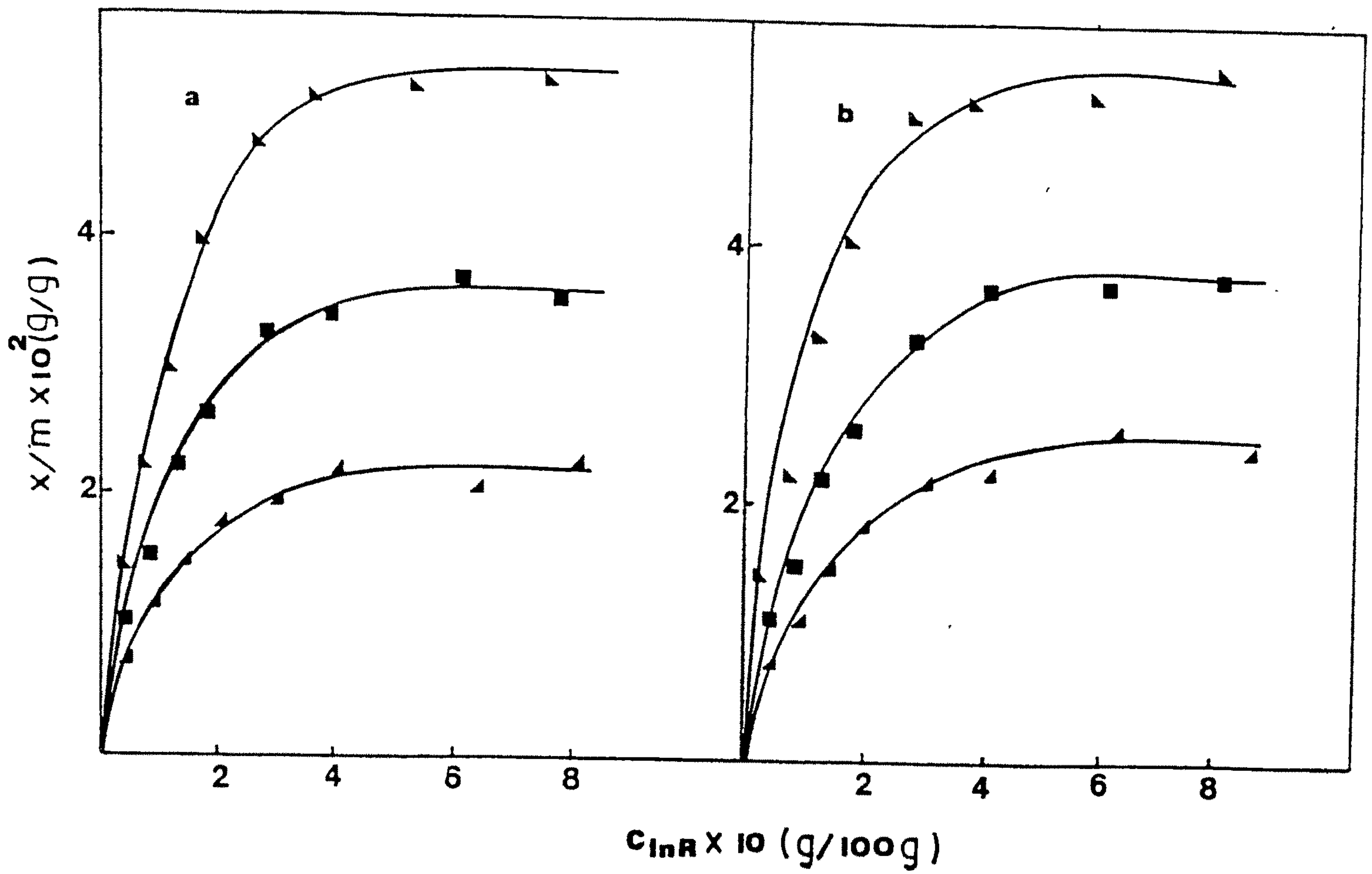


Fig.3.4.6 Plot of specific adsorption against the equilibrium concentration of InR from 20CB:80T at various temperatures : (a) alumina and (b) silica gel

◣ 30°C ■ 35°C ◢ 40°C

where C_{InR} is the equilibrium concentration of InR in g/100g of polymer in solution. ΔG^{o}_{ads}, ΔH^{o}_{ads} and ΔS^{o}_{ads} were calculated, as in previous sections. All the values are compiled in Table 3.4.1. Negative values of ΔG^{o}_{ads} indicate that adsorption of InR is a spontaneous one. The negative values of ΔH^{o}_{ads} and ΔS^{o}_{ads} indicate that adsorption process is exothermic, and the polymer molecules show lower degree of randomness after adsorption, compared to that in solution phase. Though the adsorption process is exothermic, it is relatively less so and less randomised in mixed solvents than in pure solvents. The variation in the thermodynamic quantities ΔH^{o}_{ads} and ΔS^{o}_{ads} with the percentage composition of the mixed solvents are shown in Figs.3.4.7 and 3.4.8. This tells us that the mixture of liquids is a better solvent than the pure ones. The plots in Figs.3.4.7 and 3.4.8 show maxima. The difference in the maxima for alumina and silica gel is due to polymer-adsorbent interaction coming into play. As can be seen from these figures as well as earlier Figs.3.2.1 and 3.3.2 the heat of adsorption is a complicated function of solvent, polymer and adsorbent, and no clear correlation is obtainable. The amount [A] of InR adsorbed per 100g of adsorbent was calculated from the relation :

$$A = [(C_o - C_{InR}) \cdot V \cdot 100]/m \qquad \text{..... [1]}$$

where C_o and C_{InR} are initial and equilibrium concentrations of InR solutions in g/l;

V = Volume of InR solution taken for the adsorption study [0.015 l];

m = weight of the test sample of absolutely dry adsorbent in gram.

TABLE : 3.4.1

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

[CONCENTRATION IS EXPRESSED IN /100g OF SOLUTION]

Solvent T : CB [v/v]	$-\Delta G^{o}_{ads}$ [kJ mol^{-1}]			$-\Delta H^{o}_{ads}$ [kJ mol^{-1}]	$-\Delta S^{o}_{ads}$ [$JK^{-1} mol.^{-1}$]
	30°C	35°C	40°C		
	Alumina				
100 : 00	9.54	9.21	8.95	27.40	59.00
80 : 20	10.06	9.71	9.48	27.50	57.64
50 : 50	9.77	9.52	9.28	24.53	48.70
20 : 80	10.50	10.15	9.84	30.58	66.20
00 : 100	10.92	10.51	10.26	30.73	65.50
	Silica gel				
100 : 00	11.19	10.08	9.47	62.75	170.46
80 : 20	9.98	9.71	9.48	25.06	49.80
50 : 50	9.73	9.55	9.28	23.36	44.90
20 : 80	10.45	10.14	9.47	40.17	97.89
00 : 100	11.00	10.41	9.95	42.73	104.80

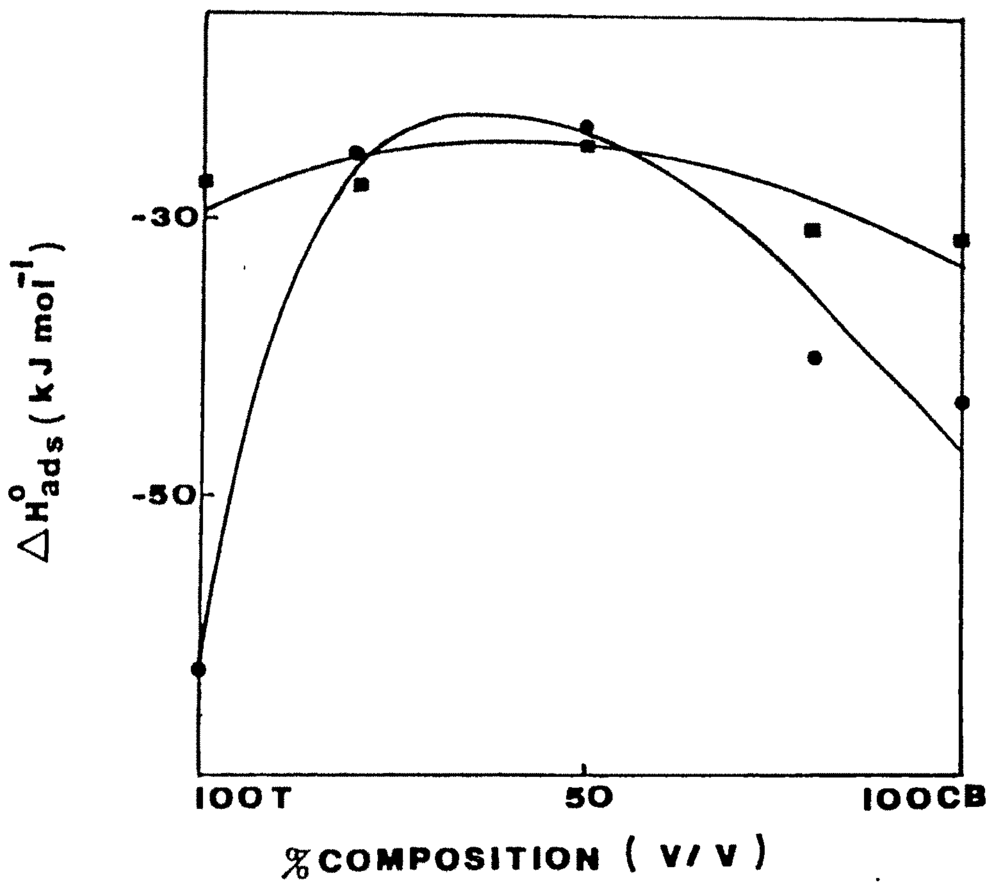


Fig.3.4.7 Plot of enthalpy of adsorption at infinite dilution ΔH^{o}_{ads} against the percentage composition of solvent mixtures

