Colloid & Polymer Science Colloid Polym Sci 272:130–140 (1994)

Studies of adsorption of polyacrylonitrile and polyacrylates at solid-liquid interface

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Abstract: The adsorption of poly(acrylonitrile), poly(methyl acrylate), poly(ethyl acrylate) and poly(butyl acrylate) was studied at different temperatures from *N,N'*-dimethyl formamide solution on various solid surfaces, i.e. silica gel, alumina and calcium carbonate. The thermodynamic quantities for adsorption processes were computed by using a) infinite dilution and b) surface coverage approaches. Both procedures tend to give similar conclusions. These reveal the importance of polymer-adsorbent interactions besides many other properties including solvent power.

Key words: Adsorption – thermodynamics – polyacrylonitrile – polyacrylates – DMF – silica gel – alumina – calcium carbonate.

Introduction

With the development of polymer science over the last few decades, studies of adsorption of macromolecules at solid-liquid interface have gained importance owing to technological prominence and academic significance [1, 2]. Study of polymer adsorption is necessary in understanding the processes of adhesion, colloid stabilization, etc. The homopolymers like poly(ethyl acrylate) and poly(butyl acrylate) are used in the automotive industry, in seals and gaskets. Polyacrylonitrile has been found to improve the oil resistance of polyacrylates and other similar polymers [3]. With this in mind, the adsorption of poly(methyl acrylate), poly(ethyl acrylate), poly(butyl acrylate), and polyacrylonitrile was studied. In this paper we report the adsorption isotherms and the related thermodynamics of adsorption of the abovementioned polymers on various solid surfaces at different temperatures.

Experimental

Poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBA), and polyacrylonitrile (PAN) were synthesized and characterized in this laboratory. The synthesis, purification, and viscosity properties of these polymers in DMF solution have been reported earlier [4]. The viscosity molecular weights of these polymers ($\bar{M}_v$) are 20.5; 21.0; 22.1, and 52.0 (10^3) respectively. The characterization of these polymers will be reported elsewhere.

Alumina (acidic, mesh size above 100) and silica gel (column chromatography grade, mesh size 60–120) were obtained from Glaxo Laboratories, India. Precipitated $CaCO_3$ was from E. Merck, India. The adsorbents were heated at 150 °C for 4 h and cooled in a dessicator before use. The surface areas of these alumina, silica gel, and $CaCO_3$ were determined by BET method (N_2 adsorption). These were 97.0, 284.2, and 25.7 m^2/g. The probability of surface impurities was checked for all adsorbents by x-ray photoelectron spectroscopy (Fig. 1) and no surface impurity was observed. The experimental details were given in our earlier paper [5].

N,N'-dimethyl formamide (DMF), AR, Glaxo Laboratories, India, was stored over 4A molecular sieves (Loba Chemie, India) before distillation, under low pressure in dry atmosphere. The distilled fraction was also stored with molecular sieves. This was distilled once again just before the use. The boiling point of the purified DMF was 151 °C (Lit. value 150–152 °C). Molecular sieves were washed with conductivity water and dried at 150 °C before use.

The experimental details of the adsorption study were reported earlier [5]. The equilibrium concentration was determined by uv spectroscopy. The λ_{max} was found to be 272 nm for all polymers in DMF.

