CHAPTER -4

PHYSICO-CHEMICAL STUDIES OF POLYMER -SURFACTANT INTERACTION

4.1 Preview

4.2 Results and Discussion

- **a) Critical aggregation concentration (cac) and polymer saturation point (psp)**
- **b) Thermodynamic Parameters**
- **c) Interfacial Parameters**
- **d) Thermodynamics of Adsorption**
- **e) Viscosity Studies**
- **f) Cloud Point Determinations**
- **g) Steady State Fluorescence Quenching**
- **h) Small Angle Neutron Scattering**

4.1 Preview

The behaviour of surfactants and polymers in aqueous solutions has been well understood[3]. Both polymers and surfactants can form a range of solutions including liquid crystalline phases and exhibit unique properties[334]. However, the properties of polymer amphiphile mixtures are quite complex and the study of their key features have gained importance only during the recent past.

The interest in polymer-surfactant interactions is mainly due to new and specific technological applications. In this aspect the physical properties of the polymer play a relevant role in determining the industrial products because they determine the degree of fluidity, the level of foaming[335], the adsorption on solid surfaces[234], etc. In continuation to the interest in this laboratory on the properties of polymers[324,336] and surfactants[85,213,214,337,338], it was decided to study their properties in presence of each other[339].

The physicochemical characterization involves determination of critical aggregation concentration (cac) and polymer saturation point (psp) by the surface tension and conductance measurements. The surface tension method affords a simple and informative method for studying mixtures of two components, one of which is highly surface active and the other relatively inactive at the air / water interface. Using conductance data, the degree of ionization 'α' and the thermodynamic parameters associated with psp at different temperatures were calculated. The surface tension data was used to evaluate surface parameters like maximum surface excess Γ_{max} and minimum area per molecule A_{min} and the thermodynamic parameters of adsorption. Viscosity measurements of polymers were carried out at various surfactant concentrations. The intrinsic viscosity $[\eta]$, shape factor, activation energy parameters at infinite dilution and the expansion factor ratios in presence of different surfactant concentrations were computed.

Cloud point determinations of nonionic surfactant Triton X100 in presence of different concentrations of polymer were done. Aggregation number (N_{agg}) determination for TX100 in presence of these polymers were carried out. Small angle neutron scattering (SANS) studies for PAA-SDS and PAA-CTAB systems were done.

4.2 Results and Discussion

(i) <u>Critical aggregation concentration (cac) and polymer saturation point (psp)</u> : The natural starting point of discussion of polymer-surfactant interactions appears to consider the effect of polymer molecules on surfactant self assembly, particularly micelle formation. The onset of aggregation of surfactant in the presence of polymer can be characterized by the critical aggregation concentration. This concept was developed by Chu and Thomas[340]. This notion indicates that the surfactant molecules form aggregates upon interaction with the surfactants. The surface tension - log concentration (log C) plots show two breakpoints (Fig. 37). As mentioned earlier, the first break is termed as cac or T_1 and on increasing the surfactant concentration a second break point is observed. This is termed as polymer saturation point (psp) or T_2. Above this concentration regular micelles are in dynamic equilibrium with polymer-surfactant aggregates[139]. The existence of two critical concentrations in case of polymer-surfactant systems was first reported by Jones[134], for the SDS/PEO system. The values of cac and psp are generally located below and above the corresponding cmc of the surfactant respectively. The micelles formed at cac have smaller aggregation number, and a higher degree of charge delocalization than those of regular micelles[341]. The polymer chains are believed to envelope the micelles with the hydrophilic regions of the chain associated with the ionic head groups and the hydrophobic regions protecting the exposed hydrophobic areas of the micelle. Such a formation which limits the exposure of hydrophobic areas of the micelles with water is obviously energetically favourable and therefore the micelles form at a lower surfactant concentration i.e. T_1. In other words, the stabilization of the interface between the hydrophobic core of the micelles and water is considered as a major driving force for polymer - micelle interactions. This lead to the development of the

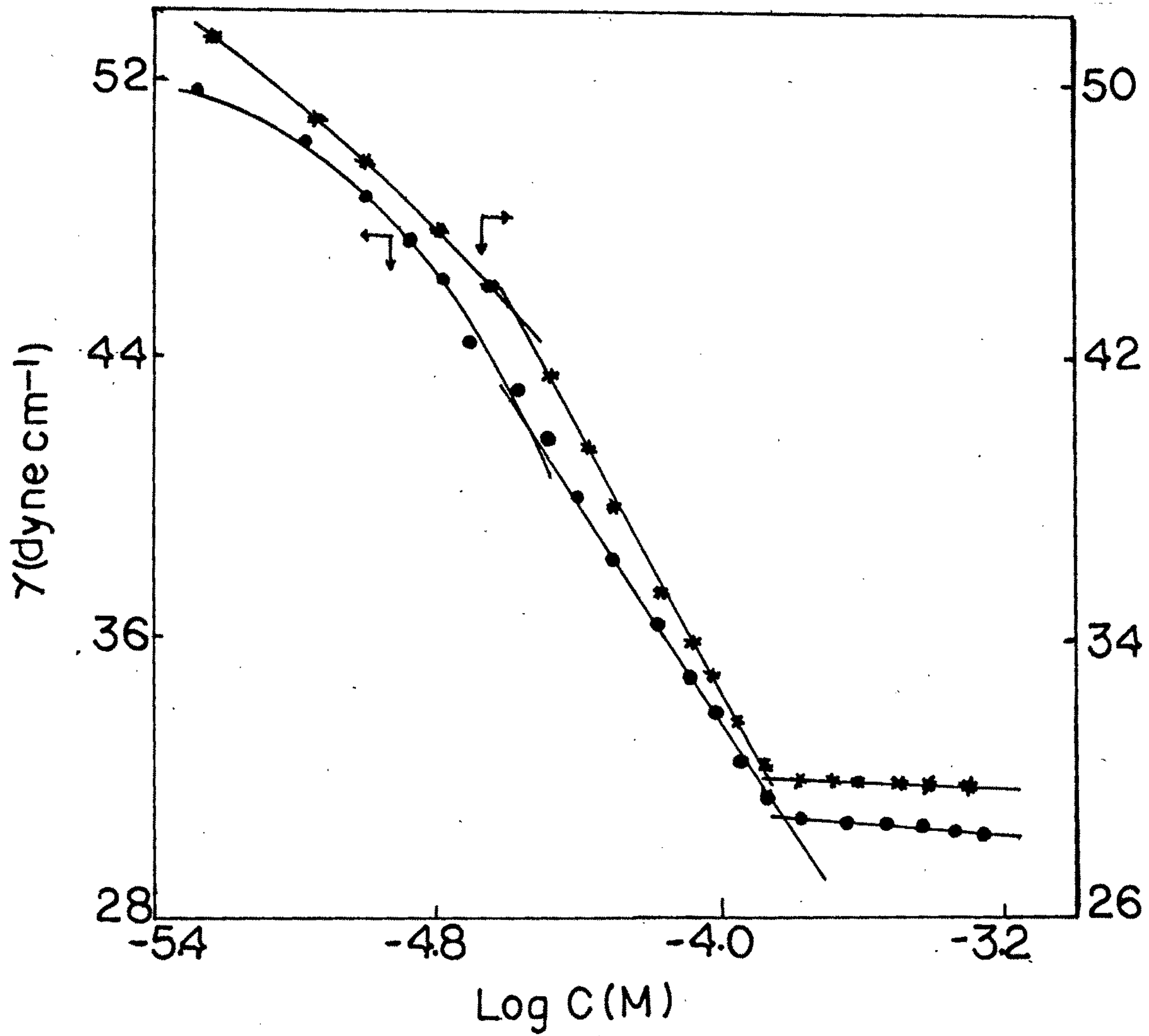

Fig. 37 : Surface tension (γ) - log C plots for polyacrylamide - TX100 systems. ● 0.0001%; ✱ 0.002% at 35°C.

'necklace model' by Shirahama[342] in which the beads are the SDS clusters and string is the polymer chain.

The homopolymers PAA, PAAc and their copolymers P(AA-AAc) in different monomer feed ratios were studied with nonionic surfactant TX100 and cationic Cetyl trimethyl ammonium bromide. In the polymers - TX100 systems the surface tension - log C profile showed two break points. But, in case of PAA - TX100 (Fig. 37) both cac and psp values are lower than the cmc of pure TX100. As the acrylic acid moiety increases in the polymers, the psp values also increase (Fig. 38,39). Table 9-13 give the cac and psp values for these polymers with TX100 from surface tension measurements. Five different polymer concentrations at four different temperatures have been studied. In case of PAA- TX100 systems, for all the concentrations studied, the psp values decrease with increase in temperature. This is probably due to the fact that PAA TX100 both being nonionic is behaving akin to a nonionic surfactant complex. Generally in case of a nonionic surfactant, cmc decreases with increasing temperature[57]. This lowering of cmc due to increasing temperature may be attributed to various factors like changes in the water structure, as well as the water-surfactant interaction, dehydration of the oxyethylene moiety of the surfactant molecule. PAA being neutral, this complex shows similar characteristics as nonionic surfactant. For PAA-TX100 systems, with increase in PAA concentrations, there is a decrease in psp values. Increase in temperature decreases the aggregation number of TX100 on the polymer and hence psp decreases. Lower psp values than cmc indicate the micelle formation even before it gets saturated. Hence, the overall variation of psp with temperature may be determined by the structure of PAA-water matrix, TX100-PAA interaction, TX100-water and TX100-PAA-water interaction[207].

