PUBLICATIONS

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[1] Thermodynamics of adsorption of polybutadiene on alumina and silica gel : effect of temperature and solvent.
V. Vangani, R. Joseph, S. Devi and A.K. Rakshit, Colloid Polym. Sci., **269**, 242, (1991).

[2] Viscosity Behaviour of Acrylonitrile - Acrylate Copolymer Solutions in Dimethyl Formamide.
R. Joseph, S. Devi, and A.K. Rakshit, Polymer International, **26**, 89, (1991).

[3] Electrical and Magnetic Properties of Doped Acrylonitrile - Acrylate Copolymers.
R. Joseph and A.K. Rakshit, IUPAC International Symposium Speciality Polymers, Preprints, p-169, Singapore (1990).

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Thermodynamics of adsorption of polybutadiene on alumina and silica gel: effect of temperature and solvent

V. Vangani, R Joseph, S. Devi* and A. K. Rakshit*

Department of Chemistry, University of Baroda, Baroda, India

Abstract The adsorption of polybutadiene (PBR) on alumina and silica gel was studied at different temperatures from cyclohexane and toluene solutions It shows that the adsorption process was dependent on temperature and solvent The adsorption isotherm and the thermodynamic quantities of adsorption were determined and it was observed that the adsorption process from both solvents was similar and the amount of adsorption increased as temperature decreased The silica gel–cyclohexane system was more exothermic than all other systems and was also relatively more ordered

Key words Adsorption, polybutadiene, thermodynamics, silica gel, alumina

Introduction

The adsorption of polymers on an adsorbent is an important phenomenon both from academic and industrial point of view. It is also different in many respects from the adsorption of small molecules [1]. A survey of literature shows that both the sophistication in theoretical developments and the range of experimental observation have been high, although they have not always kept pace with one another [2–10]. In the present study, we used the fundamental thermodynamics in the adsorption process of the title polymer, synthetic polybutadiene, on alumina and silica gel from toluene and cyclohexane solutions at 30, 35 and 40 °C.

Experimental

Polybutadiene (PBR) was obtained from Indian Petrochemicals, Vadodara, India Its composition was cis-1,4 (> 96%), trans-1,4 (1–2%), and vinyl-1,2 (1–2%) [11] This was dissolved in toluene, filtered and then re-precipitated by adding methanol The polymer so obtained was vacuum dried before further use It has narrow molecular weight distribution [11] and its viscosity molecular weight was $4\ 14 \times 10^5$ Methanol (GPR, E. Merck), toluene (synthesis grade, E Merck), and cyclohexane (chromatography grade, E Merck) were distilled before use Cyclohexane was passed through a column of activated silica gel and alumina to remove the traces of any olefinic impurities present

TLC grade silica gel (with 13% $CaSO_4$, mesh size > 100) was obtained from Acme Synthetic Chemicals, Bombay, India Alumina (acidic, mesh size > 100) was obtained from BDH (Glaxo Laboratories), India Surface areas of silica gel and alumina were 192 9 m^2/g and 97 1 m^2/g, respectively, and were obtained by BET method using nitrogen gas Both were dried for 3 h at 125 °C before use The probability of the presence of surface impurities in silica gel and alumina was checked by X-ray photoelectron spectroscopy (Fig 1) and no impurity was observed The spectra were recorded on a VG Scientific Escalab MK II spectrometer using Mg Kα radiation under vacuum, which was better than 5×10^{-7} mbar [12] The SEM photographs were taken by a Jeol JSM-T3 scanning electron microscope after gold coating by using the usual procedure

PBR solution at highest concentration was made by dissolving weighed amount in a known volume of solvent Other desired solutions were made from it by dilution The weighed amount of adsorbents were placed in a series of jacketed bottles and known amount of the desired solution was added to each one of them. These were then placed on a shaker for continuous shaking Thermostated water (± 0 1 °C) was pumped through these jacketed bottles for about 3 h before the polybutadiene was estimated The process was repeated a few times until two consecutive readings were within 2% of each other The same procedure was used at all temperatures Time required to get a reproducible value varied with system as well as temperature In most cases, it was more than 24 h In some preliminary runs, we determined the adsorption values at