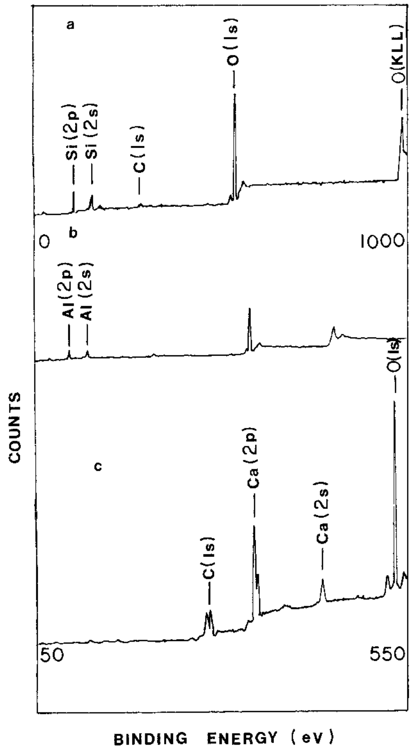

Fig. 1. ESCA of a) silica gel, b) alumina and c) $CaCO_3$

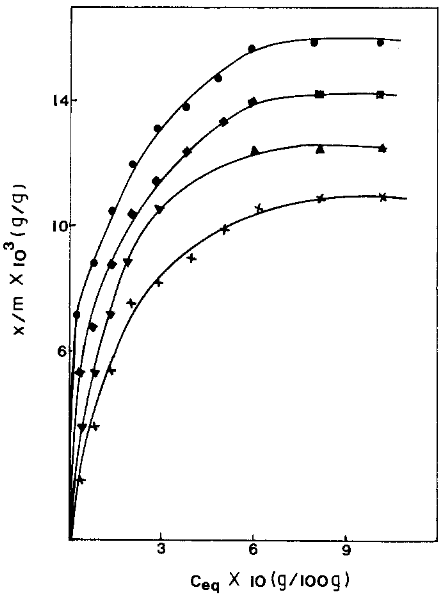

Fig. 3. Plot of specific adsorption against equilibrium concentration of PMA on $CaCO_3$. Symbols used are the same as in Fig. 2

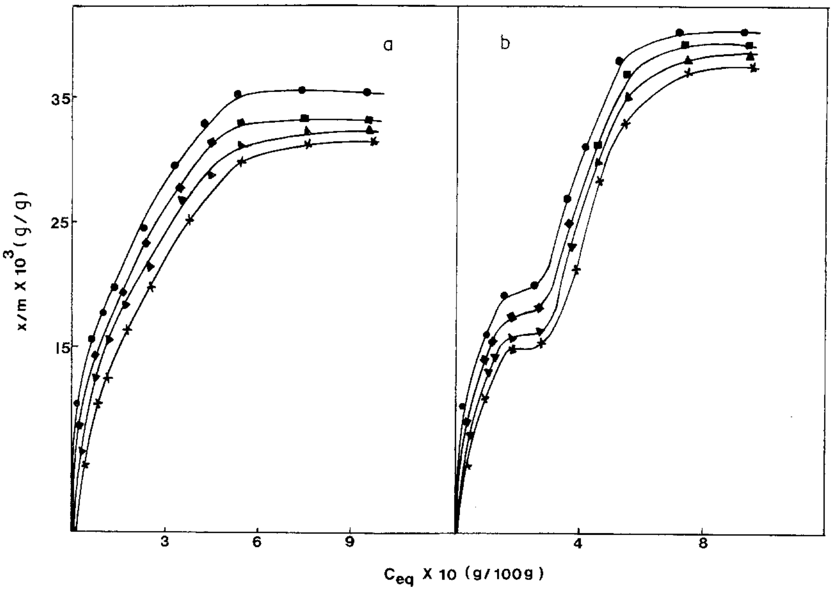

Fig. 2. Plot of specific adsorption against equilibrium concentration of a) PMA on alumina b) PMA on silica gel ● 30°C; ■ 35°C; ▲ 40°C; × 45°C

Results and discussions

Polyacrylates

Adsorption studies of PMA, PEA, and PBA onto silica gel, alumina, and calcium carbonate from DMF were carried out at 30°, 35°, 40°, and 45 °C. The adsorption isotherms are shown in Figs. 2–6. With the increase in temperature, the specific adsorption decreases in all systems. The amount of polymer adsorbed on silica gel was found to be relatively high, much less on alumina, and considerably low on $CaCO_3$ at any one temperature. This is shown in Fig. 7a for PEA adsorption on these adsorbents.

The isotherms obtained for alumina and $CaCO_3$ systems are of usual Langmuir type. The adsorption increases steeply at low concentration of polymer and finally levels off to a plateau. The isotherms on silica gel systems show an inflection after the initial steep rise (a semi plateau), then increase very steeply at higher concentrations before reaching a plateau region. These happen due to either a change in orientation at the surface [6] or the formation of multilayers [7].