However, in case of the copolymers and PAAc with TX100 this was not the case. At very low copolymers P(AA-AAc) concentrations, the cac and psp are lower than the cmc of TX100, but as acrylic acid moiety and polymer concentration were increased the psp values increase. Generally, in case of ionic surfactant systems the cmc

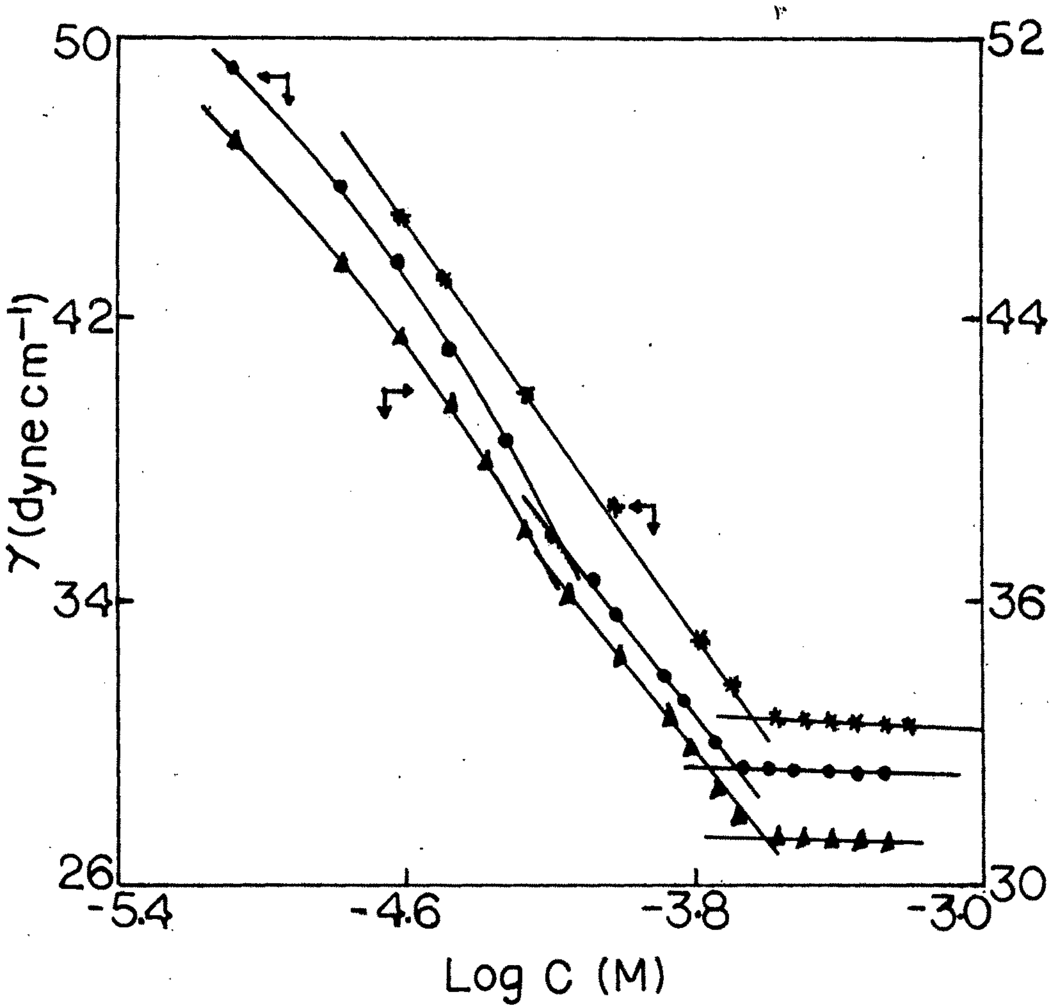

Fig. 38 : Surface tension (γ) - log C plots for copolymers - TX100 systems. ● 0.002% (AA-AAc) 85:15 copolymer; ▲ P(AA-AAc) 65:35 copolymer at 35°C.

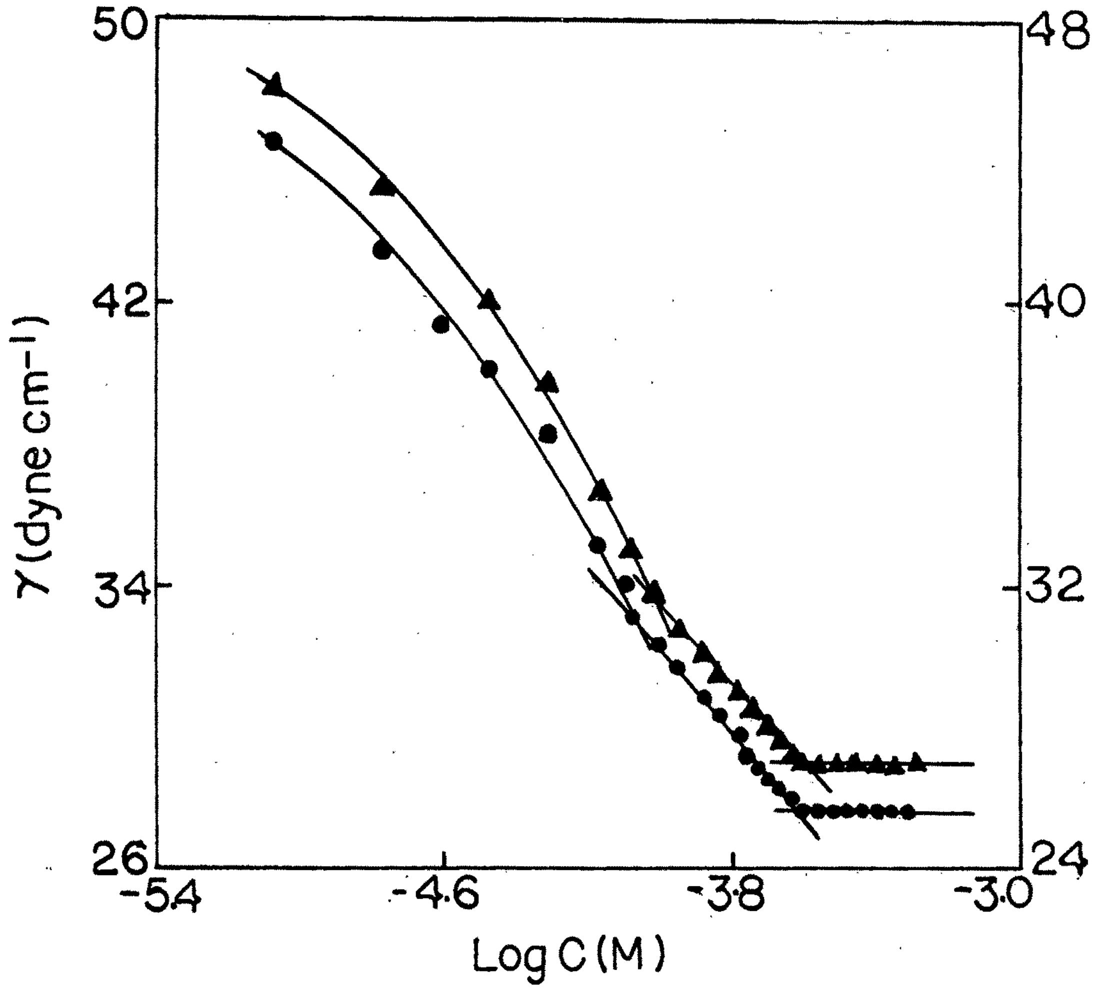

Fig. 39 : Surface tension (γ) - log C plots for polyacrylic acid - TX100 systems. ● 0.0001%; ▲ 0.002% at 35°C.

Table 9 : The critical aggregation concentration (cac) and polymer saturation point (psp) for polyacrylamide (PAA) - Triton X 100 systems at different temperatures.

Polymer Concentration (%, w/v)	**(cac mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0 (CMC)	--	--	--	--	0.234	0.221	0.214	0.195
0.0001	0.025	0.025	0.024	0.025	0.152	0.144	0.141	0.132
0.001	0.027	0.030	0.028	0.029	0.150	0.143	0.138	0.128
0.002	0.030	0.031	0.031	0.028	0.147	0.141	0.134	0.122
0.003	0.032	0.034	0.030	0.031	0.132	0.129	0.120	0.118
0.01	0.030	0.035	0.034	0.036	0.130	0.127	0.125	0.120

Table 10 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 85:15 copolymer - Triton X 100 systems at different temperatures.

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.067	0.064	0.066	0.063	0.182	0.186	0.191	0.195
0.001	0.065	0.066	0.065	0.068	0.195	0.199	0.204	0.209
0.002	0.060	0.063	0.064	0.063	0.211	0.214	0.219	0.224
0.003	0.068	0.070	0.067	0.064	0.214	0.218	0.224	0.229
0.01	0.062	0.064	0.066	0.061	0.240	0.252	0.257	0.263

Table 11 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 65:35 copolymer - Triton X 100 systems at different temperatures.

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.060	0.064	0.066	0.063	0.189	0.195	0.200	0.211
0.001	0.061	0.062	0.065	0.064	0.211	0.230	0.239	0.252
0.002	0.060	0.063	0.064	0.063	0.232	0.258	0.270	0.282
0.003	0.063	0.061	0.062	0.064	0.257	0.263	0.280	0.285
0.01	0.062	0.064	0.066	0.061	0.263	0.269	0.279	0.288

Table 12 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 50:50 copolymer - Triton X 100 systems at different temperatures.