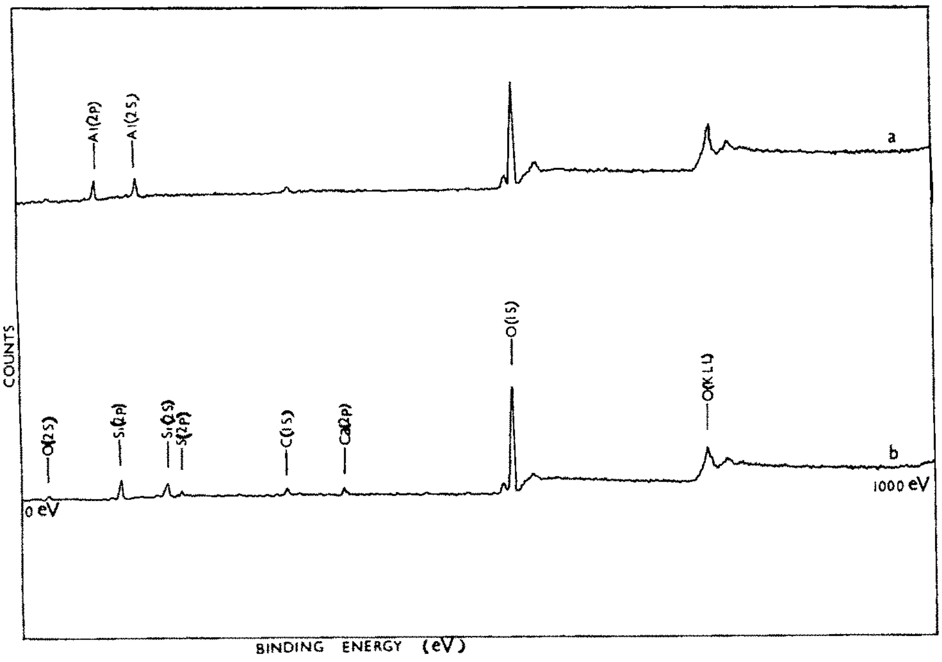

Fig 1 X-ray photo electron spectra of a) alumina, b) silica gel

intervals of 3, 5, and 7 days to check on the probable quasi-equilibrium of the systems. We feel that such problem does not exist in this study

The concentration of the polymer in solution was determined by both UV spectroscopy and gravimetry For the cyclohexane solvent system, absorbance was measured at λ_{max} (240 nm) The concentration was computed from a calibration curve obtained earlier This process was followed by gravimetry and the difference between the gravimetric and spectroscopic results was less than ± 1%. In the gravimetric procedure [13, 14], dry small-weighed beakers were taken. To obtain complete dryness, 2 ml of solution was pipetted out in a beaker and placed under low vacuum at 50 °C. The beakers were then weighed to determine the amount of residual polymer present The process was repeated until two consecutive weighings gave the same result Each point was duplicated simultaneously to check for the reproducibility of the result Duplicate blank experiments were also conducted with pure solvents PBR concentration studied ranged from 0.05% (w/v) to 1 2% (w/v). As UV spectroscopy could not be used when toluene was solvent, only the gravimetric procedure was used.

Results and discussion

In Figs. 2–4, the amount of PBR adsorbed per gram of adsorbent are plotted against the equilibrium concentration of PBR (C_{PBR}). The effects of solvent and temperature in both cases are similar although the amounts adsorbed are different. The amount of adsorption as a function of solvent is similar in both cases, with adsorption from cyclohexane being higher than that from toluene. These isotherms, which are relatively more sharp than rounded, show both maxima and minima and at higher concentration they finally become level. Such similarity of isotherms also was observed earlier [15]. It was suggested [16, 17] that as the polymer is adsorbed on the surface of the adsorbent, a second phenomenon, polymer spreading on the surface of the adsorbent, starts. The rate of adsorption is expected to be proportional to the concentration of the polymer in solution, and the rate of spreading is expected to be proportional to the concentration of the adsorbed polymer on the surface. Hence, the more the polymer spreads on the surface, the less is the amount adsorbed. The complicated nature of polymer isotherms is probably due to these two antagonistic effects, as well as some others. In Figs. 5 and 6, SEM photographs of the polymer adsorbed surface of alumina and silica gel are shown respectively. In both cases, the adsorbent was removed from the jacketed bottle after 24 h, dried, divided into two parts and then a SEM photograph was taken of one part. The SEM of the second part was taken after two more days. It can

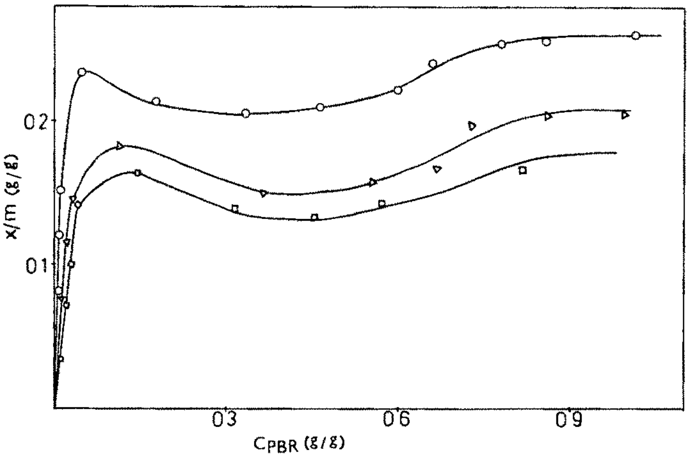

Fig 2. Plot of adsorption per gram of silica gel (x/m) against equilibrium concentration of PBR in cyclohexane at different temperatures ○ 30 °C, △ 35 °C, □ 40 °C

be concluded easily from the photographs that the system did change with time. One can see more polymer sheath on the surface and a decrease in the rough edges of the inorganic material. This we assume is a reasonably good proof of polymer spreading as well as of multilayer formation, as has been observed earlier with polystyrene [18]. Moreover, from viscosity study, voluminosity [19] was calculated and hence the Simha shape factor [20], which was 2.5 [21], thereby suggesting that the polybutadiene had a spherical conformation in solution in both solvents. It is difficult to visualize the conformational nature of the polymer at the solid–liquid interface, but as it is a linear polymer we thought that it could show the train, loop and tail segments, as was first suggested by Jenkel and Rumbach [22], 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 in solution [23].