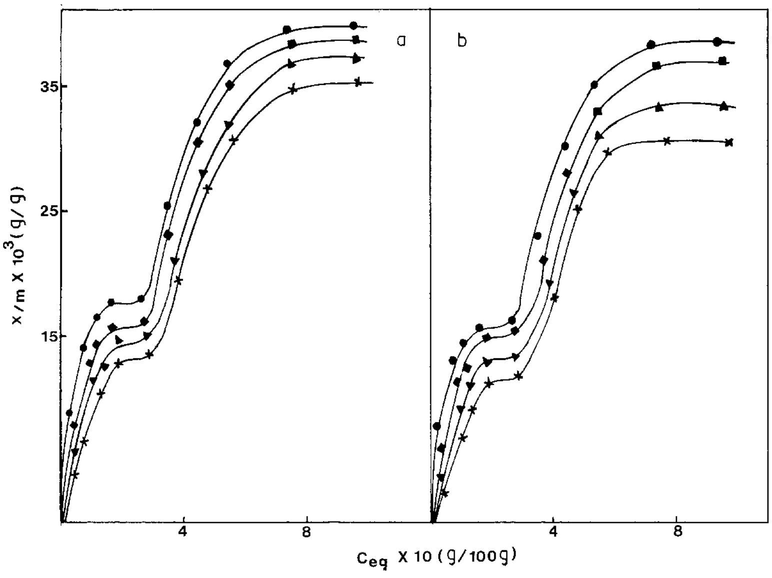

Fig. 4. Plot of specific adsorption against the equilibrium concentration of a) PEA on silica gel, b) PBA on silica gel. Symbols used are the same as in Fig. 2

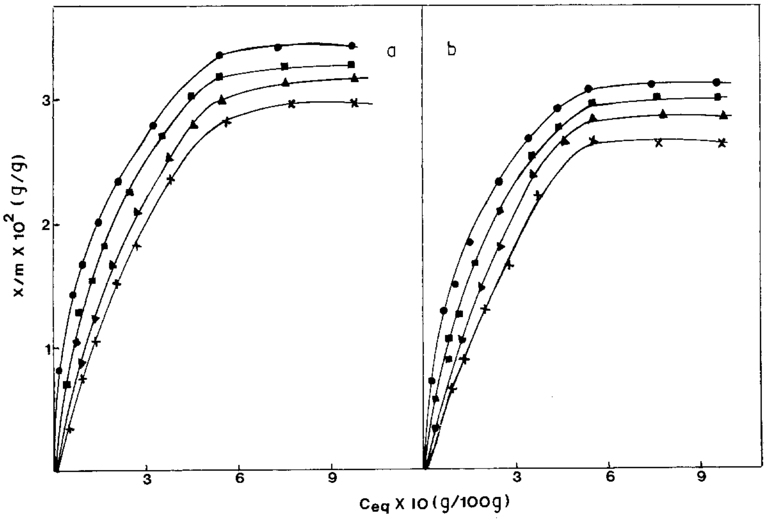

Fig. 5. Plot of specific adsorption against the equilibrium concentration of a) PEA on alumina, b) PBA on alumina. Symbols used are the same as in Fig. 2

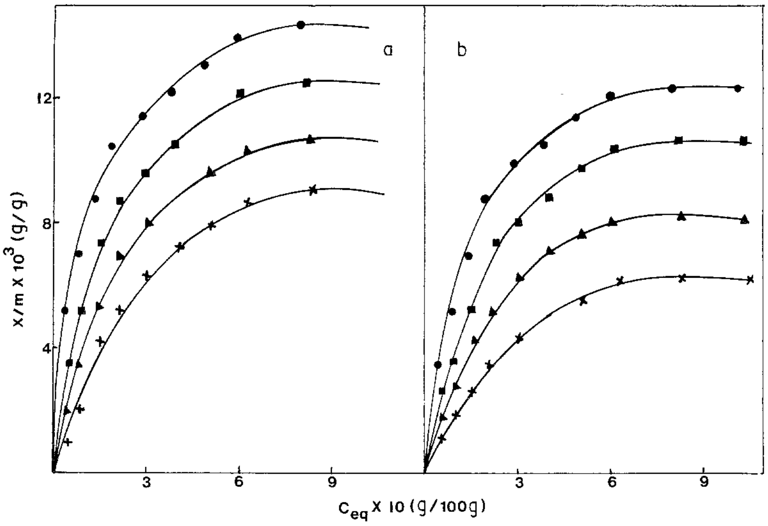

Fig. 6. Plot of specific adsorption against the equilibrium concentration of a) PEA on $CaCO_3$, b) PBA on $CaCO_3$. Symbols used are the same as in Fig. 2