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.081	0.091	0.091	0.100	0.200	0.209	0.219	0.229
0.001	0.090	0.100	0.098	0.096	0.208	0.221	0.234	0.240
0.002	0.096	0.100	0.098	0.094	0.234	0.260	0.272	0.284
0.003	0.098	0.096	0.099	0.100	0.230	0.237	0.248	0.285
0.01	0.100	0.099	0.100	0.098	0.265	0.269	0.278	0.288

Table 13 : The critical aggregation concentration (cac) and polymer saturation point (psp) for polyacrylic acid (PAAc) - Triton X 100 systems at different temperatures.

Polymer Concentration (%, w/v)	cac (mM)				psp (mM)			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
0.0001	0.100	0.098	0.094	0.098	0.229	0.245	0.263	0.275
0.001	0.098	0.099	0.096	0.098	0.234	0.257	0.272	0.277
0.002	0.096	0.100	0.098	0.094	0.237	0.263	0.275	0.288
0.003	0.098	0.095	0.099	0.100	0.248	0.269	0.278	0.290
0.01	0.100	0.099	0.100	0.098	0.257	0.272	0.282	0.294

increases with increase in temperature[266]. Similarly, ionic repulsions due to their polyelectrolyte like nature play an important role in variation of psp in these systems. The cac values are found around a particular concentration range for a polymer system[91]. The values of cac are weakly dependent on the amount of polymer in solution[109], while the psp varies linearly with it. The increase in psp values with increase in polymer concentration suggests the availability of more binding sites for the surfactant to interact resulting in higher psp values[36].. In the PAAc-TX100 systems the psp values are comparatively higher than the cmc of TX100.Similar results were observed for PAAc and nonionic surfactants of the C_iE_j type by Saito etal.[188] These results indicate structural differences between PAA and the other polymers containing the acrylic acid moiety.

In all these polymer-TX100 systems, the surface tension γ values at psp are not same for pure TX100. Goddard[90] suggests that when the surfactant is present in excess and the concentration of micelles are relatively high, the micelle / water and the air / water interface compete progressively for the polymer i.e. the interface is free of polymer at this point. Thus, surface tension values are somewhat different from pure surfactant solutions at psp and are at higher concentrations, hence we suggest that the complete transfer of polymer does not occur from air-water interface and the air-water interface is saturated with polymer-surfactant complex and not only with polymer or surfactant. Even the interfacial tension values between cyclohexane / aquo TX100 suggest that in presence of polymer (PAA) the values are higher than at its absence (Fig. 40).

The same polymers were studied with CTAB to study the changes of cac and psp, both by surface tension (Fig. 41) and conductance measurements (Fig. 42). However, we were unable to carry out surface tension or conductance measurements for PAAc-CTAB systems in this required concentration range. In polyelectrolyte - oppositely charged surfactant systems (i.e. PAAc-CTAB), the interactions clearly results from strong coulombic forces[343]. In contrast to nonionic polymers, the interaction leads to phase separation. This fact limits the studies to surfactant concentrations close to the

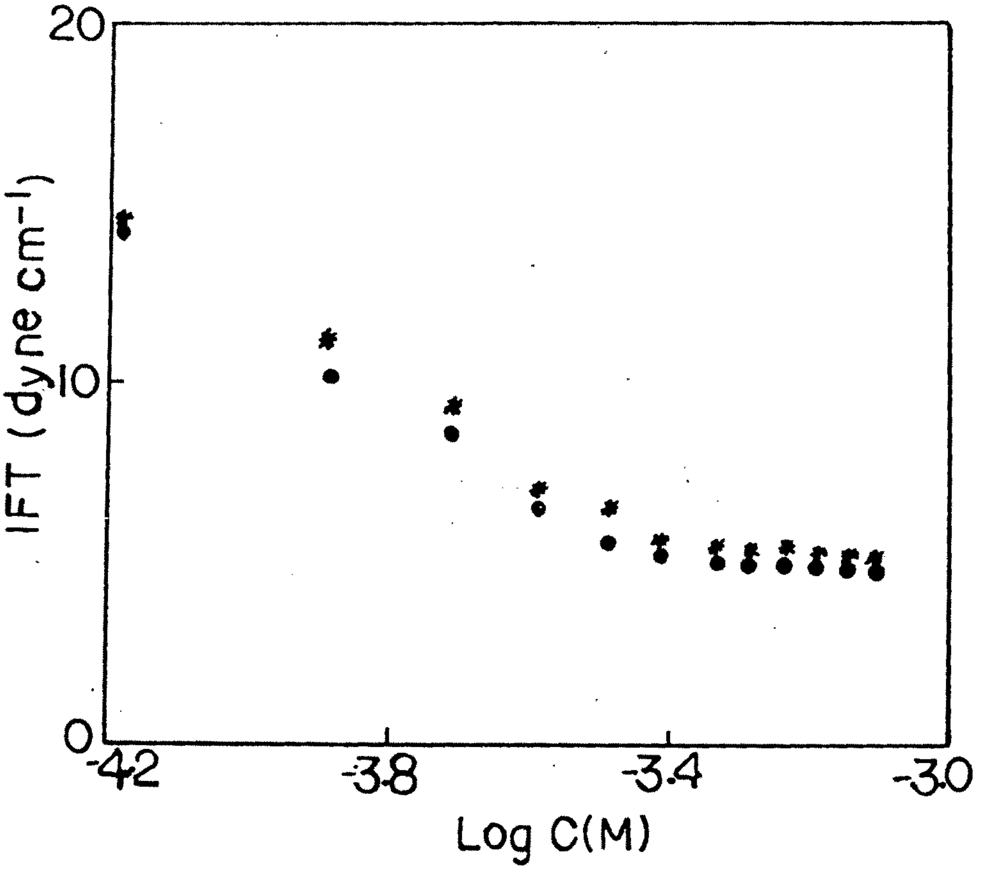

Fig. 40 : Interfacial tension (γ) - log C plots for ● aquo TX100 / cyclohexane system; ✱ aquo cyclohexane / TX100 in presence of polyacrylamide.

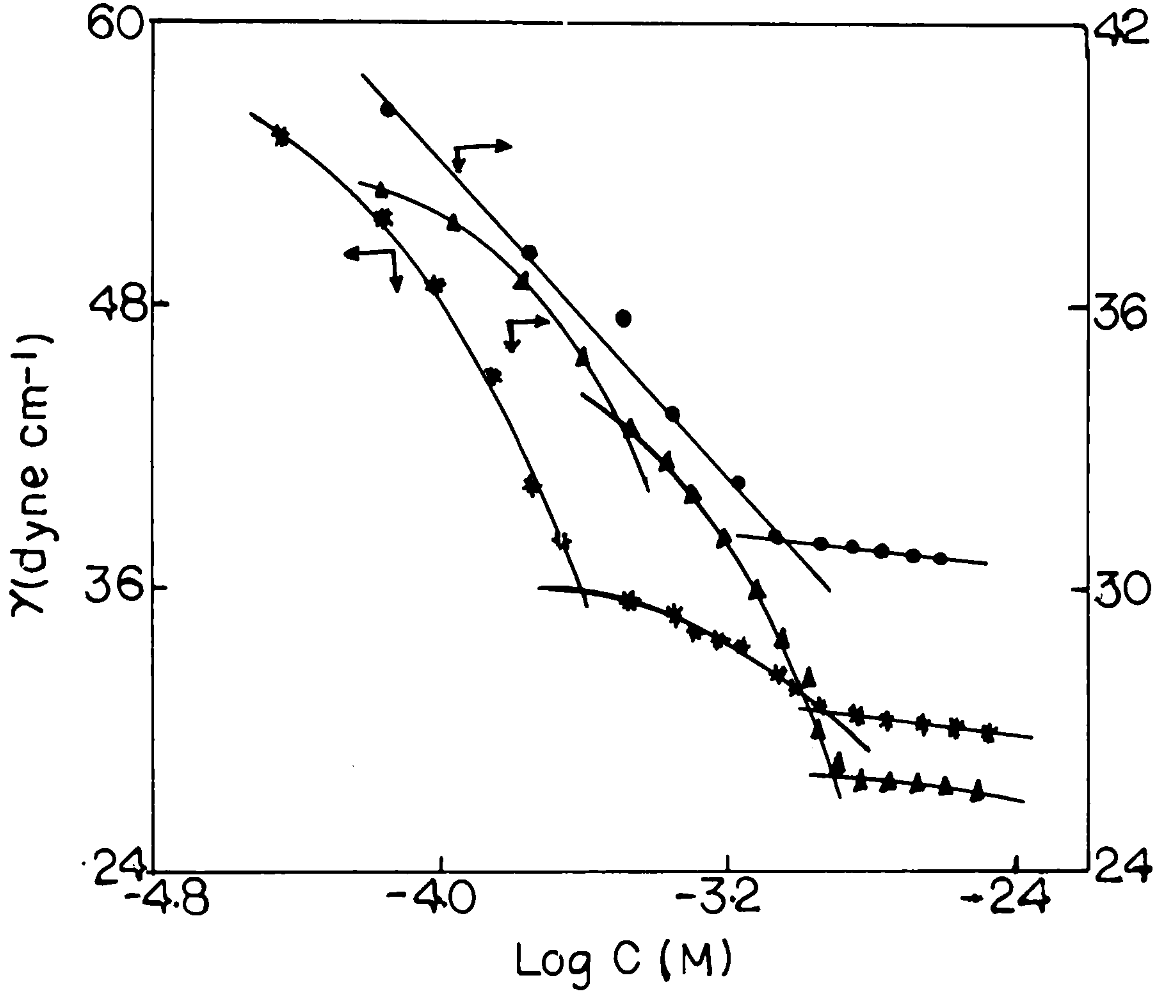

Fig. 41 : Surface tension (γ) - log C plot for polyacrylamide CTAB system for ● aqueous CTAB; ▲ 0.003% PAA; ✱ PAA at 35°C.