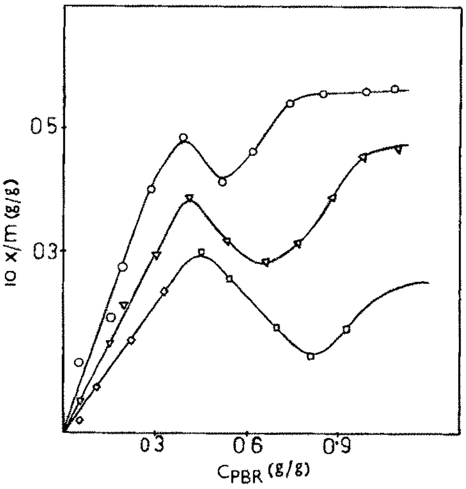

Fig. 3 Plot of adsorption per gram of silica gel (x/m) against equilibrium concentration of PBR in toluene at different temperatures. ○ 30 °C, △ 35 °C, □ 40 °C

The adsorption can be written in the following way:

$$\mathrm{A\ (solid) + PBR\,(solution) \rightleftharpoons APBR\,(solid)}\ ,$$

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

$$K = 1/a_{\mathrm{PBR\,(solution)}} \simeq 1/C_{\mathrm{PBR\,(solution)}}\ .$$

Therefore, the free energy of adsorption is

$$\Delta G_{\mathrm{ads}} = -RT \ln K = RT \ln C_{\mathrm{PBR}}\ ,$$

where R and T have their usual significance. To obtain the free energy of adsorption at infinite dilution $\Delta G^0_{\mathrm{ads}}$, the ΔG_{ads} values in the low concentration region were plotted against C_{PBR}, linearity was observed and the line was extrapolated to $C = 0$. We believe that $\Delta G^0_{\mathrm{ads}}$ values represent relative variation in the system and indicate the free energy change at a given temperature from an infinitely dilute solution (reference state) at atmospheric pressure onto a solid surface. The $\Delta G^0_{\mathrm{ads}} - T$ plot showed linearity, the slope and intercept being $-\Delta S^0_{\mathrm{ads}}$ and $\Delta H^0_{\mathrm{ads}}$, respectively. In Table 1, we present the thermodynamic values so calculated. It is obvious from the data that all

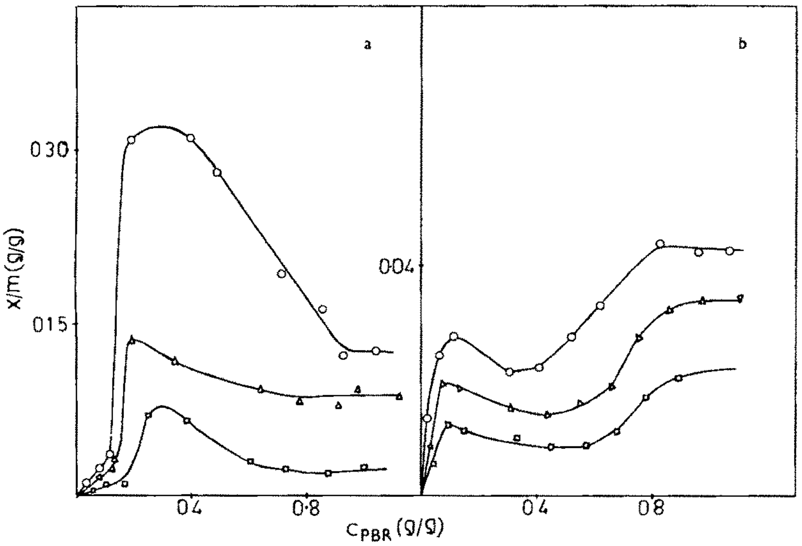

Fig. 4 Plot of adsorption per gram of alumina (x/m) against equilibrium concentration of PBR a) in cyclohexane and b) in toluene at different temperatures ○ 30 °C, △ 35 °C, □ 40 °C

adsorption processes are 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. We have already mentioned the possibility of spreading of adsorbed polymer on the adsorbent surface. Moreover, the i) polymer–solvent, ii) solvent–adsorbent and iii) polymer–adsorbent interactions also complicate the systems.