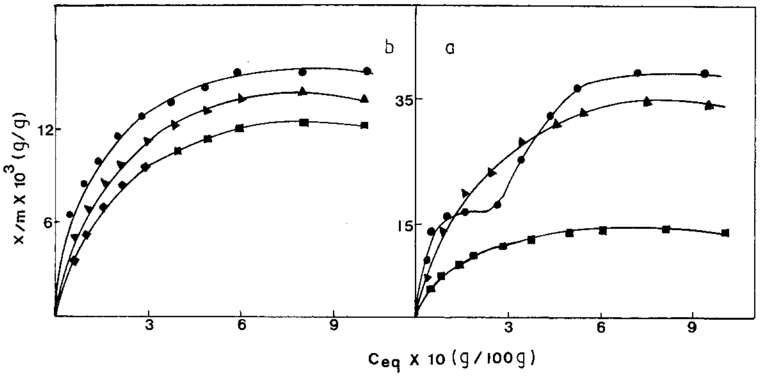

Fig. 7. Plot of specific adsorption against the equilibrium concentration of (at 35°C) a) PEA on ● silica gel; ▲ alumina; ■ $CaCO_3$; b) polyacrylates on $CaCO_3$; ● PMA; ▲ PEA; ■ PBA

The nature of these isotherms is because of polydispersity of the polymer samples and also the specific interaction of adsorbent and polymer. Though molecular weight distribution of these polymers could not be obtained, we assume that the polyacrylates were reasonably polydisperse as they were not fractionated and were prepared by free radical initiation mechanism. In such systems the low molecular weight species were adsorbed initially. These were later displaced by larger molecular weight species. Hence the molecular weight distribution on the adsorbed layer changes with the amount of adsorption.

The ladder-type or S-type isotherms were observed for protein adsorption [8]. This was attributed to the conformational alteration of the proteins during the process of adsorption or due to strong lateral attraction 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 [9, 10].

Polymer adsorption is usually discussed in terms of loop-train-tail conformation, with each chain attached to the surface at one site or at some sites. This is referred to as monolayer coverage [11]. On the other hand, multilayer adsorption is ubiquitous in polymeric systems. Multilayer formation does occur if macromolecules are present as a part of the surface phase, with none of the segments in actual contact with the surface. Nearly two decades ago, calculations by Silberberg [12] anticipated the possibility of multilayer formation. Priel and Silberberg [13] observed multilayer in polystyrene adsorption. The conclusion was drawn from the enhanced (but still microscopic) adsorption observed as non solvent was added to polystyrene solutions.

Table 1. Saturation adsorption values at 30 °C of different polymers on various adsorbents

Polymers	Adsorbed amount on					
	Silica gel	Alumina	$CaCO_3$	Silica gel	Alumina	$CaCO_3$
		(g/g) 10^3			(g/m^2) 10^4	
PMA	48.1	35.7	16.1	1.7	3.7	6.3
PEA	40.0	34.4	14.3	1.4	3.5	5.5
PBA	39.0	30.4	12.9	1.4	3.1	5.0
PAN	91.8	80.0	35.3	3.2	8.2	13.7