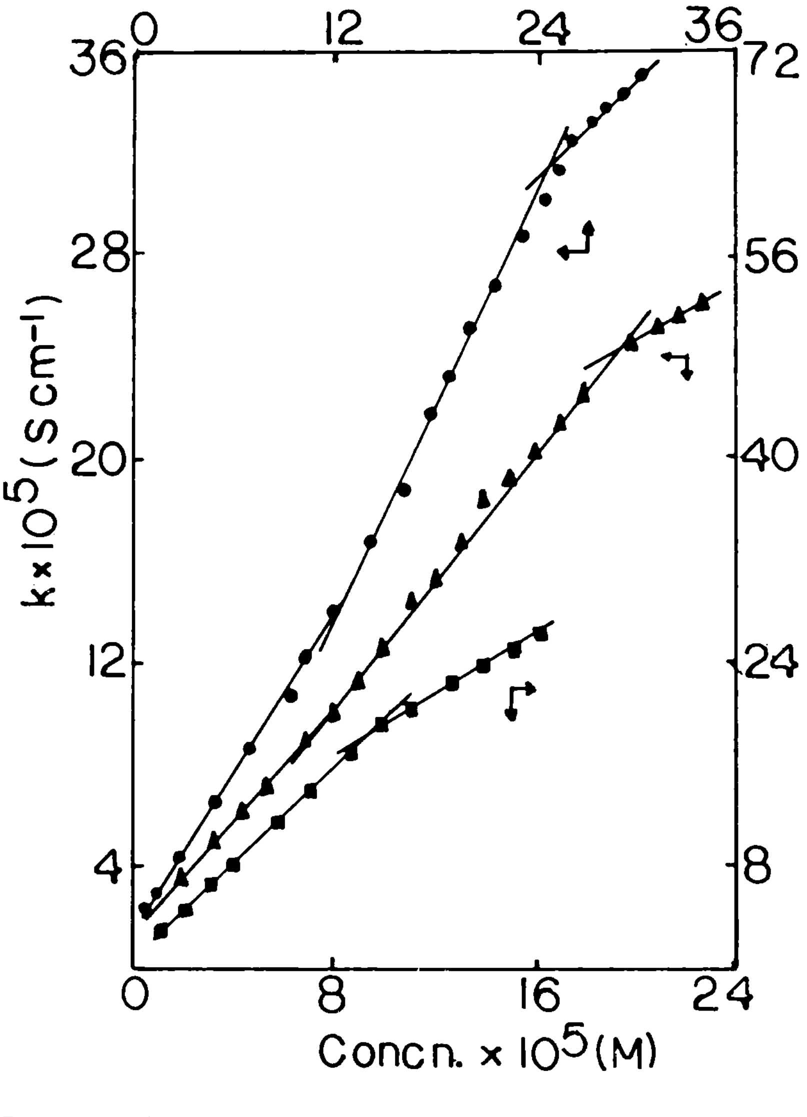

Fig. 42 : Representative plot of specific conductance - concentration plot for CTAB-polymer system. ■ aqueous CTAB at 35°C; ▲ 0.001% PAA; ● 0.003% PAA at 30°C.

critical micelle concentration (cmc) of the surfactant[221]. However, for the copolymers, which has large number of acrylamide moiety, the surface tension and conductance measurements were possible. Tables 14-17 give cac and psp values for PAA, copolymers-CTAB systems from the conductance measurements whereas values from surface tension data are given in Tables 18-21. The cac values obtained from surface tension measurements are comparatively lower than conductance data. Repeated experiments gave similar results. The reason for this discrepancy is not understood. However, the psp values obtained by both the methods are in agreement. Again, the cac values obtained by each of the methods remain over a certain concentration range independent of temperature and polymer concentration[91]. The values of psp obtained in case of PAA-CTAB decrease with increasing temperature. The psp values reach faster with increasing temperature indicate saturation of polymer at lower temperature. As mentioned earlier, presence of micelles like beads around the polymer chains form necklace[178] like structure and the neutral molecule decreases the ion-ion repulsions. Increase in temperature does not have much effect on this necklace but the aggregation member of the surfactant decreases and hence the psp decreases. The psp values increase with polymer concentration suggest more binding sites are available for binding, hence more surfactant is needed[36,178].

In case of the copolymer-CTAB systems, the psp values increase with increasing temperature and polymer concentration. Interaction with the surfactant begins at surfactant concentrations much below the cmc of the surfactant. Similar to the surface tension - log C plots which give two break points, the specific conductance concentration plots exhibit three linear regions: below the cac, between the cac and psp where micelle like aggregates begin to develop and above the psp where co-existence of dynamic equilibrium of a surfactant saturated polymer and regular micelles occur[139] (Fig. 42). The binding studies of oppositely charged-surfactant systems have been done earlier also. The binding of a polyelectrolyte and oppositely charged-surfactant results in synergistic lowering of surface tension at very low surfactant concentration, implying formation of a very surface active species[115]. A

Table 14 : The critical aggregation concentration (cac) and polymer saturation point (psp) for polyacrylamide (PAA)-CTAB system at different temperatures (by conductivity method).

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0	--	--	--	--	0.933	1.05	1.15	1.21
0.00001	--	--	--	--	0.82	0.65	0.44	0.34
0.0001	0.85	0.76	0.72	0.68	1.70	1.43	1.19	1.10
0.001	0.83	0.64	0.56	0.47	1.94	1.47	1.09	0.67
0.002	0.83	0.79	0.64	0.58	2.40	1.90	1.46	1.14
0.003	0.86	0.80	0.65	0.60	2.42	2.18	1.49	1.05

Table 15 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 85:15 copolymer - CTAB system at different temperatures (by conductivity method).

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.40	0.38	0.37	0.38	0.92	0.97	1.06	1.10
0.001	0.33	0.37	0.43	0.44	0.99	1.04	1.08	1.14
0.002	0.50	0.49	0.54	0.52	1.09	1.13	1.17	1.21
0.003	0.44	0.45	0.42	0.44	1.15	1.19	1.23	1.28
0.01	0.50	0.55	0.41	0.38	1.19	1.23	1.26	1.30

Table 16 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 65:35 copolymer - CTAB system at different temperatures (by conductivity method).

Polymer Concentration (%, w/v)	cac (mM)				psp (mM)			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
0.0001	0.36	0.32	0.40	0.43	0.98	1.03	1.06	1.10
0.001	0.45	0.42	0.45	0.48	1.04	1.09	1.12	1.18
0.002	0.37	0.38	0.44	0.43	1.08	1.13	1.16	1.19
0.003	0.40	0.43	0.45	0.47	1.13	1.16	1.20	1.24
0.01	0.55	0.40	0.46	0.43	1.21	1.25	1.29	1.34

Table 17 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 50:50 copolymer - CTAB system at different temperatures (by conductivity method).

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.42	0.34	0.37	0.35	1.07	1.13	1.17	1.20
0.001	0.52	0.42	0.44	0.40	1.10	1.15	1.19	1.21
0.002	0.44	0.37	0.38	0.41	1.12	1.16	1.21	1.24
0.003	0.32	0.34	0.41	0.38	1.16	1.17	1.23	1.28
0.01	0.38	0.47	0.42	0.34	1.20	1.26	1.29	1.35

Table 18 : The critical aggregation concentration (cac) and polymer saturation point (psp) for polyacrylamide PAA - CTAB system at different temperatures (by surface tension method).

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0	--	--	--	--	0.930	1.04	1.16	1.20
0.00001	0.275	0.214	0.256	0.264	0.82	0.67	0.40	0.34
0.0001	0.301	0.275	0.269	0.270	1.78	1.24	1.10	0.98
0.001	0.218	0.200	0.223	0.275	1.92	1.39	1.10	0.66
0.002	0.251	0.250	0.245	0.263	2.40	1.91	1.46	1.07
0.003	0.257	0.223	0.245	0.260	2.40	2.18	1.49	1.05

Table 19 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 85:15 copolymer- CTAB systems at different temperatures (by surface tension method).

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.223	0.229	0.239	0.160	0.95	0.98	1.06	1.09
0.001	0.138	0.170	0.140	0.142	1.00	1.05	1.09	1.15
0.002	0.138	0.173	0.158	0.165	1.09	1.15	1.19	1.23
0.003	0.140	0.182	0.158	0.142	1.12	1.20	1.26	1.29
0.01	0.145	0.145	0.132	0.130	1.20	1.23	1.28	1.30

Table 20 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 65:35 copolymer - CTAB system at different temperatures (by surface tension method).

Polymer Concentration (%, w/v)	cac (mM)				psp (mM)			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
0.0001	0.230	0.200	0.200	0.288	0.96	1.0	1.05	1.10
0.001	0.138	0.148	0.132	0.144	1.05	1.08	1.12	1.17
0.002	0.138	0.145	0.140	0.132	1.07	1.12	1.15	1.20
0.003	0.132	0.130	0.138	0.151	1.10	1.17	1.20	1.25
0.01	0.223	0.130	0.140	0.130	1.21	1.25	1.30	1.35

Table 21 : The critical aggregation concentration (cac) and polymer saturation point (psp) for P(AA-AAc) 50:50 copolymer - CTAB system at different temperatures (by surface tension method).