Table 1 Free energy ΔG^0_{ads}, the enthalpy ΔH^0_{ads} and the entropy ΔS^0_{ads} of PBR adsorption at infinite dilution for different systems (Concentration is expressed in g/100 g solution)

System	Temp (°C)	ΔG^0_{ads} (kJ)	ΔH^0_{ads} (kJ)	ΔS^0_{ads} (JK^{-1})
1 Silica gel	30	− 9.36		
+	35	− 9.03	− 31.8	− 74.0
toluene	40	− 8.66		
2. Alumina	30	− 10.62		
+	35	− 9.79	− 46.0	− 116.7
toluene	40	− 9.49		
3 Silica gel	30	− 16.48		
+	35	− 14.14	− 158.5	− 468.4
cyclohexane	40	− 11.79		
4 Alumina	30	− 8.95		
+	35	− 8.61	− 28.7	− 65.2
cyclohexane	40	− 8.32		

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 poor [16, 24]. It is well known that the adsorption is more from a poor solvent than from a good solvent [25]. We determined that the intrinsic viscosities of the cyclohexane–PBR and the toluene–PBR systems are 2.38 and 2.48 at 30 °C, respectively [21], signifying that toluene is a good solvent and, hence, there will be less adsorption from this solvent system. The solubility parameter is another criterion used to characterize the solvent [26]. The solubility parameter 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 [27, 28], which is contrary to what we expected from intrinsic viscosity. This type of conflicting observation was also observed earlier [6].

The other complicating factor is solvent-adsorbent interaction. The characteristics of adsorbent surfaces are important. It is a well-known fact that the aromatics are easily adsorbed on the alumina surface, and the adsorption occurs on the Al^{3+} site of the alumina [29]. Hence, qualitatively we expected that the toluene will be adsorbed on

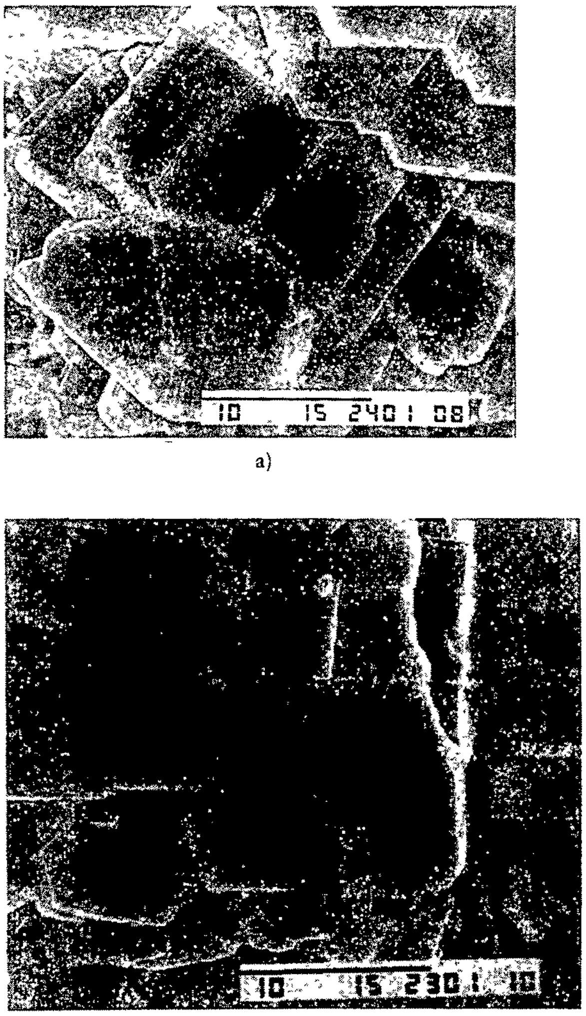

Fig 5 Scanning electron micrograph of polybutadiene adsorbed on alumina a) after 2 days, b) after 4 days

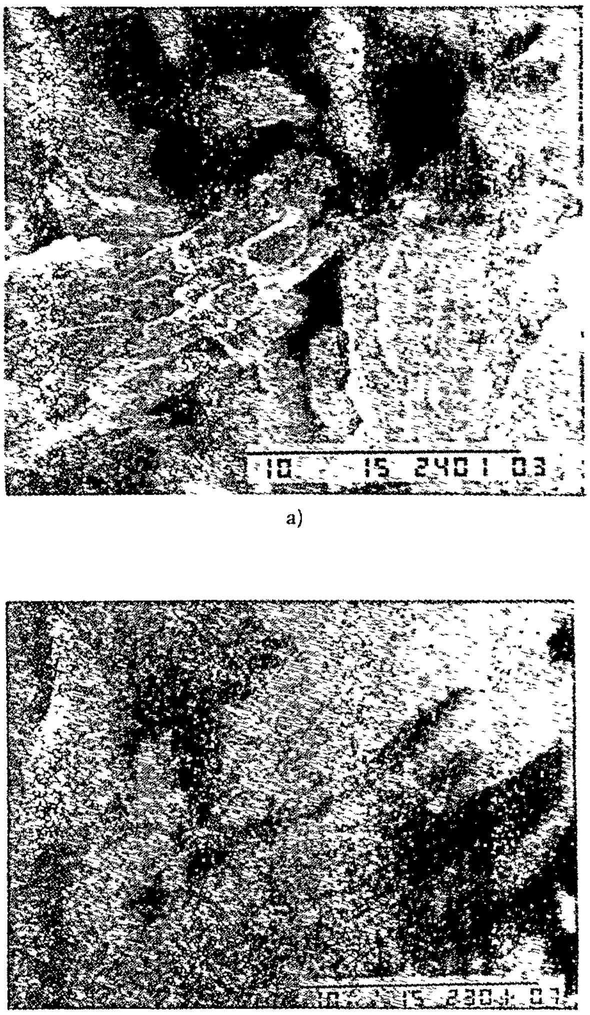

Fig 6 Scanning electron micrograph of polybutadiene adsorbed on silica gel a) after 2 days, b) after 4 days