● silica gel ■ alumina

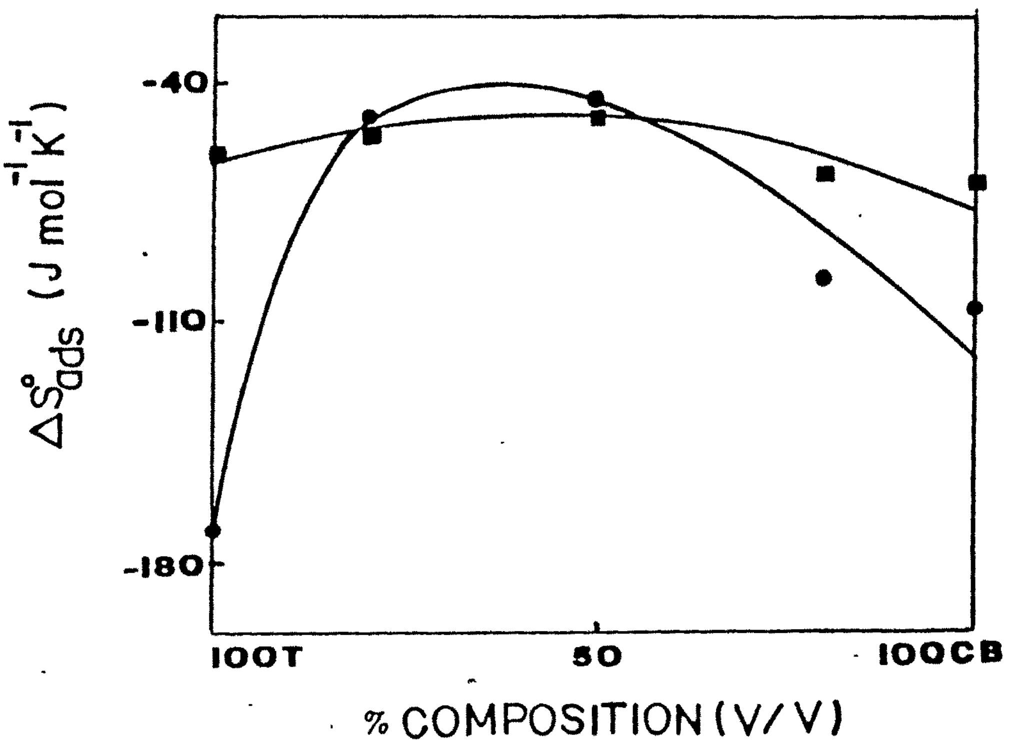


Fig.3.4.8 Plot of entropy of adsorption at infinite dilution ΔS^{o}_{ads} against the percentage composition of solvent mixtures

● silica gel ■ alumina

We calculated earlier [Sections 3.2.2 and 3.2.3] by assuming

$K_A = 1/C_{InR}$

and Tjumkin's isotherm $A = 2.3/f \log K_o + 2.3/f \log C_{InR}$

where the coefficient of heterogeneity f, energetic heretogenity coefficient C, constant relating to entropy factor m, infinitely dilute isosteric enthalpy, $\triangle H_o$, and infinitely dilute isosteric entropy $\triangle S_o$. Similar calculations were done for this system also and the computed values are given in Tables 3.4.2-3.4.6. The variations in above quantities are shown in Figs.3.4.9-3.4.13.

From these figures and tables, we find that for InR too, the heterogeneity of the adsorbents increases with temperature. The energetic coefficient C, which is independent of temperature seems to be a function of system, adsorbent, and solvent composition. In almost all cases the plot of C shows a convex curve, for both adsorbents, with solvent composition signifying that the mixed systems are more heterogeneous in nature.

The isosteric heat $\triangle H_A$ values indicate the exothermicity which decreases with increase in adsorption. Similarly, the entropy change $\triangle S_A$ also decreases with increase in adsorption. The same trend was also observed for PBR and GR.

The existence of compensation effect was observed by a linear

TABLE : 3.4.2

THERMODYNAMIC PARAMETERS OF ADSORPTION ON InR FROM PURE SOLVENTS

Solvent System	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$[303K] [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$ [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
Alumina								
Chloro-benzene (CB)	1.00	47.6	144.9	3.7	42.4	125.0	4.5	2.4
	2.00	52.6	165.3	2.5				
	3.00	58.3	187.5	1.5				
	4.00	63.0	205.1	0.9				
Toluene (T)	0.25	103.8	320.6	6.7	95.9	290.2	8.0	13.6
	0.50	109.2	343.2	5.2				
	0.75	118.4	378.0	3.9				
	1.00	125.0	403.9	2.6				
Silica gel								
CB	1.00	77.0	239.4	4.5	70.2	213.6	5.5	3.1
	2.00	83.8	265.5	3.4				
	3.00	90.4	291.4	2.1				
	4.00	97.5	317.0	1.4				
T	0.50	124.0	384.6	7.5	117.2	358.7	8.6	6.6
	1.00	131.2	413.3	6.0				
	1.50	138.7	442.1	4.7				
	2.00	144.8	465.3	3.8				

TABLE : 3.4.3

THERMODYNAMIC PARAMETERS OF ADORPTION OF InR ON ALUMINA FROM MIXED SOLVENTS SYSTEMS

Solvent System CB : T	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$[303K] [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$ [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
80 : 20	0.50	107.5	334.8	6.1	102.0	310.5	8.0	5.7
	0.75	109.6	346.1	4.7				
	1.00	113.0	359.7	4.0				
	1.25	115.3	370.5	3.0				
50 : 50	0.50	149.3	472.4	6.2	145.6	454.1	8.0	4.7
	0.75	151.8	484.8	4.9				
	1.00	153.3	492.1	4.2				
	1.25	155.3	502.1	3.2				
20 : 80	0.50	126.0	393.8	6.6	112.8	344.1	8.5	12.1
	0.75	132.7	420.1	5.4				
	1.00	140.0	446.6	4.6				
	1.25	145.8	469.0	3.6				

TABLE : 3.4.4

THERMODYNAMIC PARAMETERS OF ADSORPTION OF InR ON SILICA GEL FROM MIXED SOLVENT SYSTEMS

Solvent System T : CB	A [g/100g]	$-\Delta H_A$ [kJ mol^{-1}]	$-\Delta S_A$ [J mol^{-1}K^{-1}]	$-\Delta G_A$ [kJ mol^{-1}]	$-\Delta H_o$ [kJ mol^{-1}]	$-\Delta S_o$ [J mol^{-1}K^{-1}]	$-\Delta G_o$[303K] [kJ mol^{-1}]	$-f_o$ [gl^{-1}]
80 : 20	0.50	90.6	280.4	5.6	79.2	238.0	7.1	10.4
	0.75	96.8	304.0	4.7				
	1.00	102.4	324.7	4.0				
	1.25	108.1	345.6	3.3				
50 : 50	0.50	139.2	440.7	5.6	127.5	397.4	7.1	10.8
	0.75	146.1	466.8	4.6				
	1.00	151.2	486.4	3.8				
	1.25	157.4	508.7	3.2				
20 : 80	0.50	158.5	500.8	6.8	146.3	454.4	8.7	11.0
	0.75	163.5	520.7	5.7				
	1.00	170.2	545.8	4.8				
	1.25	176.1	568.1	3.9				