Polymer Concentration (%, w/v)	**cac (mM)**				**psp (mM)**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.200	0.162	0.121	0.180	1.06	1.13	1.17	1.20
0.001	0.132	0.131	0.138	0.152	1.1	1.15	1.19	1.22
0.002	0.125	0.120	0.138	0.230	1.12	1.16	1.21	1.23
0.003	0.128	0.158	0.174	0.158	1.16	1.18	1.23	1.29
0.01	0.160	0.165	0.145	0.165	1.21	1.26	1.31	1.35

direct consequence of increased surface activity of the polycation as it binds to surfactant is its increased foaming property[194]. The earliest work on the interaction of surfactants and serum albumin with opposite charges were carried out by Putnam and Neurath[344], that lead to the precipitation on the acid side of its isoelectric point and soluble complex formation on the basic side. The combined system of polyelectrolytes and oppositely charged surfactant passes through various regions of clear, turbid, precipitate, slightly precipitate and clear again[132]. This was observed for the copolymers with CTAB and at the point it clears, the psp occured. Thus, eventually the surface tension curve coincides with the polymer free surfactant system in the micellar region. For these systems the psp values increase with increasing temperature. This is quite common in ionic surfactant systems, as micellization is due to hydrophobic interaction[211]. Increase in temperature results in ionic repulsions or increase in mobility of ions, and hence higher concentration is required for micelle formation. The psp values increase with temperature and increasing polymer concentration.

(ii) Thermodynamic parameters :

The knowledge of the energetics of the process serve as a measure of the nature of interaction. In case of surfactant systems, the thermodynamic parameters associated with micellization are evaluated, similarly for polymer-surfactant systems the thermodynamic parameters can be evaluated at cac as well as at psp. The free energy of micellization at psp, ΔG°_{psp} for a nonionic system is given by[266]

$$\Delta G^{\circ}_{psp} = RT \ln C_{psp}$$

The free energy of micellization at psp is directly proportional to psp (taken in the mole fraction scale). Even in the case of copolymers and PAAc i.e. the polyelectrolytes TX100 systems, the free energy of micellization was evaluated by the above equation because the specific conductance - TX100 concentration plots in these systems do not show any change in conductance values with changing TX100 concentration.

Tables 22-26 give the free energy, enthalpy and entropy values for the TX100 polymer systems. In case of pure TX100, the free energy values become more negative with increase in temperature, indicating spontaneous micelle formation. Even in the presence of polymers the ΔG°_{psp} values become more negative with increase in temperature. This is because the change in the magnitude of the logarithm of cmc is more than compensated by the change in RT values[214]. The ΔG°_{psp} are always found to be much more negative compared to ΔG°_m values indicating micelle formation in presence of the polymers is more favourable compared to normal micelle.

The enthalpy and entropy of micelle formation in presence of polymers are given by the well known relation

$$\Delta G^\circ_{psp} = \Delta H^\circ_{psp} - T\Delta S^\circ_{psp}$$

From tables 22-26, it can be noted that micellization of TX100 in presence of PAA is endothermic whereas in presence of PAAc and the copolymers it is exothermic. The exothermicity and endothermicity of micellization are specific to the surfactant, the nature of the added compound[213,214,345], in this case a polymer and temperature of micellization. The presence of the polymer effects the endothermic or exothermic nature of the compound.

Similarly, the entropy changes correspond with changes in the polymer from PAA to the copolymers to PAAc. As the systems become more polyelectrolytic due to the presence of charges in the system, the randomness decreases and the magnitude of entropy ΔS°_{psp} is reduced. Changes in entropy of any system can be explained by various schools of thought. In case of nonionic surfactant, the entropy gained by the destruction of the structured water shell is commonly credited as providing the driving force for the process. Moreover, with temperature increase, the entropic gain is greater than the enthalpic gain hence free energy becomes more negative[346]. As temperature increase leads to dehydration of the oxyethylene groups, there are more number of nonpolar conformations available which thus provide an entropic driving

Table 22 : Thermodynamic parameters associated with the polymer saturation point (psp) for polyacrylamide (PAA) - Triton X 100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^\circ_{psp}$ (kJ mol^{-1})**				**ΔH°_{psp} (kJ mol^{-1})**	**ΔS°_{psp} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0	31.2	31.8	32.4	33.2	9.2	133.2
0.0001	32.3	32.9	33.5	34.2	7.2	130.2
0.001	32.3	33.0	33.6	34.3	7.8	132.3
0.002	32.4	32.9	33.7	34.4	9.8	138.8
0.003	32.6	33.2	33.9	34.6	8.2	134.5
0.01	32.6	33.2	33.8	34.4	3.4	118.0

Table 23 : Thermodynamic parameters associated with the polymer saturation point (psp) for P(AA-AAc) 85:15 copolymer - Triton X 100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{psp}$ (kJ mol^{-1})**				**ΔH°_{psp} (kJ mol^{-1})**	**ΔS°_{psp} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	31.8	32.3	32.7	33.2	3.76	92.6
0.001	31.6	32.1	32.6	33.0	3.73	92.1
0.002	31.4	31.9	32.3	32.8	3.23	93.1
0.003	31.4	31.8	32.3	32.8	3.70	92.0
0.01	31.1	31.5	32.0	32.4	4.58	87.5

Table 24 : Thermodynamic parameters associated with the polymer saturation point (psp) for P(AA-AAc) 65:35 copolymer - Triton X 100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{psp}$ (kJ mol^{-1})**				**ΔH°_{psp} (kJ mol^{-1})**	**ΔS°_{psp} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	31.7	32.2	32.6	33.0	7.6	79.8
0.001	31.5	31.7	32.1	32.5	9.5	72.2
0.002	31.2	31.5	31.8	32.2	10.1	69.6
0.003	30.9	31.2	31.7	32.1	8.8	73.2
0.01	30.9	31.3	31.8	32.2	4.4	87.4

Table 25 : Thermodynamic parameters associated with the polymer saturation point (psp) for P(AA-AAc) 50:50 copolymer - Triton X 100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^\circ_{psp}$ (kJ mol^{-1})**				**ΔH°_{psp} (kJ mol^{-1})**	**ΔS°_{psp} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	31.6	32.0	32.4	32.8	7.15	80.6
0.001	31.5	31.8	32.2	32.7	7.2	80.0
0.002	31.2	31.4	31.8	32.2	9.9	70.2
0.003	31.2	31.7	32.1	32.2	10.9	67.0
0.01	30.9	31.3	31.8	32.2	4.6	87.0

Table 26 : Thermodynamic parameters associated with the polymer saturation point (psp) for polyacrylic acid (PAAc) - Triton X 100 system at different polymer concentration.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{psp}$ (kJ mol^{-1})**				**ΔH°_{psp} (kJ mol^{-1})**	**ΔS°_{psp} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	31.2	31.6	31.9	32.3	9.9	70.4
0.001	31.1	31.5	31.8	32.3	8.6	74.2
0.002	31.2	31.4	31.8	32.1	10.1	69.4
0.003	31.0	31.3	31.8	32.2	6.5	80.8
0.01	31.0	31.3	31.7	32.1	7.0	78.9

force for the conformational changes[347]. However, it is expected that high entropy changes are generally associated with phase changes. Shaw[17] has suggested that the high entropy change may be due to the freedom of movement of the hydrocarbon chain in the core of the micelle. However, we are not very clear how this movement of hydrocarbon chains in the core of the micellar aggregates can have a dominating effect on entropy values, which is a macroscopic property. According to Rosen[207] the presence of hydrated oxyethylene groups of the surfactant in the solution introduces structure in the liquid water phase and the decrease in the surfactant-water contact because of micellization results in an increase in the overall randomness and hence increase in entropy. In the case of PAA-TX100 system, both being nonionic, their complex formed shows similar tendencies. However, the copolymers and PAAc due to the presence of charges, hinders the freedom of movement thereby lowering the entropy values. The large positive $T\Delta S^\circ_{psp}$ dominate over small ΔH°_{psp} values indicating that the micellization process is entropy driven.

For ionic surfactant systems, the free energy of micellization is given by

$$\Delta G^\circ_{psp} = (2-\alpha)\,RT \ln C_{psp}$$

where C_{psp} is taken in the mole fraction scale. α is the degree of ionization of the micelle and is usually obtained from the slopes of the conductivity - concentration plots above and below the cmc. Several techniques have been used to determine the α values for ionic micelles, but the value depends on the method[222]. Conductometric determination of 'α' is based on the 'method of slopes'[348]. The value of α calculated by this method are higher because the micellar contribution to the conductance is assumed to be the same as that of an equivalent number of monomeric ions, the sum of whose charges is equal to the micellar charge. Several workers have found 'α' values of polymer-surfactant systems in this manner. Zana et al.[96] found α values of 0.85 and 0.65 for PVP-SDS complex and PEO-SDS complex respectively. Witte and Engberts[145] estimated α-values of 0.58 for PEO-SDS complex. In case of CTAB-polymers systems, we got values around 0.5-0.75.

In these systems the ΔG°_{psp} values are found to become more negative with increase in temperature indicating spontaneous micelle formation (Tables 27-30). A linear ΔG°_{psp}-T plot ($r = 0.989$-0.999) was used to compute ΔH°_{psp} and ΔS°_{psp} values. The enthalpy values for ionic surfactant systems are negative. In PAA-CTAB systems, low negative values are found but at higher PAA concentrations the values become positive. The nonionic nature of the polymer, probably may be a reason for the positive enthalpy values at high PAA concentrations. However, in case of the copolymers and CTAB, negative values of enthalpy indicate the process to be highly exothermic.