the surface and thereby the polybutadiene will be less adsorbed from toluene solution than from cyclohexane solution. This is also true for silica gel, where the surface 'OH' groups on which the adsorption occurs are not all equivalent [29]. The experimental observation, the prediction from the solvent strength parameter values of eleutropic series [30] 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, contributed to the overall thermodynamic quantities obtained.

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Authors' address

Prof. A K Rakshit
Department of Chemistry
Faculty of Science
M S. University of Baroda
Baroda 390 002, India

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Viscosity Behaviour of Acrylonitrile–Acrylate Copolymer Solutions in Dimethyl Formamide

Roychen Joseph, Surekha Devi & Animesh Kumar Rakshit*

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda 390 002, India

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Abstract: The viscosities of dimethyl formamide solutions of acrylonitrile–acrylate copolymers were determined at 30, 35, 40 and 45°C using an Ubbelohde viscometer. The viscosities of homopolymer solutions were also studied. The homopolymers of acrylonitrile and also of methyl, ethyl and butyl acrylates were synthesised in the laboratory. The random copolymers were synthesised by a solution polymerisation technique keeping the acrylonitrile:acrylate ratio as 1:1, 1:2 and 1:3 (w/w). The intrinsic viscosity for each system was computed as a function of temperature. The activation parameters of viscous flow were calculated using the Frenkel–Eyring equation. Voluminosity for all systems was also computed. From intrinsic viscosity and voluminosity data it was concluded that the polymer molecules are spherical in the dimethyl formamide solutions.

Key words: acrylates, acrylonitrile, copolymer, viscosity, DMF, shape factor

INTRODUCTION

In continuation of our studies of adsorption of polymers[1] on inorganic substrates, which are used in the paint industry, or are used as fillers, a series of homopolymers and copolymers of acrylonitrile and different acrylates, e.g. methyl acrylate (MA), ethyl acrylate (EA) and butyl acrylate (BA), have been synthesised in various monomer ratios. Difficulty in moulding of polyacrylonitrile has restricted its application in the homopolymer form because of its high glass transition temperature. Improvement in various properties to a large extent can be achieved through copolymerisation with a suitable monomer. Acrylates have comparatively low T_g values and hence acrylonitrile–acrylate copolymers are expected to show better processibility. Hence these copolymers were chosen for our study. Characterisation of these polymers is needed to understand the overall process of adsorption. The determination of rheological properties of polymer solutions is an important tool for characterisation. In this paper results of viscosity studies of homopolymer and copolymer solutions in dimethyl formamide (DMF) at four different temperatures are presented. Polymer solutions show both Newtonian and non-Newtonian flow,[2] the latter at higher concentrations. At lower concentrations Newtonian laminar flow is observed. From viscosity data at different temperatures, the activation entropy and enthalpy of viscous flow were calculated. The intrinsic viscosities of the polymer solutions at all temperatures were also computed. The polymer–solvent interaction is an important parameter and is a function of the placement of the monomer units in the copolymer.[3] This will affect the conformation of the polymers and hence the viscosity of the polymer solutions[4,5] and thereby the intrinsic viscosity. Hence we studied the viscosity of these polymer solutions in dimethyl formamide to get an insight of the conformational changes in these polymers.

EXPERIMENTAL

Acrylonitrile (Fluka) and methyl, ethyl and butyl acrylates (National Chemicals, Baroda, India) were

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* Author to whom all correspondence should be addressed.

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purified by washing with 1% NaOH aqueous solution and then with distilled water until free of NaOH. They were then dried over $CaCl_2$, distilled and the middle fraction was used. A solution polymerisation technique was used for synthesising the copolymers and homopolymers. The acrylonitrile acrylate ratios for the various copolymers were varied. They were 1 1, 1 2 and 1 3 (w/w) symbolised as $ANXA_{11}$, $ANXA_{12}$ and $ANXA_{13}$ where X stands for methyl, ethyl or butyl. The monomers were dissolved in the required weight ratios in four times the quantity of dimethyl formamide (DMF). Benzoyl peroxide (1% w/w) was used as initiator, and the mixture was kept at 85°C with continuous stirring for 6 h. The product was precipitated in an excess quantity of methanol and dried over vacuum. The product was then Soxhlet extracted with toluene to remove homopolymers of the acrylates, dried thoroughly and dissolved in acetone. The copolymers were soluble in acetone but polyacrylonitrile (PAN) was not and hence the copolymers could be separated from this homopolymer. The copolymers were then precipitated out in methanol, and dried in vacuum to a constant weight. The experimental mole ratios of acrylonitrile and acrylates were then calculated from the observed nitrogen concentrations.