TABLE : 3.4.5

COMPARISON OF PARAMETERS OBTAINED FROM TWO DIFFERENT EQUATIONS

Solvent System CB : T	- C [kJ mol^{-1}] [From Eq.5]*	- C [kJ mol^{-1}] [From Eq.9]*	- m [J $mol^{-1}K^{-1}$] [From Eq.6]*	- m [J $mol^{-1}K^{-1}$] [From Eq.10]*
	Alumina system			
100 : 00	5.18	5.04	20.29	19.88
80 : 20	10.70	10.49	48.35	47.76
50 : 50	7.81	7.87	38.55	38.94
20 : 80	26.63	26.47	100.84	100.44
00 : 100	29.11	28.98	113.90	113.47
	Silica gel system			
100 : 00	6.80	6.67	25.88	25.49
80 : 20	23.70	23.79	90.84	91.26
50 : 50	23.94	23.91	89.42	89.49
20 : 80	23.24	23.18	86.49	86.35
00 : 100	13.95	14.28	54.13	55.31

* Equation Nos. are from Section 3.3

TABLE : 3.4.6

'f' VALUES FOR DIFFERENT SYSTEMS

Solvent System T : CB	30°C	35°C	40°C
	Alumina		
100 : 00	2.13	2.35	2.50
80 : 20	1.57	1.75	1.90
50 : 50	1.56	1.61	1.66
20 : 80	1.58	1.64	1.71
00 : 100	0.39	0.43	0.45
	Silica gel		
100 : 00	0.98	1.08	1.17
80 : 20	1.19	1.33	1.48
50 : 50	1.27	1.43	1.58
20 : 80	1.54	1.68	1.84
00 : 100	0.42	0.46	0.50

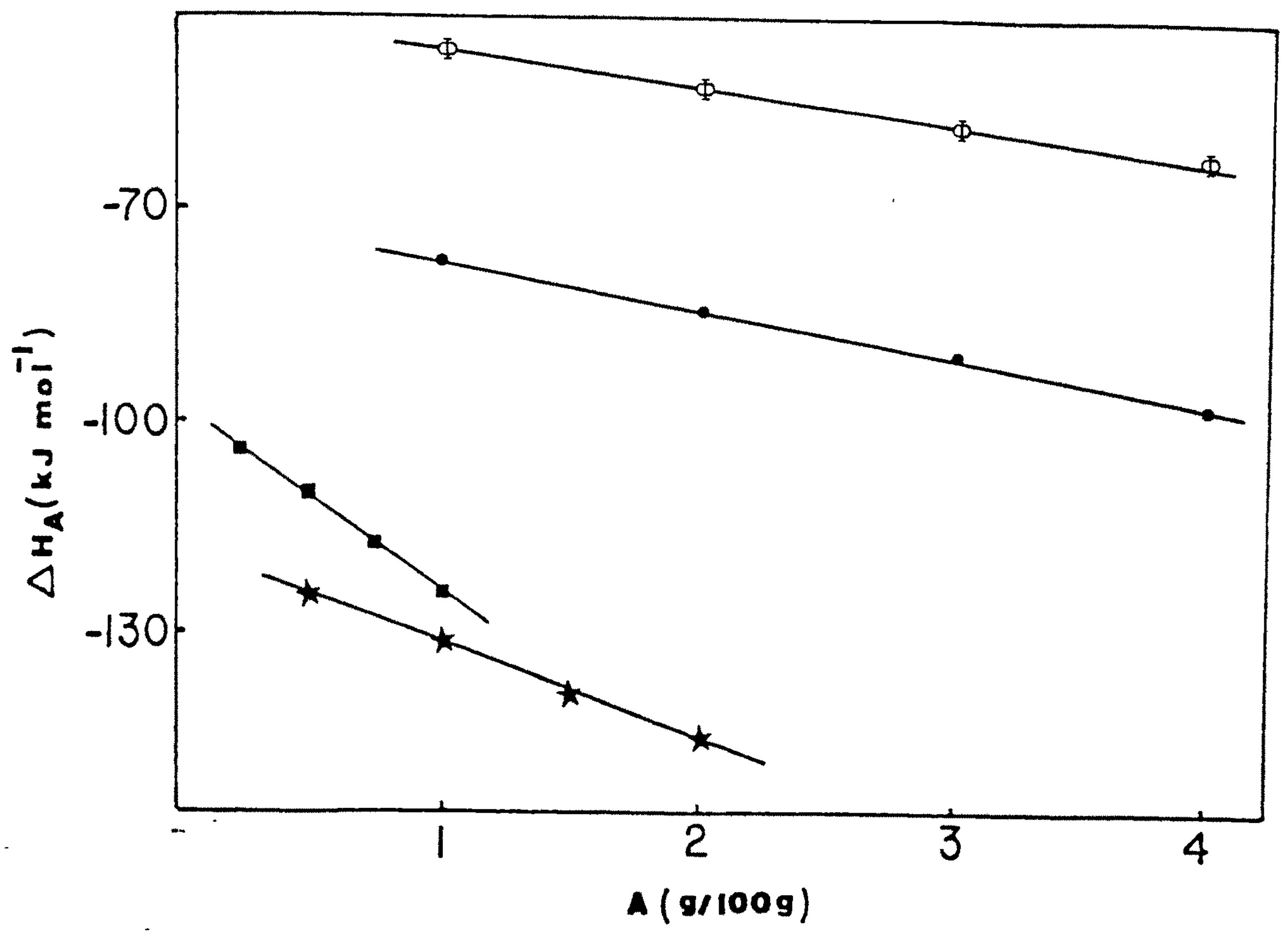


Fig.3.4.9 Change in ΔH_A with change in amount of InR adsorbed, A, on silica gel from ● 100CB:00T ★ 00CB:100T and alumina from Φ 100CB:00T ■ 00CB:100T

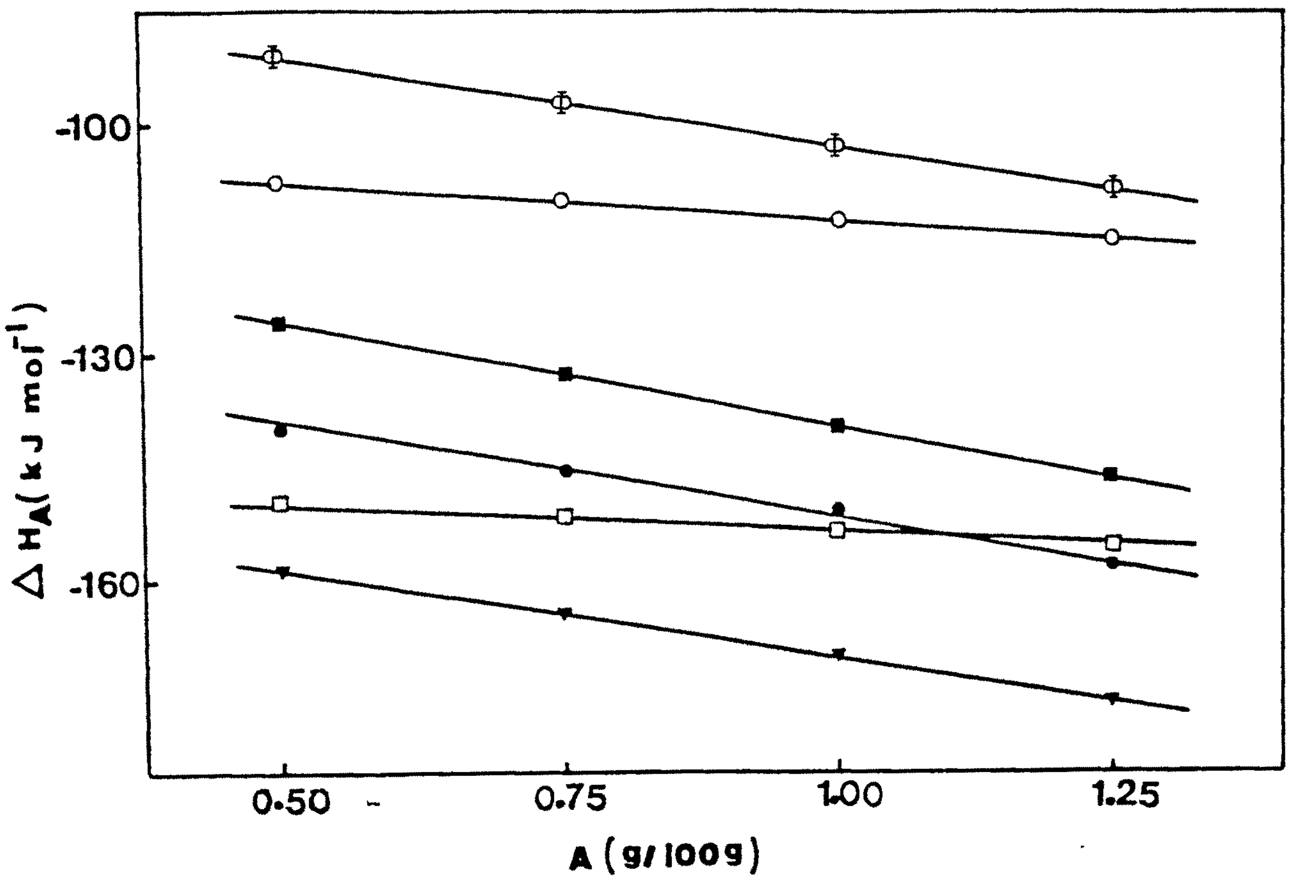


Fig.3.4.10 Change in ΔH_A with change in amount of InR adsorbed, A, on silica gel from Φ 80CB:20T ● 50CB:50T ▼ 20CB:80T and alumina from ○ 80CB:20T □ 50CB:50T ■ 20CB:80T