The ΔS°_{m} values for a ionic surfactant system are much lower compared to that of nonionic surfactant system. The presence of charges results in lowered degree of randomness. For the ionic surfactant CTAB-copolymer system the magnitude in ΔS°_{psp} values are much lower compared to TX100-copolymer systems. Again the presence of charges of polymer and ionic surfactants results in low ΔS°_{psp} values in these systems.

A linear correlation was observed between ΔH°_{psp} and ΔS°_{psp} (Fig. 43 and 44) for the TX100-polymer and also CTAB-polymer systems. The slope of these lines were 310 K and 375 K respectively. According to Lumry and Rajender[349], the micellization can be described as consisting of two forces, one due to the desolvation i.e. due to the dehydration of hydrocarbon tail of the surfactant molecules and second due to the 'chemical' part i.e. the aggregation of the tails of the surfactant molecules to form micelles. In general, this compensation phenomenon between the enthalpy change ΔH°_{psp} and the entropy change ΔS°_{psp} in various process can be written as follows

$$\Delta H^{\circ}_{psp} = b_1 + b_2\, \Delta S^{\circ}_{psp}$$

From the thermodynamics

$$\Delta G^{\circ}_{psp} = \Delta H^{\circ}_{psp} - T\Delta S^{\circ}_{psp}$$

therefore by substituting for ΔH°_{psp} in the general thermodynamic relation :-

$$\Delta G^{\circ}_{psp} = b_1 + (b_2 - T)\, \Delta S^{\circ}_{psp}$$

Table 27 : Thermodynamic parameters associated with polymer saturation point (psp) for polyacrylamide (PAA) - CTAB systems at different polymer concentrations.

Polymer Concentration (%, w/v)	$-\Delta G^{\circ}_{psp}$ (kJ mol^{-1})				ΔH°_{psp} (kJ mol^{-1})	ΔS°_{psp} (J mol^{-1} K^{-1})	α (35°C)
	30°C	**35°C**	**40°C**	**45°C**			
0.0	46.1	46.4	46.8	47.0	-27.8	60.4	0.33
0.00001	36.6	37.2	37.8	38.4	-2.1	114	0.72
0.0001	35.6	36.2	36.8	37.4	-1.1	114	0.68
0.001	36.5	37.1	37.6	38.2	-3.8	108	0.63
0.002	36.5	37.2	37.5	38.0	-5.9	101	0.59
0.003	36.3	36.9	37.6	38.2	3.4	131	0.58

Table 28 : Thermodynamic parameters associated with polymer saturation point (psp) for P(AA-AAc) 85:15 copolymer - CTAB systems at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^\circ_{psp}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{psp}$ (kJ mol^{-1})**	**ΔS°_{psp} (J mol^{-1} K^{-1})**	**α (35°C)**
	30°C	**35°C**	**40°C**	**45°C**			
0.0001	40.7	41.0	41.2	41.7	24.1	54.9	0.53
0.001	45.9	46.1	46.3	46.5	34.3	38.4	0.34
0.002	42.9	43.4	43.6	44.0	22.2	68.8	0.43
0.003	42.7	42.9	43.1	43.4	28.8	45.8	0.44
0.01	41.6	41.8	42.0	42.3	28.9	42.0	0.48

Table 29 : Thermodynamic parameters associated with polymer saturation point (psp) for P(AA-AAC) 65:35 copolymer- CTAB systems at different polymer concentrations.

Polymer Concentration (%, w/v)	$-\Delta G^{\circ}_{psp}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{psp}$ (kJ mol^{-1})	ΔS°_{psp} (J mol^{-1} K^{-1})	α (35°C)
	30°C	35°C	40°C	45°C			
0.0001	43.8	43.9	44.1	44.1	38.0	19.2	0.41
0.001	45.1	46.3	46.4	46.6	35.1	36.2	0.33
0.002	42.5	42.9	43.2	43.5	23.3	63.4	0.45
0.003	43.0	43.1	43.3	43.4	35.8	24.0	0.44
0.01	42.6	42.8	43.0	43.3	28.2	47.6	0.44

Table 30 : Thermodynamic parameters associated with polymer saturation point (psp) for P(AA-AAC) 50:50 copolymer - CTAB systems at different polymer concentrations.

Polymer Concentration (%, w/v)	$-\Delta G^\circ_{psp}$ (kJ mol^{-1})				$-\Delta H^\circ_{psp}$ (kJ mol^{-1})	ΔS°_{psp} (J mol^{-1} K^{-1})	α (35°C)
	30°C	35°C	40°C	45°C			
0.0001	44.9	45.2	45.5	45.9	24.5	67.0	0.50
0.001	45.2	45.5	45.8	46.1	26.4	62.2	0.33
0.002	45.8	45.9	46.3	46.6	26.2	64.4	0.33
0.003	45.6	45.9	46.2	46.5	26.5	63.0	0.25
0.01	45.6	46.0	46.3	46.6	25.5	66.4	0.64

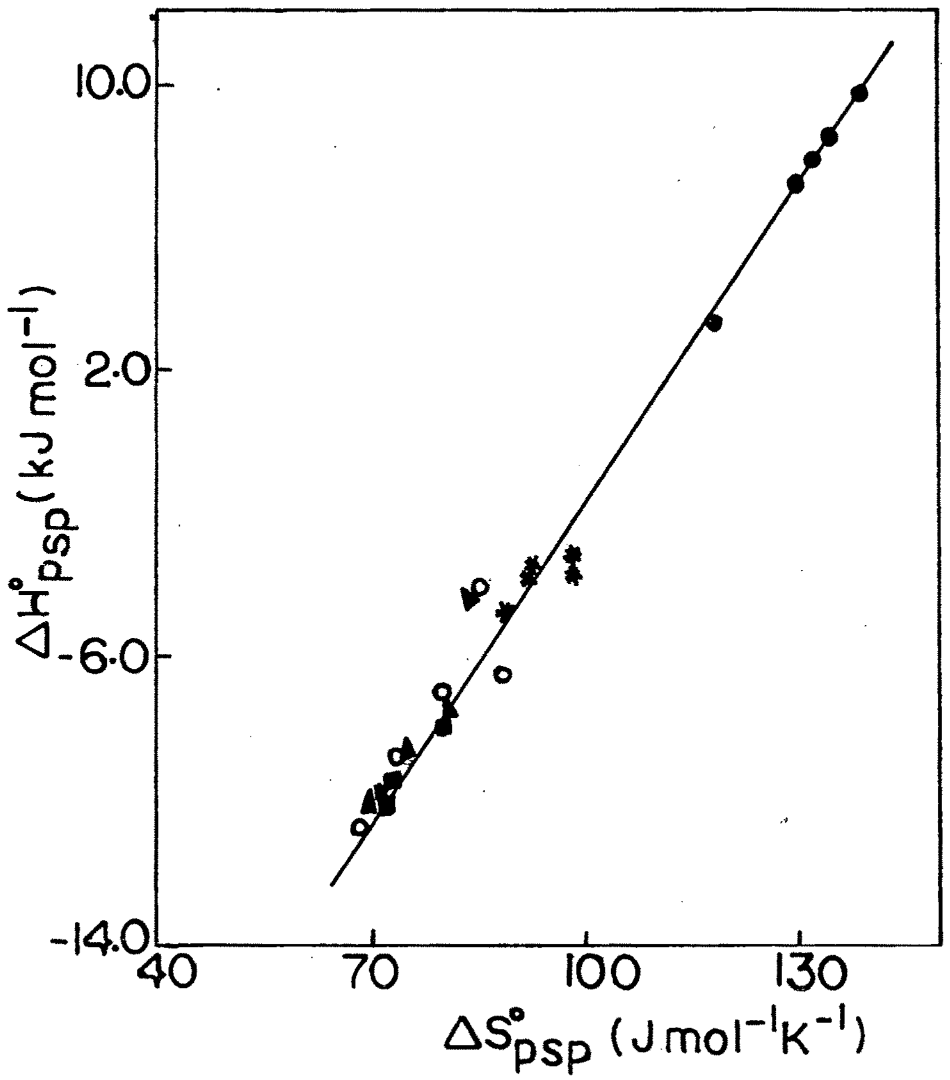

Fig. 43 : Enthalpy-entropy compensation plots for all polymers - TX100 systems. ● PAA; ✱ P(AA-AAc) 85:15; ▲ P(AA-AAc) 65:35; ■ P(AA-AAc) 50:50; ○ PAAc.