The viscosity, η, of these homopolymer and copolymer solutions in dimethyl formamide was determined using an Ubbelohde viscometer kept vertically in a thermostatted bath at the required temperature (±0 05°C). The range of concentration of polymer solutions was from 0 2 to 0 8 g/dl. The efflux flow time for all solutions was more than 100 s. The density of the polymer solutions was taken to be that of the solvent.

RESULTS AND DISCUSSION

In Table 1, the intrinsic viscosities, $[\eta]$, of all the systems at various temperatures are given. They were computed by a well known procedure.[6] The correlation coefficient was always 0 99 or better. It can be seen that $[\eta]$ decreases as the temperature increases and $[\eta]$–T plots are always linear with negative slope. A few representative plots are shown in Fig 1. This indicates that the swelling of the polymer coils is not great in these systems and that there are lower critical solution temperatures (LCST) for these polymer solutions. A critical look at the intrinsic viscosity data (Table 1) shows that in general as the weight ratio of acrylonitrile in the copolymers decreases, the intrinsic viscosity also decreases at all temperatures, the only exception being for the acrylonitrile ethyl acrylate copolymers. In this case a minimum occurs as the ratio decreases, but at higher temperatures the minimum becomes less prominent. The intrinsic viscosity change with temperature for homopolymer solutions is similar to that for copolymer solutions. The higher the intrinsic viscosity, the better the solvent at that temperature.[7] DMF is a better solvent for the ethyl acrylate systems and PAN than for the other systems. It is also seen from Table 1 that

TABLE 1 Intrinsic viscosity of various copolymers and homopolymers at different temperatures in dimethyl formamide solution

Sample no	Polymers (feed ratio) g/g (AN XA)	Expt mole ratio (AN XA)	Intrinsic viscosity $[\eta]$ (dl/g)			
			30 C	35 C	40°C	45°C
S1	$ANMA_{11}$	1 0 86	0 294	0 283	0 274	0 266
S2	$ANMA_{12}$	1 1 40	0 258	0 251	0 242	0 237
S3	$ANMA_{13}$	1 2 27	0 249	0 240	0 229	0 221
S4	$ANEA_{11}$	1 0 58	0 385	0 381	0 375	0 372
S5	$ANEA_{12}$	1 0 98	0 336	0 331	0 328	0 320
S6	$ANEA_{13}$	1 1 36	0 365	0 353	0 342	0 327
S7	$ANBA_{11}$	1 0 52	0 295	0 289	0 281	0 275
S8	$ANBA_{12}$	1 0 82	0 288	0 282	0 275	0 270
S9	$ANBA_{13}$	1 0 96	0 267	0 255	0 250	0 245
S10	PMA		0 255	0 251	0 248	0 245
S11	PEA		0 347	0 343	0 339	0 335
S12	PBA		0 256	0 252	0 249	0 245
S13	PAN		0 727	0 721	0 712	0 704

[a] AN = acrylonitrile, MA = methyl acrylate, EA = ethyl acrylate, BA = butyl acrylate. Subscripts 11, 12 and 13 signify 1 g of AN and 1, 2 or 3 g of second component in the copolymer

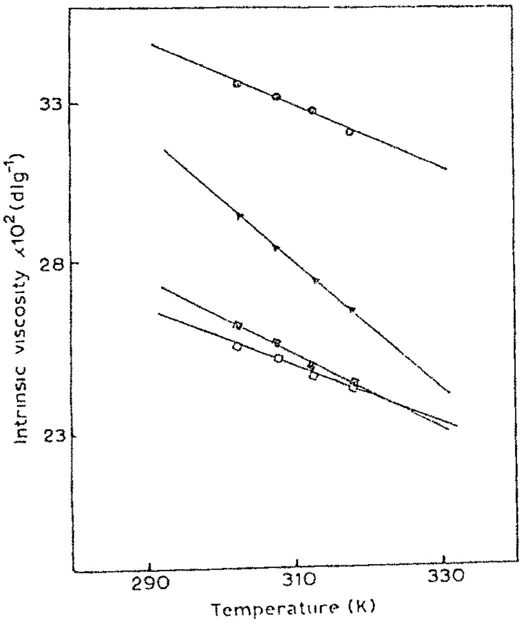

Fig 1 Plots of intrinsic viscosity (dl/g) against temperature ⊛ S5 ▲ S1 ▨ S9 ☐ S10

as the composition of the copolymers changes, with increasing acrylate concentration DMF is a little worse solvent. This is true for all the copolymer systems.