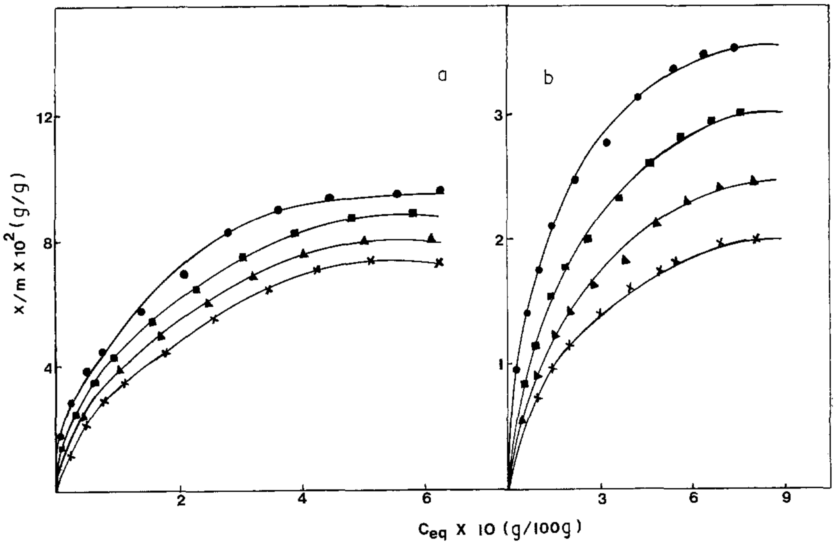

Fig. 8. Plot of specific adsorption against equilibrium concentration of a) PAN on silica gel, b) PAN on $CaCO_3$. Symbols are as in Fig. 2.

When the surface areas of the adsorbents are higher, a larger number of adsorbent sites is available on the surface of the adsorbents. From the surface area determinations, the areas were found to be 284.2, 97.1, and 25.7 m^2/g for silica gel, alumina, and $CaCO_3$, respectively, as mentioned earlier. Hence, it is clear that the silica gel with the highest surface area has more active sites for adsorption, and thus accounts for the highest adsorption among these adsorbents. On the other hand, on the basis of adsorption per unit surface area, the adsorption picture changes drastically where adsorption on $CaCO_3$ is maximum and is least on silica gel (Table 1). This is because at a given total amount of polymer, if the surface area of the adsorbent is small, only very high molecular weight fraction of polymers get adsorbed on the surface and hence the amount adsorbed per unit surface area is high. For $CaCO_3$ that is the case. But when more area is available, as in silica gel, then lower molecular weight species also get adsorbed on the surface. That is, $CaCO_3$ is a better adsorbent on g/m^2 basis because of the preferential adsorption of high molecular weight fraction.

Another interesting feature of the isotherms was the amount of adsorbed polymer decreased with higher alkyl acrylates. Similar observation was reported earlier by Polonskii [14]. This is because 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 polyacrylates, reducing the number of adsorbent sites available for adsorption and, hence, the specific adsorption. The effect is more pronounced in higher alkyl acrylates. This effect is shown in Fig. 7b for polyacrylates–$CaCO_3$ systems.

Polyacrylonitrile

The adsorption isotherms of PAN on silica gel, alumina and calcium carbonate are of general Langmuir type (Figs. 8 and 9). However, the amount of polymer adsorbed is much higher

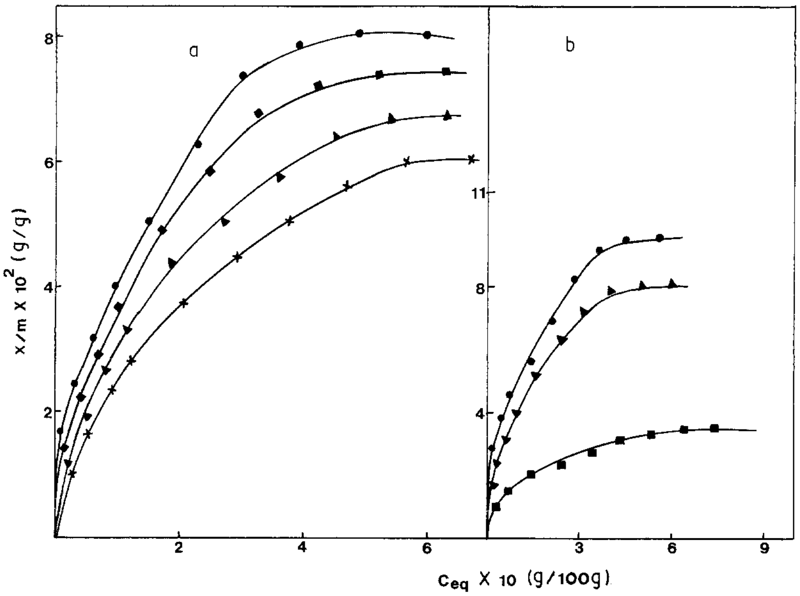

Fig. 9. Plot of specific adsorption against equilibrium concentration of PAN on a) alumina (symbols are as in Fig. 2), b) ● silica gel; ▲ alumina; ■ $CaCO_3$ at 35°C.

compared to the polyacrylates. The semi plateau regions of polyacrylate–silica gel adsorption isotherms were not observed in PAN–silica gel systems. We think that strong lateral attractive forces existing between adsorbed polymer molecules is the reason for this plateau region. Residual forces were not strong enough for other systems. The nitrile moiety is much smaller in size than all acrylate moieties considered here. Hence, relatively more surface active sites were available for PAN adsorption. However, all the PAN molecules adsorbed can be accommodated in a monolayer, resulting in the high affinity isotherms. 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 for on the basis of polymer–adsorbent interactions alone as the studies were conducted in presence of a single solvent.