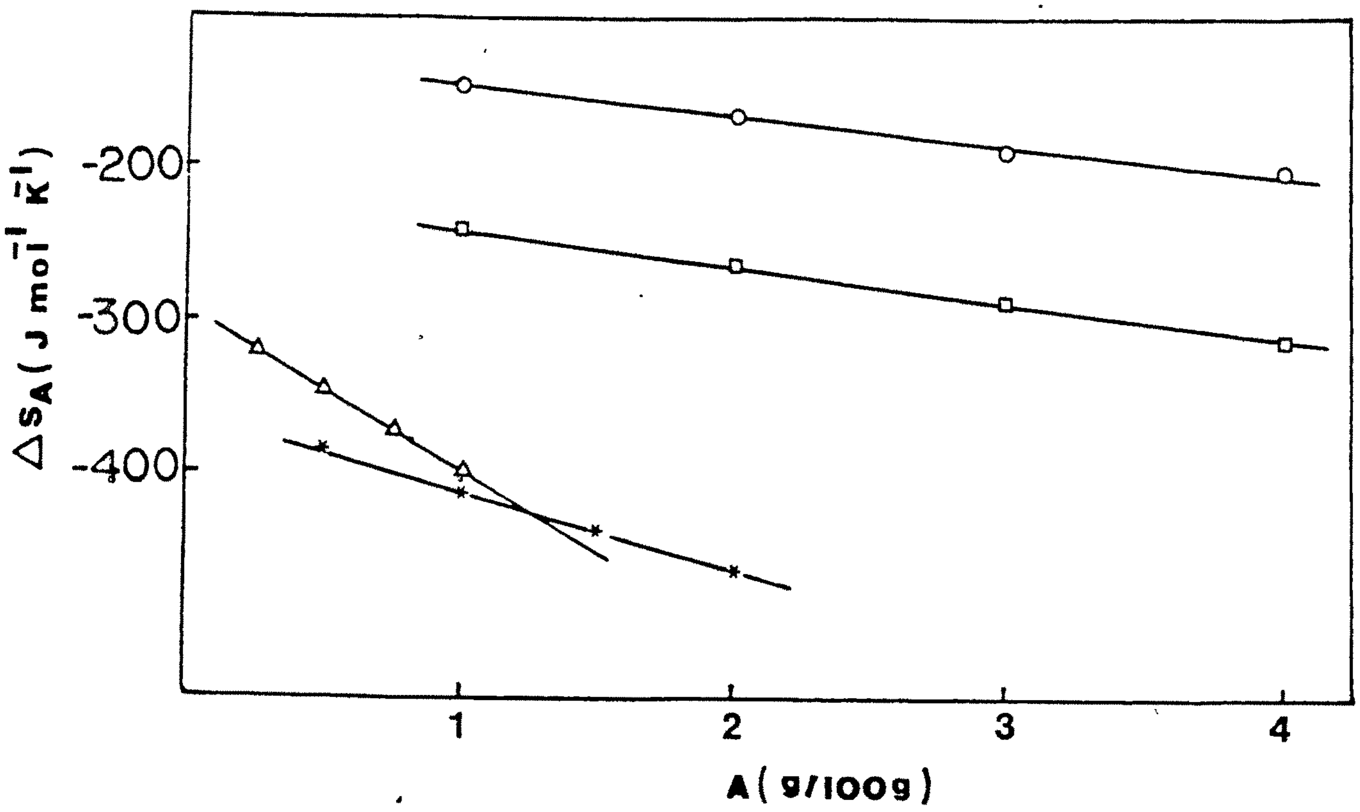


Fig.3.4.11 Change in ΔS_A with A on silica gel from □ 100CB:00T ✱ 00CB:100T and alumina from ○ 100CB:00T △ 00CB:100T

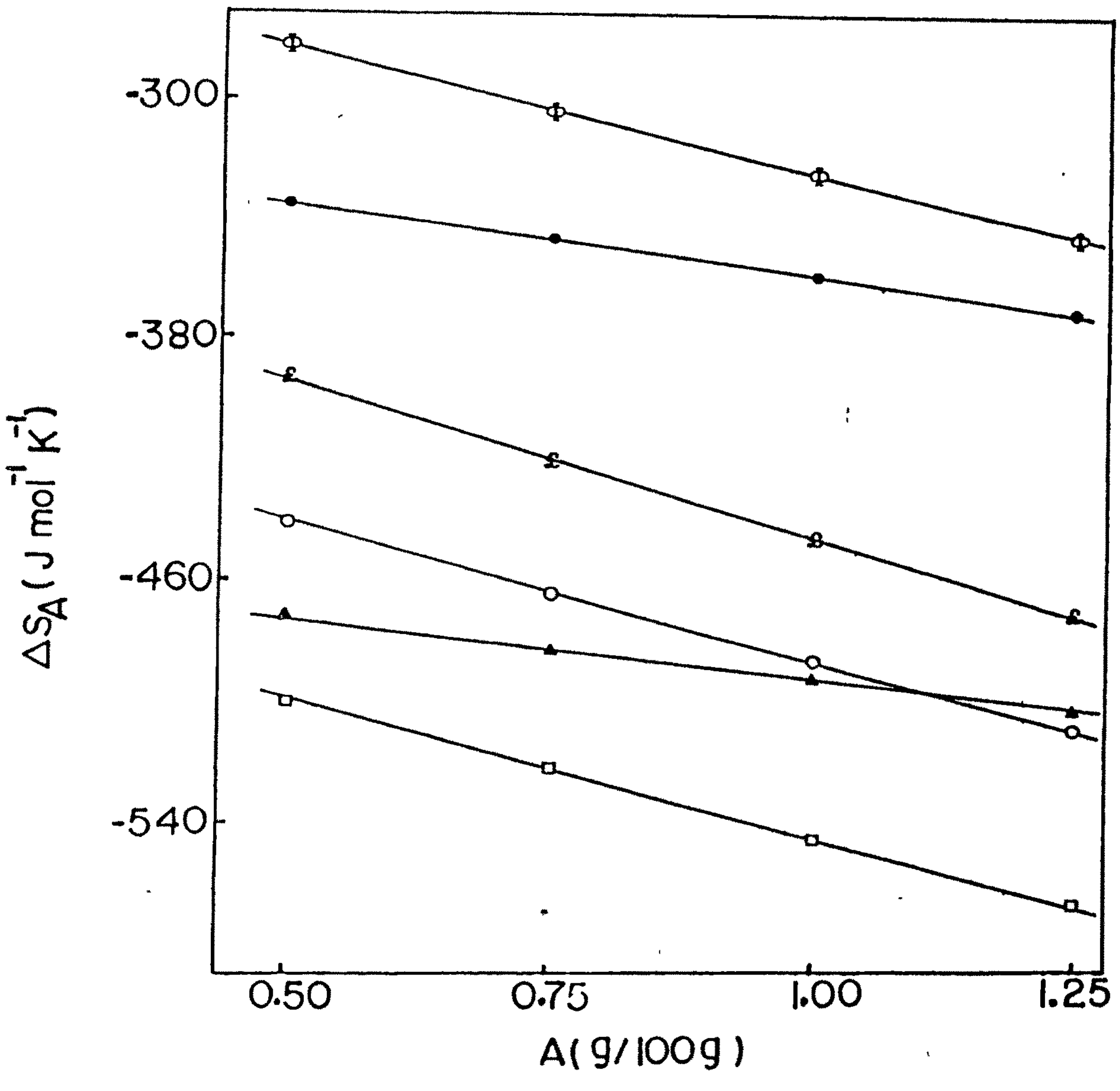


Fig.3.4.12 Change in ΔS_A with A on silica gel from Φ 80CB:20T ○ 50CB:50T □ 20CB:80T and alumina from ● 80CB:20T ▲ 50CB:50T £ 20CB:80T