The viscosities of the polymer solutions were determined at different temperatures for different concentrations. The viscosity is affected by the variation in the temperature. The well known Frenkel–Eyring equation[8] for viscous flow is

$$\eta = (Nh/V)\exp(\Delta G^{\ddagger}_{\text{vis}}/RT) \qquad (1)$$

where V is the molar volume of solution, N is Avogadro's number, h is Planck's constant, R is the gas constant, T is temperature and $\Delta G^{\ddagger}_{\text{vis}}$ is the activation free energy for the viscous flow. Equation (1) can be rewritten as

$$\begin{aligned}\ln(\eta V/Nh) &= (\Delta G^{\ddagger}_{\text{vis}}/RT)\\ &= (\Delta H^{\ddagger}_{\text{vis}}/RT) - (\Delta S^{\ddagger}_{\text{vis}}/R) \qquad (2)\end{aligned}$$

where $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ are the activation enthalpy and entropy change for the viscous flow $\ln(\eta V/Nh)$ was plotted against T^{-1} and the plot was linear with correlation coefficient 0·99 or better for all systems The $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ quantities were thus computed for all systems Some representative plots are shown in Fig. 2

The values of $\Delta G^{\ddagger}_{\text{vis}}$, $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ are presented in Table 2. V is the molar volume of the solution, but the molar volume of a polymer solution is an enigma and hence the molar volume of the solvent was used in the calculations because the density of the polymer solution and that of the solvent are generally the same[9] In all these systems $\Delta H^{\ddagger}_{\text{vis}}$ and $\Delta S^{\ddagger}_{\text{vis}}$ are constant quantities, independent of temperature, which signifies that the systems are not cross-linked It is also observed that the heats of activation of viscous flow are generally positive and decrease as the concentration of the polymer in solution decreases (Table 3) The values are not large, the highest value observed was around 10 kJ/mol for PAN at 0 8 g/dl concentration The entropies of activation of the viscous flow process are also low and negative, indicating that the polymer structures are poorly ordered in this solvent system Although there seems to be a decrease in $\Delta S^{\ddagger}_{\text{vis}}$ values for almost all the systems as a function of polymer concentration with the exception of PAN, we believe that the changes are not significant and that at least in these copolymer systems it can be safely assumed that $\Delta S^{\ddagger}_{\text{vis}}$ is constant independent of composition and concentration The free energy of activation of viscous flow, $\Delta G^{\ddagger}_{\text{vis}}$, has also been calculated for all the conditions From Table 2 it can be seen that $\Delta G^{\ddagger}_{\text{vis}}$ is independent of temperature and is similar for all the systems

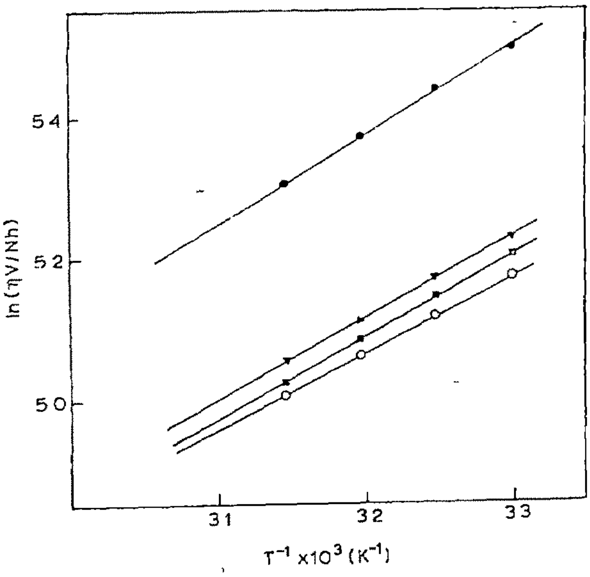

Fig. 2. Plot of $\ln(\eta V/Nh)$ versus T^{-1} ●, S13, ▲, S5, ■, S1, ○, S9

TABLE 2. Free energy $\Delta G^{\ddagger}_{\text{vis}}$, enthalpy $\Delta H^{\ddagger}_{\text{vis}}$ and entropy $\Delta S^{\ddagger}_{\text{vis}}$ of activation for the viscous flow of the copolymers in dimethyl formamide (0 8 g/dl) solution

Sample	$\Delta G^{\ddagger}_{\text{vis}}$ (kJ/mol)				$\Delta H^{\ddagger}_{\text{vis}}$ (kJ/mol)	$\Delta S^{\ddagger}_{\text{vis}}$ (J/mol deg)
	30°C	35°C	40°C	45°C		
S1	13 1	13 2	13 2	13 3	9 4	−12 3
S2	13 1	13 1	13 2	13 3	9 2	−12 9
S3	13 0	13 1	13 2	13 3	8 9	−13 6
S4	13 3	13 4	13 4	13 5	9 4	−13 0
S5	13 2	13 3	13 3	13 4	9 1	−13·6
S6	13 2	13 3	13 4	13 4	9 6	−12·1
S7	13 1	13 2	13 3	13 3	9 0	−13 7
S8	13 1	13 2	13 2	13 3	9 1	−13 3
S9	13 1	13 1	13 2	13 2	9 0	−13 3
S10	13 0	13 1	13 2	13 3	8 9	−13 8
S11	13 2	13 3	13 3	13 4	8 9	−14 0
S12	13 1	13 1	13 2	13 3	9 0	−13 5
S13	13 9	13 9	14 0	14 1	10 4	−11 4