As discussed before, the higher surface area of silica gel contains more active sites for the polymer molecules to adsorb. Hence, a greater amount of polymer could be accommodated, thus increasing the specific adsorption on this substrate. The surface area of the adsorbents follows the order silica gel > alumina > $CaCO_3$, as mentioned before. The specific adsorption also follows a similar pattern and is represented in Fig. 9b. The amount of polymer adsorbed is generally a function of molecular weight, and the plateau region for the higher molecular weight polymer sometimes extends over the entire experimentally accessible range of concentrations [15, 16]. The viscosity average molecular weight of PAN is more than double that of polyacrylates and the specific amount adsorbed is much higher, too. This indicates that higher PAN molecular weight may also be responsible for the difference in PAN adsorption isotherms with those of acrylates. The isotherm plateau of PAN was at lower equilibrium concentration on all three adsorbents in comparison to those of polyacrylates (Figs. 2–6).

The thermodynamic parameters of adsorption were calculated using the adsorption data obtained at four different temperatures on various adsorbents. The adsorption equilibrium can be written as

$$\text{AD (solid)} + \text{P(Solution)} \rightleftharpoons \text{ADP(Solid)} \qquad (1)$$

where AD is adsorbent and P is polymer. Therefore, the equilibrium constant K is

$$\mathrm{K} = a_{\mathrm{ADP(solid)}}/(a_{\mathrm{AD(solid)}} \cdot a_{\mathrm{p(solution)}}), \qquad (2)$$

where a represents activity. By definition, the activity of any pure solid is taken to be unity. Hence, $a_{\mathrm{AD(solid)}}$ is unity. At very low concentration region where polymer adsorption was of the order of 3 mg or less per gram of the adsorbent (i.e., less than 3 mg in 25.7 m^2 of $CaCO_3$ surface and the ratio further decrease for alumina and silica gel), the solid ADP may be assumed to be almost pure and hence activity would be unity. Therefore, Eq. (2) can be written as

$$K = 1/a_{\mathrm{P(solution)}} = 1/c_{\mathrm{P(solution)}} \,, \tag{3}$$

where C_{P} is the concentration of the polymer solution at the equilibrium condition. The free energy of adsorption ΔG_{ads} can be written as

$$\Delta G_{\mathrm{ads}} = -RT \ln K = RT \ln C_{\mathrm{P}} \,, \tag{4}$$

where R and T have their usual significance. The computation procedure was described in detail in an earlier paper [5]. These relations are valid only at the very dilute region (less than 0.1 g polymer/100 ml solvent) at which it was used. The reproducibility and reversibility of the adsorption process were checked to our satisfaction. The plot of ΔG_{ads} at low concentration region against original concentration was linear (correlation coefficient 0.99). This was extrapolated to original concentration equal to zero and hence the free energy of adsorption at infinite dilution $\Delta G^0_{\mathrm{ads}}$ was obtained. This indicates the free energy change at a given temperature for the adsorption process when that occurs from an infinitely dilute solution (reference state) at atmospheric pressure onto a solid surface. The variation of $\Delta G^0_{\mathrm{ads}}$ with temperature gives $\Delta S^0_{\mathrm{ads}}$ and hence $\Delta H^0_{\mathrm{ads}}$, the entropy and enthalpy of adsorption at infinite dilution respectively.