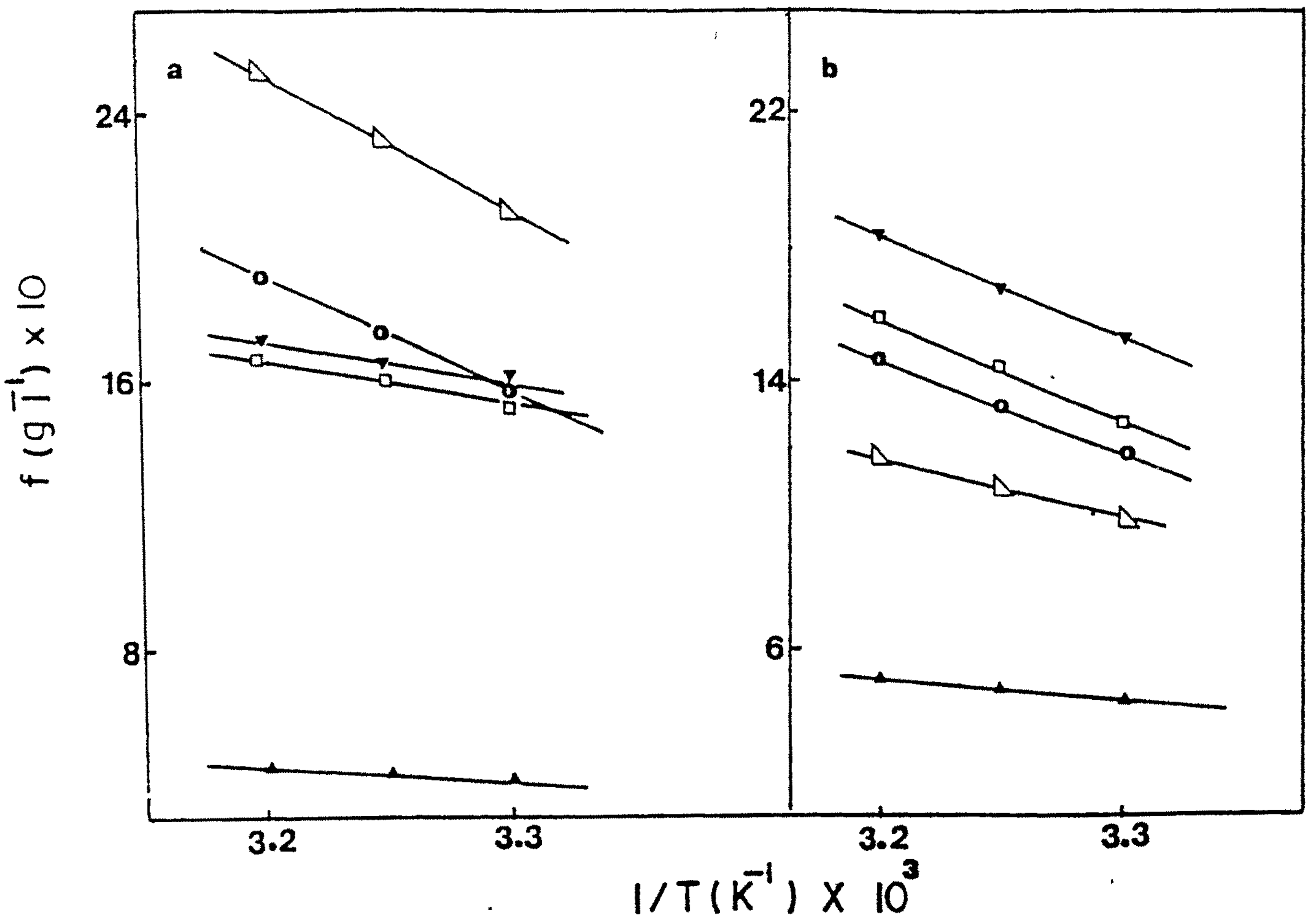


Fig.3.4.13 Change in 'f' values with temperature for (a) alumina and (b) silica gel

△ 100CB:00T ○ 80CB:20T □ 50CB:50T ▼ 20CB:80T

▲ 00CB:100T

relationship between ΔS_A and ΔH_A. This indicates that the adsorption process under study takes place with the simultaneous change in the entropy and enthalpy factors. The change in free energy was determined using the equation :

$$\Delta G_A = \Delta H_A - T\Delta S_A$$

The ΔG_A values so obtained, at a particular temperature, have been listed in Tables 3.4.2-3.4.4. The ΔG_A values when plotted against A, the intercept yield ΔG_0. The ΔG_0 values are also tabulated in Tables 3.4.2-3.4.4. This isosteric infinitely dilute free energy of adsorption, ΔG_0, seems to be independent of the solvent composition indicating that the over all process [though not ΔH_0 or ΔS_0] is independent of any significant variable.

The ΔH^O_{ads} obtained by the extrapolation method for all the systems studied were plotted against the similarly obtained ΔS^O_{ads}. The linear plot obtained is shown in Fig.3.4.14. The slope of the plot yielded a temperature value of 321 K. Similarly, the isosteric ΔH_0 values for all the adsorption systems studied were plotted against the corresponding ΔS_0 values. The linear plot obtained is shown in Fig.3.4.15. The slope of the plot yielded a temperature value of 319 K.

This can be mathematically explained as follows /402b/ :