TABLE 3. Free energy $\Delta G^{\ddagger}_{\text{vis}}$, enthalpy $\Delta H^{\ddagger}_{\text{vis}}$ and entropy $\Delta S^{\ddagger}_{\text{vis}}$ for the viscous flow at 30°C with various concentration of polymer ANMA$_{11}$ (Sample S1)

Concentration of Polymer soln (g/dl)	$\Delta G^{\ddagger}_{\text{vis}}$ (kJ/mol)	$\Delta H^{\ddagger}_{\text{vis}}$ (kJ/mol)	$-\Delta S^{\ddagger}_{\text{vis}}$ (J/mol deg)
0 8	13 11	9 4	12 32
0 6	12 95	9 2	12 48
0 48	12 89	9 0	12 88
0 40	12 81	8 9	12 90
0 20	12 71	8 8	12 96

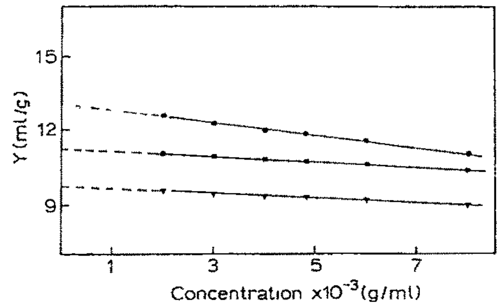

Fig 3 Plot of Y versus concentration (g/ml) where $Y=(\eta_r^{0.5}-1)/[C(1.35\eta_r^{0.5}-0.1)]$
●, S5, ■, S7, ▼, S2

The Frenkel–Eyring equation of viscous flow has also been written as[10]

$$\eta = A\exp(\Delta G^{\ddagger}_{\mathrm{vis}}/RT) \tag{3}$$

where the pre-exponential factor A was difficult to determine. It has been suggested though that A is approximately equal to 10^{-3} poise[11] Comparing this relation with eqn (1) it is clear that $A \simeq (Nh/V)$ Using appropriate units it is observed that (Nh) itself is approximately equal to 10^{-3} signifying that the molar volume is 1 ml This seems to be unlikely and hence we suggest that eqn (2) should always be used to compute the activation parameters of the viscous flow with V as the molar volume of the solvent The relative viscosity data at any concentration, η_r, helps us in calculating the voluminosity V_E of polymer solutions Recently it has been used[12] to determine the shape of protein molecules in a solution V_E was calculated by plotting Y against C where C is concentration in g/ml and

$$Y=(\eta_r^{0.5}-1)/[C(1.35\eta_r^{0.5}-0.1)]$$

The plot was linear and was extrapolated to $C \to 0$ (Fig 3) and V_E was obtained from the intercept The intrinsic viscosity $[\eta]=\nu V_E$ where ν is the shape factor[13] The shape factor is a quantity which gives an idea of the shape of the particles in the solution If it is 2·5, the particles are spherical in nature If the particles in solution are oblate, or prolate, the ν values are different[14,15] For all systems studied at all temperatures ν was found to be equal to 2.5 (Table 4) indicating that in dilute solutions the copolymers of acrylonitrile and the acrylates are spherical in nature The voluminosity (ml/g at infinite dilution) is a function of temperature and is a measure of the volume of the solvated polymer molecules As the temperature increases the solvation decreases and hence V_E decreases. This decrease is linear in nature though the rates of change are different This indicates that the effects of temperature on the polymer–solvent interaction are different Moreover, in general, the higher the amount of acrylate in the copolymer the less the solvation Hence we can conclude that the polymer–solvent interaction is affected by the copolymer composition, temperature, etc, although the conformation of the polymer molecules in dimethyl formamide solution is spherical at all temperatures regardless of the amount of acrylate and type of acrylate present

TABLE 4 Voluminosity V_E at different temperatures and the shape factor ν at 40°C

Sample	V_E (ml/g)				$\nu_{40\,°C}$
	30°C	35°C	40°C	45°C	
S1	11.68	11.29	10.92	10.62	2.51
S2	10.32	9.97	9.70	9.46	2.49
S3	9.95	9.58	9.30	8.99	2.46
S4	15.35	14.99	14.62	14.48	2.56
S5	13.39	13.31	13.00	12.97	2.51
S6	14.45	14.16	13.61	12.99	2.51
S7	11.74	11.54	11.22	11.04	2.51
S8	11.46	11.18	10.91	10.78	2.52
S9	10.30	10.16	9.95	9.69	2.51
S10	28.27	27.72	27.05	26.85	2.55
S11	10.19	9.95	9.90	9.69	2.50
S12	13.64	13.51	13.40	13.25	2.53
S13	10.18	10.01	9.90	9.78	2.51

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