The computed thermodynamic quantities of adsorption, as mentioned above, are compiled in Tables 2 and 3. It is obvious that the adsorption processes were exothermic with negative entropy changes. Both enthalpy and entropy change follow the order silica gel > alumina > $CaCO_3$ for polyacrylates and PAN. The free energy values were negative, indicating spontaneous processes and they were found to decrease with higher alkyl acrylates. The observations were similar on all three adsorbents. Both in $CaCO_3$–polyacrylates

Table 3. The free energy ($\Delta G^0_{\mathrm{ads}}$), enthalpy $\Delta H^0_{\mathrm{ads}}$, and entropy $\Delta S^0_{\mathrm{ads}}$ of adsorption of polyacrylonitrile at infinite dilution on different adsorbents. (Concentration expressed in g/100 g of solution)

Adsorbent	Temp. °C	$-\Delta G^0_{\mathrm{ads}}$ (kJ mol^{-1})	$-\Delta H^0_{\mathrm{ads}}$ (kJ mol^{-1}	$-\Delta S^0_{\mathrm{ads}}$ (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		

Table 2. The free energy $\Delta G^0_{\mathrm{ads}}$, enthalpy $\Delta H^0_{\mathrm{ads}}$, and entropy $\Delta S^0_{\mathrm{ads}}$ of adsorption of polyacrylates at infinite dilution on silica gel, alumina and $CaCO_3$. (Concentration expressed in g/100 g of solution)

System	$-\Delta G^0_{\mathrm{ads}}$ kJ mol^{-1}				$-\Delta H^0_{\mathrm{ads}}$	$-\Delta S^0_{\mathrm{ads}}$
	30°C	35°C	40°C	45°C	(kJ mol^{-1})	(J mol^{-1}K^{-1})
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

and in $CaCO_3$–PAN systems, the free energy change with temperature was much less prominent in comparison to silica gel and also alumina systems. These data therefore indicate that the interactions of these polymers with silica gel and alumina are much stronger in comparison to the interactions of these polymers with $CaCO_3$. The free energy, enthalpy and entropy of adsorption at infinite dilution for PAN on all adsorbents used were much higher than the corresponding values for the acrylate adsorption. From a study of Tables 2 and 3 it can be surmised that the adsorption processes were enthalpy-driven rather than entropy.

The thermodynamic quantities were also calculated as a function of surface coverage. The amount of polymer adsorbed per unit weight of the adsorbent was kept constant in such calculation (column 2 of Tables 4–7). As the procedure for such calculation is already available [17], we will not present the details here. In calculating thermodynamic quantities by this method, it is inherently expected that the polymer conformation did not change on adsorption. Characteristic IR frequencies of polymers did not show any perceptible change after adsorption, thus indicating the same conformation as before [18]. The thermodynamic parameters computed are compiled in Tables 4–7. The negative isosteric heats obtained indicate that the adsorption processes are exothermic. As more polymer gets adsorbed, the isosteric heat (ΔH_A) decreases linearly. The entropy (ΔS_A) also behaves similarly. That is, the polymer adsorption on the adsorbent surface is an

Table 4. Thermodynamic parameters of adsorption of polyacrylate–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})	$-\Delta H_0$ (kJ mol^{-1})	$-\Delta S_0$ (J mol^{-1}K^{-1})	$-\Delta G_0$(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 5. 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})	$-\Delta H_0$ (kJ mol^{-1})	$-\Delta S_0$ (J mol^{-1}K^{-1})	$-\Delta G_0$(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 6. 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})	$-\Delta H_0$ (kJ mol^{-1})	$-\Delta S_0$ (J $mol^{-1}K^{-1}$)	$-\Delta G_0$(303°K) (kJ mol^{-1})
PMA	0.30	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			

Table 7. 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})	$-\Delta H_0$ (kJ mol^{-1})	$-\Delta S_0$ (J $mol^{-1}K^{-1}$)	$-\Delta G_0$(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			

exothermic process and it could be seen (Tables 4–7) that higher amount of polymer adsorption was associated with more exothermic heat change.