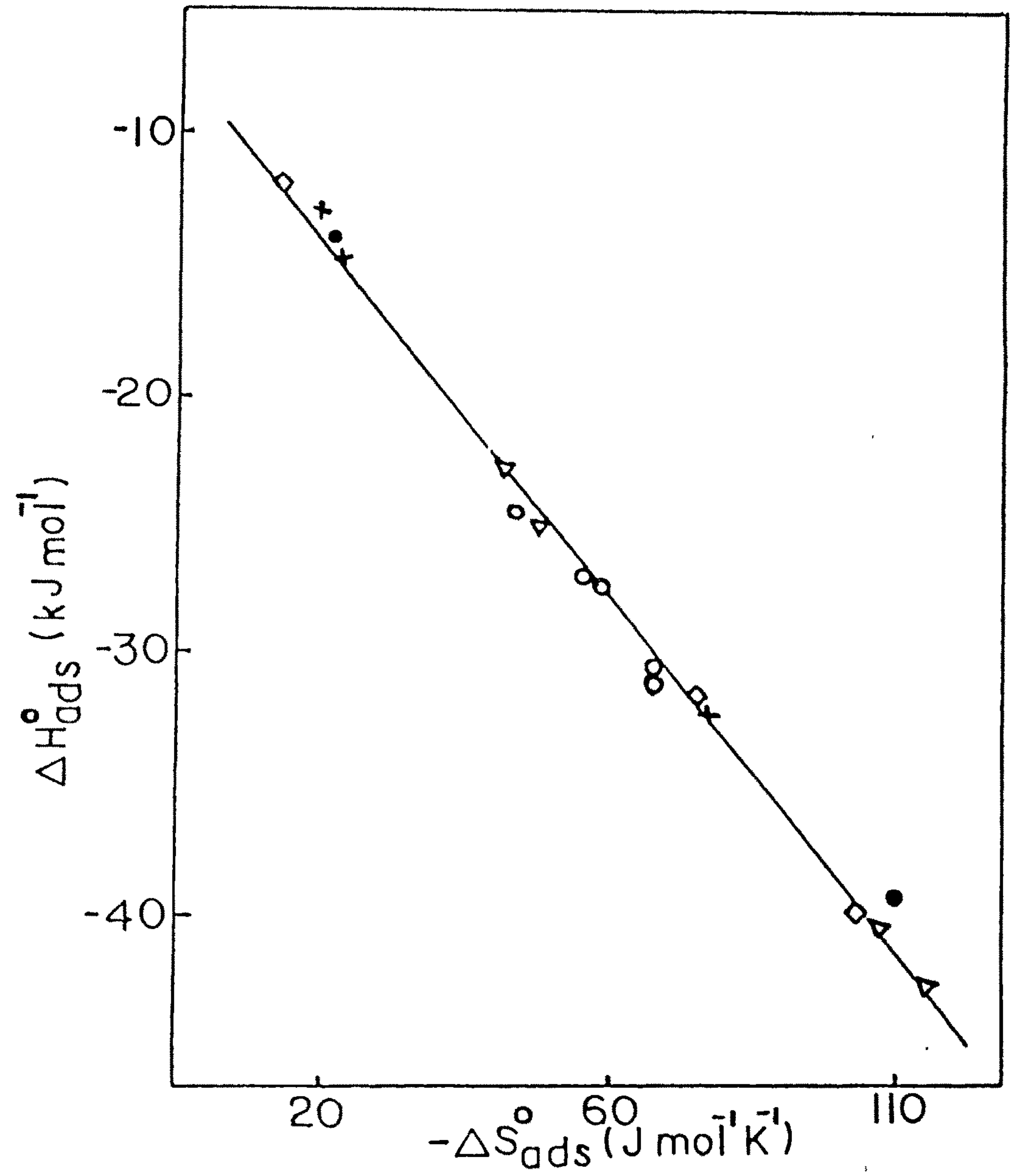


Fig.3.4.14 Plot of ΔH^{o}_{ads} against ΔS^{o}_{ads} for different systems

□ GR on silica gel; ● GR on alumina

△ InR on silica gel; ○ InR on alumina

× PBR on silica gel

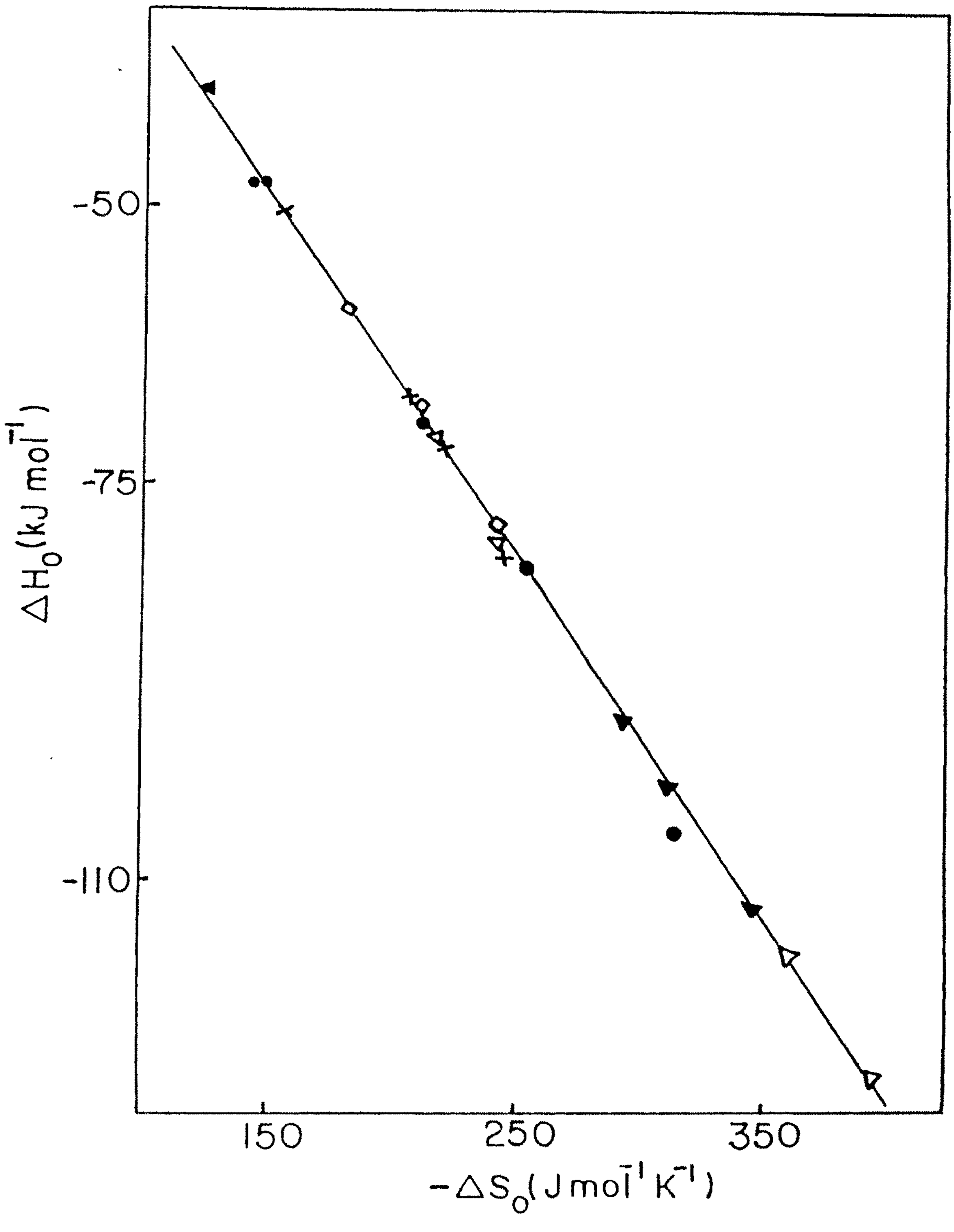


Fig.3.4.15 Plot of ΔH_0 against ΔS_0 for different systems

✕ GR on silica gel; ☐ GR on alumina;

△ InR on silica gel; ▲ InR on alumina;

● PBR on silica gel

$$\Delta H = K_1 + K_2 \Delta S$$

$$\Delta G = \Delta H - T \Delta S$$

$$\therefore \Delta G = K_1 + K_2 \Delta S - T \Delta S$$

$$\therefore \Delta G = K_1 + \Delta S [K_2 - T]$$

$$\Delta G = K_1 \text{ when } K_2 = T$$

Thus, at a temperature of 320 K, the free energy of adsorption becomes independent of the entropic forces and is solely governed by the enthalpic forces.

Two different thermodynamic approaches gave similar values of slope i.e. 320 K, independent of the solvent. This indicates that this temperature is characteristic of the adsorption of natural and synthetic rubbers on oxide substrates.

3.5 POLYMER-SURFACTANT INTERACTION

Preview

The spontaneous molecular association of ionic surfactants in aqueous solution can be detected readily by electrical conductivity measurements. The chief advantages of this method are :

[1] availability of a suitable instrument

[2] absence of any need to add additional substances to the solutions being measured.

But this is not so for nonionic surface-active agents, in organic media. Nonionic surfactants may form reverse micelles in liquid hydrocarbons. One of the best methods chosen for the determination of critical reverse micelle concentration [cmc] of the nonionic surfactant systems is based on the colour change of iodine that takes place when nonionic associated surfactants [i.e. the so called "reverse micelles"] are added to an iodine solution, i.e. the iodine solubilization method /403/. This method is equally applicable to the determination of cmc in aqueous or in non-aqueous solutions /404/. Secondly, iodine has the advantage of small molecular size compared to the molecule of surface active agent; it is less likely, therefore, to affect the micelle formation as much as the large dye molecules, customarily used do, for cmc determination by spectral shift /403/. However, this method is applicable to only unionized surface active agents, systems devoid of any interaction between surfactant and added solute molecules /405/.

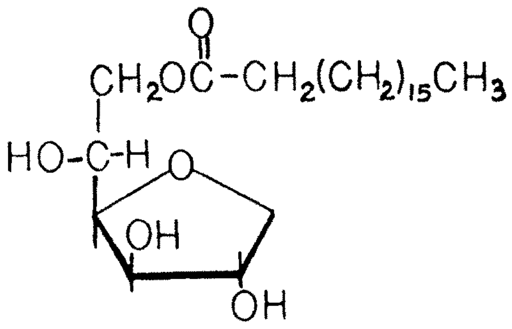
Among the nonionic surfactants, micellization of Triton X-100, in the presence and absence of different additives, in aqueous solutions, has been extensively studied /406/. Comparatively, less work has been done on the behaviour of Span 60 in organic media. Hence we determined the cmc [or so called "reverse micelle concentration"] of Span 60 in toluene at various temperatures of 20, 25, 30, 35 & 40°C. Various thermodynamic quantities of reverse micellization were computed and discussed.

Interactions between polymer and surfactant play an important role in variety of fields, like mineral processing and in enhanced oil recovery. In mineral processing, interactions between surface active collector species and long chain polymeric molecules are encountered. Selectivity in mineral processing operations can be affected through modifications caused by these interactions in the polymer solution properties, as well as in interfacial properties, such as adsorption of different species at the solid-liquid and liquid-gas interfaces /407,408/.

The critical reverse micelle concentration of Span 60 in presence of synthetic and natural rubbers was determined. The study was done at different temperatures. Free energy of micellization [ΔG_m], enthalpy of micellization [ΔH_m] and entropy of micellization [ΔS_m] were then computed.

Material

Iodine [AR, Sarabhai] was resublimed before use. Sorbitan monostearate - Span 60 [Koch-Light Laboratories Ltd, England] was used without any further treatment. The structure of Span 60 is shown below :



Sorbitan Monostearate

[Span 60, mol. wt. 430.63]

Spectronic 20 was used for absorption studies.

Methods

The iodine solubilization method was used for the determination of the cmc of Span 60 /404/. A stock solution of iodine [A] was selected to transmit 80% of the light transmitted by the pure solvent. The λmax of I_2 in toluene was found to be 410 nm. The stock solution of the Span 60 [B] contained a known concentration of the surfactant well above its cmc, prepared in the solution A. By diluting B with A, a series of concentrations of Span 60, having the same concentration of iodine were obtained. The series ofcourse included concentrations well above and below the cmc to be determined. The λmax of iodine solution in presence of Span 60, above cmc, was found to be 435 nm. The absorption in presence of iodine and Span 60 were obtained at 435 nm, and solution A as the standard for 100% transmittance. This is shown in Fig.3.5.1.