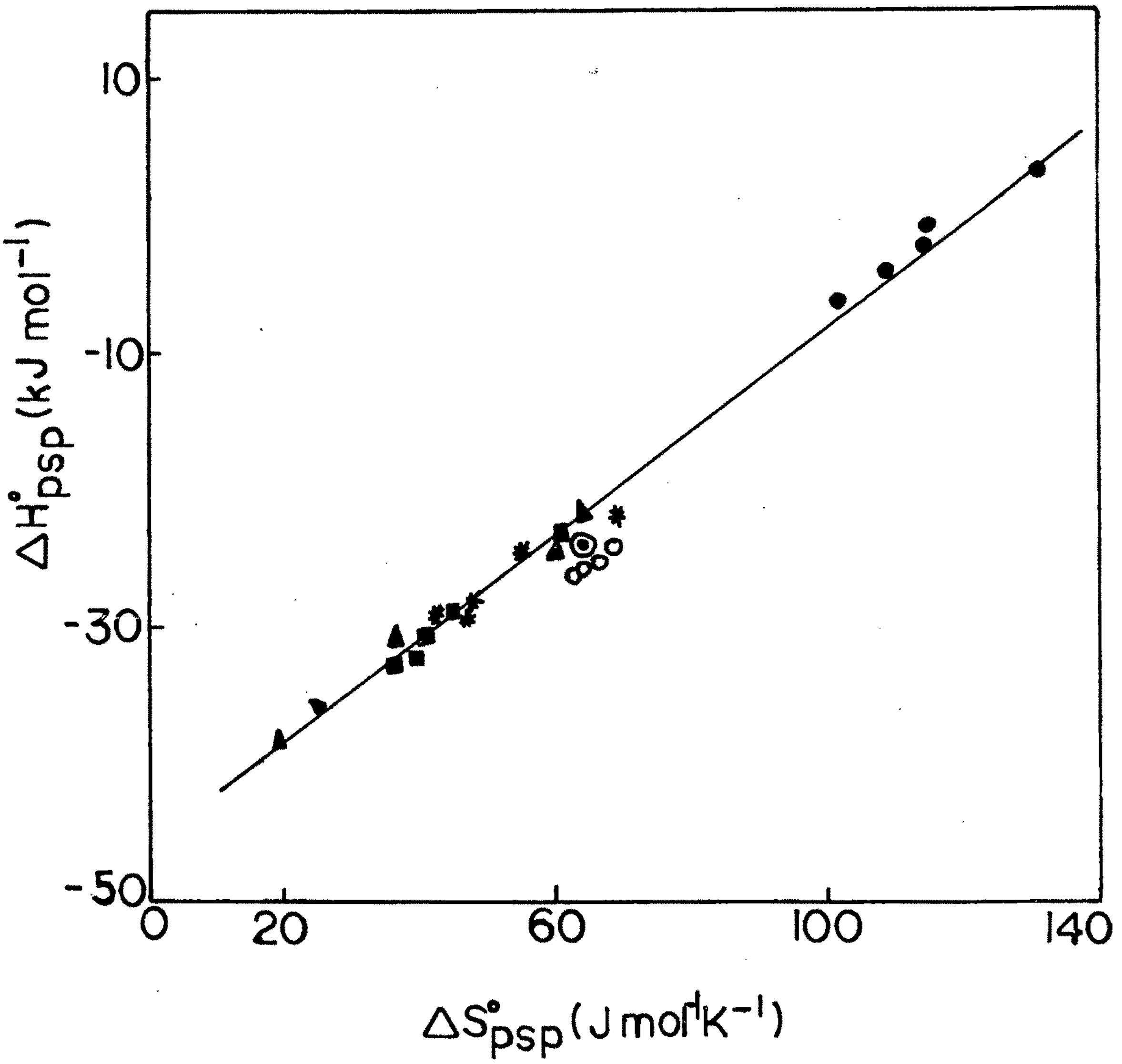

Fig. 44 : Enthalpy-entropy compensation plot for all polymers - CTAB system. ⊙ CTAB; ● PAA; ✱ P(AA-AAc) 85:15; ■ P(AA-AAc) 65:35; ○ P(AA-AAc) 50:50.

At b_2 = T the $\Delta G°_{psp}$ will be independent of entropic effect i.e. there will be no structural effect. The b_2 is therefore called isostructural temperature. This can be obtained from the slope of $\Delta H°_{psp}$ vs $\Delta S°_{psp}$ plots. It was suggested by Lumry et al.[349] that the value of b_2 in water solution would be between 270-294 K. As seen from Fig. 43 and 44 the value for the TX100-polymer system is around these temperatures. Such enthalpy-entropy compensation was observed for many physicochemical processes including micellization[211,213] and monolayer formation[350]. However, the CTAB- polymer systems gave very high compensation temperature (375 K), it is difficult to explain this high value though it probably means that some specific interaction is present in the system.The isostructural temperature has a thermodynamic significance. It is said to be characteristic of solute-solute and solvent-solvent interactions i.e. proposed as a measure of the "desolvation" part of the micellization process, whereas the intercept b_1 characterizes the solute-solute interaction, i.e. considered as index of the chemical part of the micellization process. Hence, the intercept represents the enthalpy effect under the condition $\Delta S°_{psp}$=0 i.e. $\Delta G°_{psp}$=b_1 (at the isostructural temperature, the micellization process is totally independent of any structural change in the system). Hence, it is felt that micellization is the bulk structural property of the solvent and addition of polymers at these concentrations do not have much effect on the bulk property[351].

Engberts et al.[219] have observed that for n-octyl-β-D-thio glucopyranoside (OTG) - the free energy of micellization in presence of PPO does not change much. The endothermic interaction enthalpy is compensated by a positive entropy change. They concluded that this ΔH / ΔS compensatory behaviour, probably originated largely from the release of water molecules from the hydrophobic hydration shells of the polymers upon interaction with the micelles.

The free energy of micellization $\Delta G°_{mic}$ in the absence of the polymer and the free energy of aggregation $\Delta G°_{agg}$ in the presence of polymer can be calculated by the following relations[58,352]

$$\Delta G^\circ_{mic} = (2-\alpha)\, RT \ln[cmc]$$

$$\Delta G^\circ_{agg} = (2-\alpha)\, RT \ln\, [cac]$$

where α is the degree of ionization of the micelle. Since the values of ΔG°_{mic}, ΔH°_{mic}, ΔG°_{agg} and ΔH°_{agg} have been obtained, the entropy changes of the corresponding process ΔS°_{mic} and ΔS°_{agg} can easily be calculated. The addition of surfactant to a polymer solution results in the formation of aggregation. The free energy of aggregate formation ΔG°_{agg} would then be related to free energy of micelle formation ΔG°_m by

$$\Delta G^\circ_{agg} = \Delta G^\circ_m + \Delta G^\circ_{ps}$$

where ΔG°_{ps} is the measure of polymer-surfactant interaction. Therefore, one can write

$$\Delta G^\circ_{ps} = (2-\alpha)\, RT \ln \frac{cac}{cmc}$$

The values of ΔG°_{ps} for polymer - TX100 systems are given in Tables 31-35. The cac values for definite polymer - TX100 systems lie around a particular concentration range irrespective of temperature or polymer concentration. The major contributing factors for the lower values of cac may be (i) the hydrophobic interactions between surfactant alkyl chains, which is the main driving force[224], (ii) the hydrophobic interactions between the polymer and surfactant alkyl chains, the magnitude of which depends on the hydrophobicity of the polymer, (iii) the existence of specific interactions between the polymer segments and the surfactant hydrophilic moieties. The values of cac depends on the overall effect of all the above factors. It can be noted from the Tables 31-35 that the ΔG°_{ps} values for the PAA - TX100 systems are much more negative than those of the copolymers and PAAc, which indicate differences in binding patterns of PAA with nonionic TX100. Due to very low cac values for PAA-TX100 systems, there are more negative ΔG°_{ps} values. Wang et al.[224] observed similar kind of results for the systems of PAA and hydrophobically modified PAA with both SDS and CTAB. Interestingly, the magnitude of ΔG°_{ps} obtained by calorimetric method are similar to our values[224]. Even for CTAB-polymer systems

Table 31 : ΔG°_{ps} and ΔG°_{t} for polyacrylamide (PAA) - Triton X 100 system at different temperatures.

Polymer Concentration (%, w/v)	$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})				$-\Delta G^{\circ}_{t}$ (kJ mol^{-1})			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
0.0001	5.63	5.57	5.60	5.43	1.1	1.1	1.1	1.0
0.001	5.44	5.11	5.30	5.04	1.1	1.2	1.1	1.1
0.002	5.17	5.03	5.02	5.10	1.2	1.2	1.3	1.2
0.003	5.01	4.80	5.13	4.86	1.4	1.4	1.5	1.4
0.01	5.15	4.80	4.72	4.46	1.4	1.4	1.4	1.2

Table 32 : ΔG°_{ps} and ΔG°_{t} for P(AA-AAc) 85:15 copolymer - Triton X 100 system at different temperatures.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})**				**ΔG°_{t} (kJ mol^{-1})**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	3.15	3.17	3.06	2.98	-0.6	-0.5	-0.3	0
0.001	3.23	3.09	3.10	3.00	-0.5	-0.3	-0.1	-0.2
0.002	3.43	3.21	3.14	2.98	-0.2	-0.1	0.1	0.4
0.003	3.11	2.94	3.02	2.98	-0.2	-0.1	0.1	0.4
0.01	3.08	3.17	3.06	3.07	0.1	0.3	0.4	0.8

Table 33 : ΔG°_{ps} and ΔG°_{t} for P(AA-AAc) 65:35 copolymer - Triton X 100 system at different temperatures.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})**				**ΔG°_{t} (kJ mol^{-1})**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	3.20	3.15	3.10	2.98	-0.6	0.4	0.2	- 0.2
0.001	3.38	3.26	3.10	2.99	0.3	- 0.5	0.3	0.6
0.002	3.42	3.21	3.12	2.98	0	- 0.3	- 0.6	-1.0
0.003	3.31	3.30	3.22	2.95	0.2	0.6	0.8	0.7
0.01	3.36	3.17	3.10	3.07	0.4	0.5	0.5	0.7

Table 34 : ΔG°_{ps} and ΔG°_t for P(AA-AAc) 50:50 copolymer- Triton X 100 system at different temperatures.