Similar studies were done with hydrolyzed PAN on different types of cellulose [17]. The thermodynamic quantities reported were much lower than the pure PAN systems discussed here. The difference arises because of the lower surface coverage, as the amount adsorbed was less, besides the variation in adsorbate and adsorbent characteristics. The Temkin equation can be written as [17]

$$A \cdot f = 2.3 \log K_0 + 2.3 \log C_{eq} \,, \tag{5}$$

where A, f, K_0, and C_{eq} are amount adsorbed, coefficient of heterogeneity, equilibrium constant at infinite dilution, and equilibrium concentration, respectively. A plot of A vs log C_{eq} taken from the rising part of the curve (i.e., very dilute solution as defined earlier) is linear and, hence, f can be determined at a particular temperature. The energetic heterogeneity of the adsorbent surfaces C' is related with the coefficient of heterogeneity, f, by the relation [17]

$$f = C'/RT - f_0 \,, \tag{6}$$

where f_0 is the coefficient of heterogeneity at infinite temperature. The two quantities C' and f are given in Tables 8 and 9. The slope of ΔS_A-A plot (A is the amount of polymer adsorbed) is m. It has been observed earlier [17] as well as in this study that m is almost equal to f_0R. The m and C' increased as the adsorption decreased. These

Table 8. Surface characteristic parameters obtained for polyacrylates on silica gel, alumina, and $CaCO_3$ by surface coverage approach

System	$f(\mathrm{gl}^{-1})$				$-f_0$	$-m$	$-C$
	30 °C	35 °C	40 °C	45 °C	(gl^{-1})	$(\mathrm{J\,mol}^{-1}\mathrm{K}^{-1})$	$(\mathrm{kJ\,mol}^{-1})$
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	4.56	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

Table 9. Surface characteristic parameters of adsorption of PAN by surface coverage approach

Adsorbents	$f(\mathrm{gl}^{-1})$				$-f_0$	$-m$	$-C$
	30 °C	35 °C	40 °C	45 °C	(gl^{-1})	$(\mathrm{J\,mol}^{-1}\mathrm{K}^{-1})$	$(\mathrm{kJ\,mol}^{-1})$
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

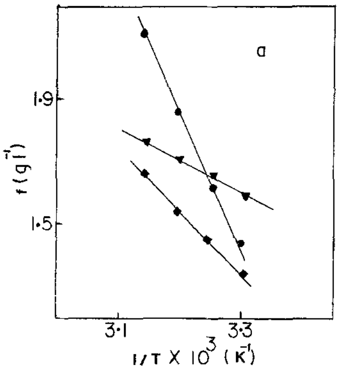

Fig. 10a. Temperature dependence of f for PAN on ● $CaCO_3$; ▲ silica gel; ■ alumina.

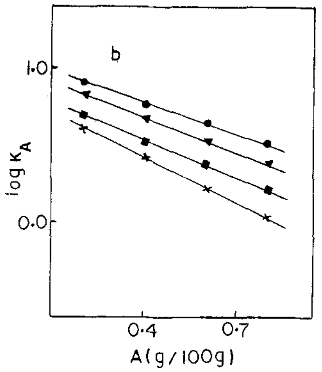

Fig. 10b. Plot of log K_A against amount of PAN adsorbed on $CaCO_3$ at different temperatures. ● 30°C; ▲ 35°C; ■ 40°C; × 45°C

values were exceptionally high for $CaCO_3$ system. The f_0 values for the three adsorbents follow the order

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

and are 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 $>$ $CaCO_3$.

This was found to be true for all polyacrylates and PAN. It can be concluded from the above comparison that the entropy factors produce a definite effect on the process of adsorption of all these polymers used here. The *f* values are linear functions of temperature as are shown in Fig. 10a for some systems. The dependence of log K_A (K_A is the equilibrium constant of adsorption where A amount of polymer was adsorbed per unit of adsorbent) as a function of amount adsorbed was linear on all three adsorbents (Fig. 10b). The ΔS_A linearly changes with ΔH_A. This shows the presence of compensation effect. It should be mentioned here that ΔS^0_{ads} and ΔH^0_{ads} (cf. Tables 2 and 3) are also linearly related. These indicate that the processes under study take place simultaneously with the change in enthalpy and entropy factors and these have determining effects on the affinity of the polymers towards the adsorbents.

Acknowledgement

Financial assistance from the Department of Atomic Energy, Government of India (Grant no. 37/15/88-G) and University Grants Commission, New Delhi, is gratefully acknowledged. Thanks are also due to Dr. V. S. Kaushik and Dr. Unnikrishnan of IPCL, Baroda for ESCA and surface area studies respectively.

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Received September 24, 1992;
accepted May 11, 1993

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