Results and Discussion

From Fig.3.5.1, we see that the λmax of iodine in toluene shifts from 410 nm to 435 nm, on addition of Span 60, above its cmc. The logarithm of observed percent transmittance [log % T] was then plotted against concentration. The plots obtained at different temperatures are shown in Fig.3.5.2. All plots show a break point. This was taken to be the cmc of Span 60 at that particular temperature. The cmc values [in millimoles/l] obtained at various temperatures are compiled in Table 3.5.1.

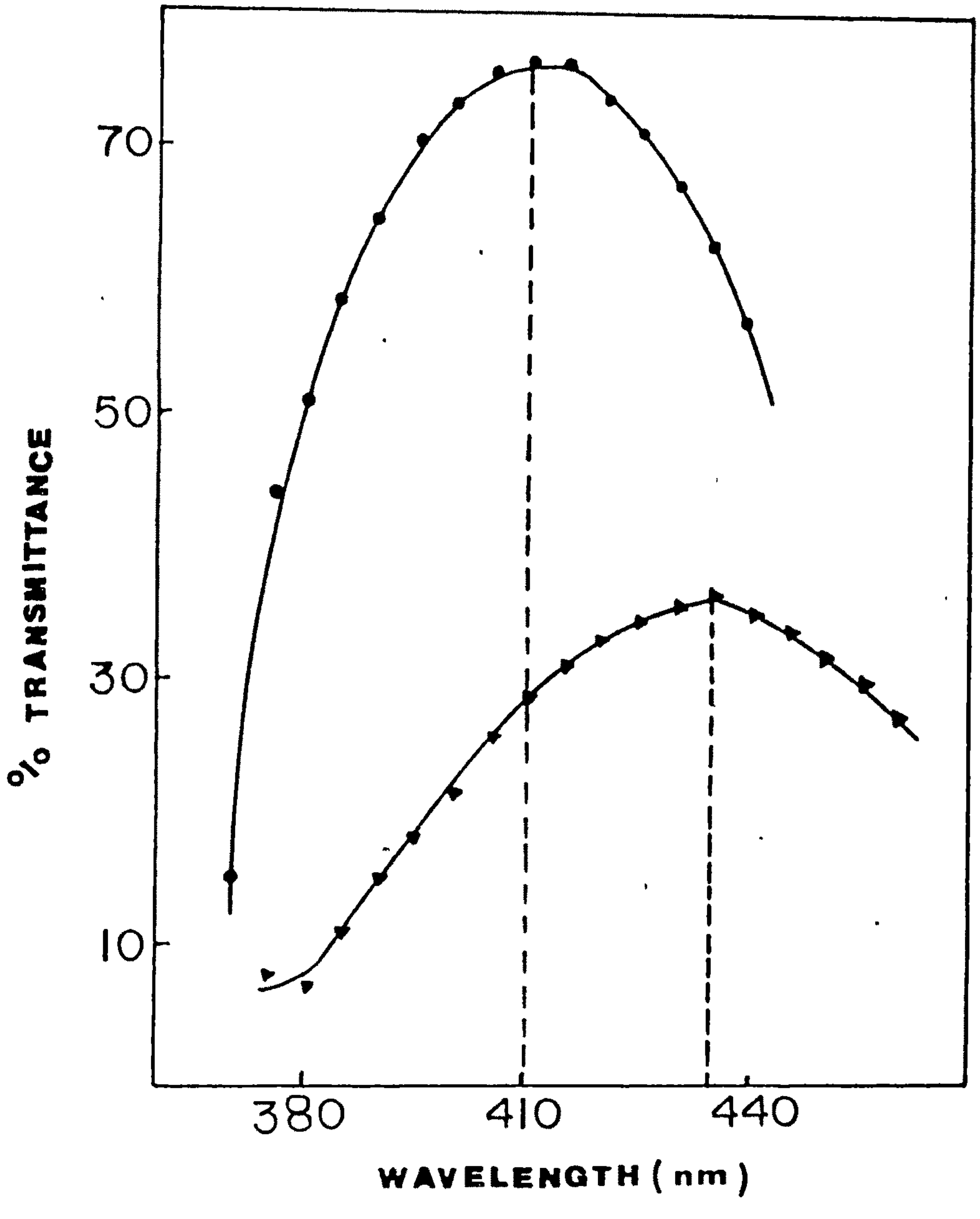


Fig.3.5.1 Absorption Spectra of Iodine in

● toluene and ▲ toluene + Span 60

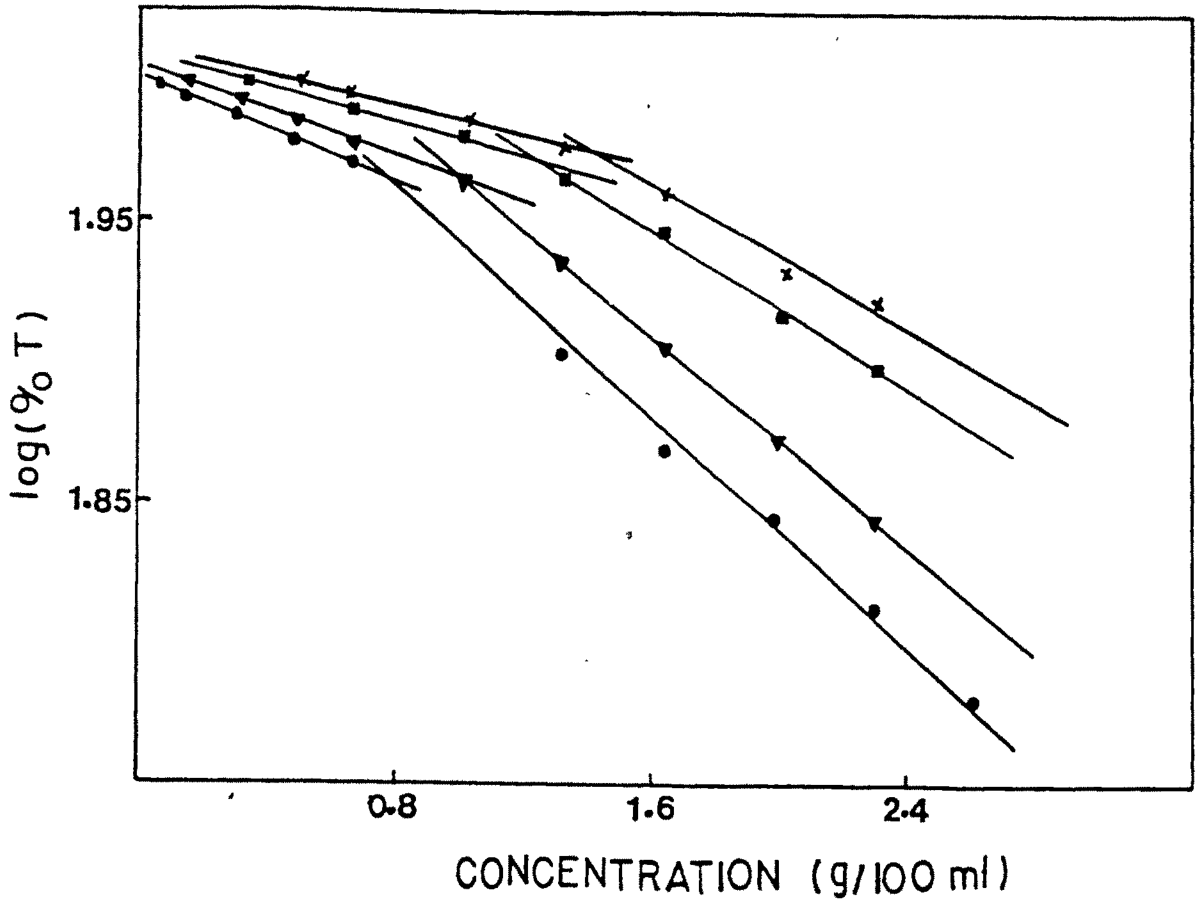


Fig.3.5.2 Plot of log percent transmittance at 435 nm of Span 60 solution in toluene vs. concentration

● 20°C ▲ 25°C ■ 30°C ✕ 35°C

The readings were recorded within 5-6 h. of making the solution. On standing for a longer time fading of colour becomes perceptible. The Span 60 solutions, of various concentrations were clamped in a thermostat, maintained at the required temperature [± 0.1°C] for an hour, with intermittent shaking. The transmittance was then read at 435 nm. This procedure was repeated for various temperatures. All points were atleast duplicated to check on the reproducibility of transmittance values.

In presence of polymers, the same procedure was adopted. Polymer solution of required concentration was prepared in solution A, resulting in stock solution C. The stock solution of Span 60 of highest concentration was then prepared in C. The other concentrations were obtained using C for the necessary dilutions.

The cmc values were seen to increase with increase in temperature. The increase in temperature increases the kinetic energy of the molecules. The molecules are thus in increased state of motion. Therefore higher concentration of surfactant is required to bring the molecules sufficiently close to result in the micelle formation and hence the increase in cmc with temperature. The cmc values were determined in presence of various concentrations of PBR, InR and GR. No change in cmc of Span 60 was observed in presence of InR and GR, even at the concentration of 1.3815% and 2.075% respectively. In presence of PBR, the cmc values were seen to increase at all temperatures in comparison to those obtained in pure solvent. The values are presented in Table 3.5.1. No shift in cmc values was

TABLE : 3.5.1

CRITICAL MICELLE CONCENTRATION (CMC) OF SPAN 60 AT DIFFERENT TEMPERATURES

System	CMC [Millimoles/Lit.]				
	20°C	25°C	30°C	35°C	40°C
Span 60 + Toluene	18.58	23.22	27.87	32.51	37.15
Span 60 + Toluene + PBR [1.0149%]	-	32.51	37.15	41.79	46.44

obtained when the concentration of PBR was less than 1%. The log % T vs. concentration plot is shown in Fig.3.5.3.

Not much interaction was as such expected between Span 60 and these rubbers. Both are hydrophobic and the medium is also quite nonpolar. At lower concentrations of PBR, the cmc of Span 60 is not affected. The PBR molecules remain in the solvent medium without any interaction with Span 60. But a further increase in concentration of PBR results in increase in hydrophobicity to a large extent, thereby the hydrophilic ends experience the repulsive force and start moving away. This results in aggregate formation with hydrophilic part in the core and hydrophobic part towards the solvent media.

The same was expected for InR and GR, but was not observed. This may be due to the polyisoprenes being relatively more hydrophobic than polybutadiene. Therefore much high concentrations of polymers will be required to cause sufficient repulsion between the hydrophobic and hydrophilic ends. To work with higher concentrations had practical limitations, hence, we were unable to do so.

The molecular weights of both the natural rubbers are much too different. This did not have any affect on cmc within the polymer concentration range studied. In Table 3.5.2, the thermodynamic quantities calculated for the above systems are given. The free energy, enthalpy, and entropy of micellization were calculated by the well known relations :

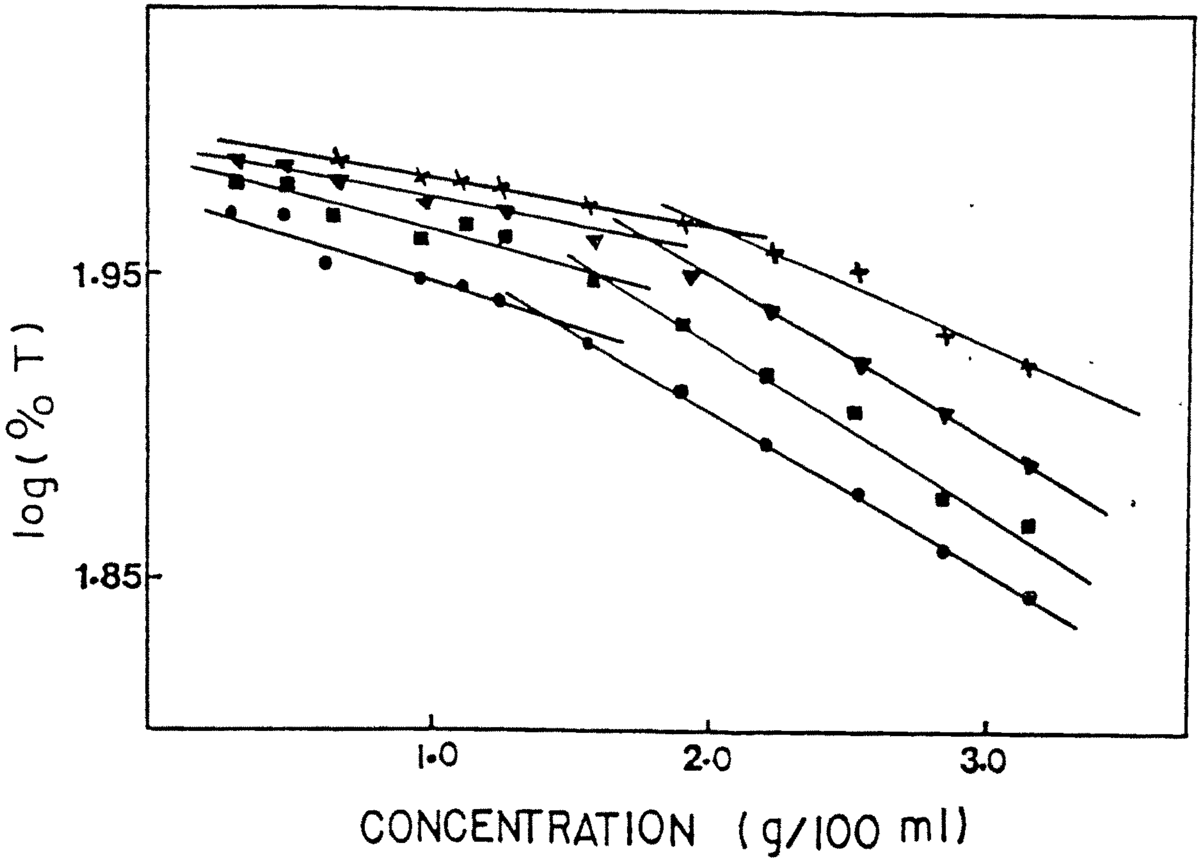


Fig.3.5.3 Plot of log percent transmittance at 435 nm of Span 60 solution in PBR + toluene vs. concentration

● 25°C ■ 30°C ▲ 35°C X 40°C

TABLE : 3.5.2

THE FREE ENERGY [$\triangle G_m$], ENTHALPY [$\triangle H_m$], AND ENTROPY [$\triangle S_m$]
OF MICELLIZATION, FOR DIFFERENT SYSTEMS

Temperature [°C]	Span 60 + Toluene			Span 60 + Toluene + PBR [1.0149%]		
	$-\triangle G_m$ [kJ mol^{-1}]	$-\triangle H_m$ [kJ mol^{-1}]	$-\triangle S_m$ [J mol^{-1}K^{-1}]	$-\triangle G_m$ [kJ mol^{-1}]	$-\triangle H_m$ [kJ mol^{-1}]	$-\triangle S_m$ [J mol^{-1}K^{-1}]
20	15.18	25.32	34.61	-	-	-
25	14.88	26.19	37.95	14.04	18.29	14.24
30	14.65	27.07	40.99	13.93	18.91	16.42
35	14.49	27.98	43.79	13.62	19.54	19.21
40	14.36	28.89	46.42	13.56	20.18	21.13

$$\triangle G_m = RT \ln [cmc] \qquad \ldots\ldots [1]$$

$$\triangle H_m = -RT^2 \, d \ln [cmc]/dT \qquad \ldots\ldots [2]$$

$$\triangle S_m = [\triangle H_m - \triangle G_m]/T \qquad \ldots\ldots [3]$$

where cmc are reverse cmcs.

The reverse cmc was always taken in the molefraction scale. To calculate $\triangle H_m$, ln [cmc] was plotted against T[°K] and the slope of the straight line obtained was d ln [cmc]/dT. $\triangle G_m$ values for all the systems are negative, indicating that micellization process is spontaneous. The enthalpy of micellization is negative for all systems, indicating that the process of micellization is exothermic. $\triangle S_m$ is negative for all the systems, indicating loss of randomness on micellization.

The contact angles values with respect to glass plate of polymer solutions with and without Span 60 are given in Table 3.5.3. The contact angle values decrease to some extent, on addition of Span 60. Then they remain constant on further addition of surfactant. This suggests a definite existence of polymer-surfactant interaction.

The contact angle values show a definite decrease with the addition of various amount of surfactant. It finally leads to a stable value without any further change. This decrease in contact angle [max. being only about 12%] shows that the interfacial energy between

TABLE : 3.5.3

CONTACT ANGLE VALUES FOR DIFFERENT SYSTEMS IN TOLUENE SOLUTION
[CONCENTRATION OF SPAN 60 $\simeq$ 1.0%]

	Polymer without Span 60 [θ]	**Polymer + Span 60 [θ]**
PBR	36.8	34.1
GR	42.7	38.5
InR	36.2	31.5

polymer and the glass surface decreases in presence of the surfactant. This indicates that polymer and surfactant do interact to some extent though it is not large. The natural rubbers as well as synthetic polybutadiene behave in the similar way though in cmc, within the concentration range studied, there was no effect of GR and InR. Even PBR showed effect only at higher concentration.