Polymer Concentration (%, w/v)	$-\Delta G^\circ_{ps}$ (kJ mol^{-1})				ΔG°_t (kJ mol^{-1})			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.68	2.27	2.22	1.76	-0.4	-0.2	0.0	0.4
0.001	2.41	2.03	2.03	1.87	-0.3	0.06	0.2	0.5
0.002	2.24	2.03	2.03	1.93	0.0	0.4	0.6	1.0
0.003	2.19	2.14	2.14	1.76	- 0.02	0.18	0.4	0.9
0.01	2.14	2.06	1.98	1.82	0.3	0.4	0.6	1.0

Table 35 : ΔG°_{ps} and ΔG°_{t} for polyacrylic acid (PAAc) - Triton X100 system at different temperatures.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})**				**ΔG°_{t} (kJ mol^{-1})**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.14	2.08	2.14	1.73	0.0	0.2	0.5	0.9
0.001	2.19	2.06	2.09	1.73	0.0	0.4	0.6	0.9
0.002	2.24	2.03	2.03	1.91	0.0	0.4	0.6	1.0
0.003	2.19	2.16	2.01	1.76	0.2	0.4	0.7	0.9
0.01	2.14	2.06	1.98	1.82	0.3	0.5	0.7	1.1

Table 36 : ΔG°_{ps} and ΔG°_{t} for polyacrylamide (PAA) - CTAB system at different temperatures.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})**				**$-\Delta G^{\circ}_{t}$ (kJ mol^{-1})**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.00001	-	-	-	-	9.9	9.2	9.3	9.0
0.0001	0.23	0.83	1.07	1.52	10.8	10.8	10.4	10.0
0.002	0.29	1.26	1.52	2.50	7.7	7.5	7.3	6.5
0.002	0.29	0.73	0.98	1.94	9.7	9.2	8.8	8.8
0.003	0.21	0.70	0.94	1.85	11.9	12.1	12.4	12.6

Table 37 : ΔG°_{ps} and ΔG°_{t} for P(AA-AAc) 85:15 - CTAB system at different temperatures.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})**				**$-\Delta G^{\circ}_{t}$ (kJ mol^{-1})**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.13	2.60	2.86	3.21	5.4	5.4	8.8	5.3
0.001	2.62	2.67	2.56	2.67	0.2	0.3	0.5	0.5
0.002	1.52	1.92	1.97	2.23	3.2	3.0	3.2	3.0
0.003	1.89	2.20	2.62	2.67	3.4	3.5	3.7	3.6
0.01	1.57	1.66	2.68	3.06	4.5	4.6	4.8	4.7

Table 38 : ΔG°_{ps} and ΔG°_{t} for P(AA-AAc) 65:35 copolymer- CTAB system at different temperatures.

Polymer Concentration (%, w/v)	$-\Delta G^{\circ}_{ps}$ (kJ mol^{-1})				ΔG°_{t} (kJ mol^{-1})			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
0.0001	2.39	3.04	2.70	2.69	2.3	2.5	2.7	2.9
0.001	1.84	2.35	2.44	2.44	1.0	0.1	0.4	0.4
0.002	2.33	2.60	2.50	2.74	3.6	3.5	3.6	3.5
0.003	2.13	2.23	2.44	2.50	3.1	3.3	3.5	3.6
0.01	1.33	2.47	2.38	1.73	3.5	3.6	3.8	3.7

Table 39 : ΔG^{o}_{ps} and ΔG^{o}_{t} for P(AA-AAc) 50:50 copolymer - CTAB system at different temperatures.

Polymer Concentration (%, w/v)	**$-\Delta G^{o}_{ps}$ (kJ mol^{-1})**				**$-\Delta G^{o}_{t}$ (kJ mol^{-1})**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.01	2.89	2.95	3.28	1.2	0.9	1.3	1.1
0.001	1.47	2.34	2.50	2.93	0.9	0.6	1.0	0.9
0.002	1.89	2.67	2.88	2.86	0.3	0.2	0.5	0.4
0.003	2.70	2.89	2.68	3.06	0.5	0.2	0.6	0.5
0.01	2.26	2.06	2.62	3.36	0.5	0.1	0.5	0.4

(Tables 36-39), especially the copolymers, the ΔG°_{ps} values are more negative compared to the homopolymers. Increased hydrophilicity in case of PAA makes the differences in binding pattern with surfactants.

We also calculated the standard free energy associated for the interaction between surfactants and polymers, ΔG°_{t} , given by the difference in Gibbs free energy of transfer of the surfactant monomer from aqueous solution to the micelle in presence of polymers[225]

$$\Delta G^{\circ}_{t} = \Delta G^{\circ}_{psp} - \Delta G^{\circ}_{m}$$

Tables 31-35 gives the ΔG°_{t} values for free energy transfer of micelles from TX100 solutions to PAA, PAAc and copolymer solutions. In all these systems, on the whole the free energy of transfer of the surfactant monomer towards the polymer-surfactant micelle is smaller than the value corresponding to pure micelles, indicating the addition of these polymers stabilizes the micelle[221]. The micelle stabilization is more pronounced in case of PAA, which is more hydrophilic compared to other polymers. Tables 36-39 represent the ΔG°_{t} values in case of CTAB-polymer systems. The large differences in the ΔG°_{t} values in case of PAA-CTAB system, indicates favourable formation of aggregates on polymer strands compared to normal micelles.

(iii) Interfacial parameters :

One of the important features of the surfactant is to get adsorbed at the air / water interface. The concentration of surfactant is always high at the surface and the Gibbs equation measures the amount of surfactant adsorbed at the air / water interface.

The Gibbs equation in case of dilute systems is given by[227]

$$\Gamma = -\frac{1}{n\,RT}\,\frac{d\gamma}{d\log C}\ \text{mol cm}^{-2}$$

For the ternary surfactant-polymer-water system, the Gibbs equation becomes[229]

$$-d\gamma = \Gamma_1\, d\mu_1 + \Gamma_2\, d\mu_2 + \Gamma_3\, d\mu_3$$

As the polymer concentration is constant, we can assume

$$\Gamma_1\, d\mu_1 + \Gamma_3\, d\mu_3 = 0$$

where Γ_1 and Γ_3 refer to water and polymer excesses. Thus, even for the ternary systems, the surface tension data can be analyzed by the Gibbs equation. Γ, γ, R T and C are surface tension, gas constant, absolute temperature and concentration respectively. The Γ_{max} values for nonionic surfactant (Table 40) increases with increase in temperature because of the hydration of the ethylene oxide segments of the nonionic surfactant decreases with rise in temperature and hence there is the tendency to locate at the air / water interface. The Table 40 also gives surface excess values of PAA-TX100 systems which show similar conformations as nonionic surfactant systems and hence Γ_{max} values increase with temperature increase. For the copolymers and PAAc the Γ_{max} values are given in Tables 41-44. For the copolymers and PAAc the increase in temperature hinders adsorption at the liquid / air interface. The surface excess quantity is lower as the polymer concentration is increased indicating that the surfactants prefer relatively more water-polymer matrix than the water-air interface. The interaction may be physical, chemical or both.

In case of the PAA-CTAB systems, n is considered as 2, which is number of particles per molecule of the surfactant whose concentration varies with surfactant bulk phase concentration[214]. Γ_{max} values increase with rise in temperature (Table 45). The increase in surface excess values with increase in temperature may be due to partial shifting of interacting surfactant molecules from the bulk to the surface due to the presence of the polymers. However, the change in Γ_{max} is irregular with change in polymer concentration. In case of the copolymers-CTAB systems the surface excess values decrease with increase in temperature (Tables 46-48), as is the characteristic of any ionic surfactant. The changes in Γ_{max} values with temperature though is not very regular, and remains almost same with temperature.

Table 40 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for polyacrylamide (PAA) - Triton X 100 system at different temperatures.

Polymer Concentration (%, w/v)	Γ_{max} X 10^{10} mol cm^{-2}				A_{min} X 10^2 nm^2			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
0.0	2.64	2.75	2.87	3.02	63	60	58	55
0.0001	2.67	2.71	2.75	2.76	62	61	60	60
0.001	2.41	2.46	2.56	2.75	69	68	65	60
0.002	2.50	2.63	2.64	2.80	66	63	63	60
0.003	2.73	2.87	2.88	2.93	60	58	57	56
0.01	2.30	2.67	2.88	3.20	72	62	57	52

Table 41 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for P(AA-AAc) 85:15 copolymer - Triton X 100 system at different temperatures.

Polymer Concentration (%, w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^{2} nm^{2}**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.41	2.20	1.84	1.81	69	75	91	92
0.001	2.24	2.20	2.0	1.81	74	75	83	92
0.002	2.10	1.95	1.67	1.64	80	85	100	101
0.003	1.93	1.74	1.67	1.61	88	98	99	103
0.01	1.72	1.70	1.51	1.48	97	98	110	112

Table 42 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for P(AA-AAc) 65:35 copolymer - Triton X100 system at different temperatures.

Polymer Concentration (%, w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^{2} nm^{2}**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.41	2.15	1.89	1.53	69	77	88	108
0.001	2.30	2.03	1.67	1.53	72	82	100	108
0.002	2.18	2.10	1.78	1.59	76	84	94	104
0.003	2.53	2.03	1.78	1.53	66	82	93	108
0.01	2.41	2.15	1.89	1.53	69	77	88	109

Table 43 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for P(AA-AAc) 50:50 copolymer - Triton X100 system at different temperatures.

Polymer Concentration (%, w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^{2} nm^{2}**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	1.95	1.90	1.84	1.64	85	87	91	101
0.001	1.90	1.84	1.66	1.56	87	90	99	106
0.002	2.10	1.95	1.71	1.64	80	86	97	101
0.003	1.72	1.53	1.50	1.48	96	108	110	112
0.01	1.55	1.52	1.42	1.11	107	108	117	120

Table 44 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for polyacrylic acid (PAAc) - Triton X100 system at different temperatures.

Polymer Concentration (%, w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^2 nm^2**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	2.07	1.95	1.83	1.48	80	85	90	112
0.001	2.06	1.52	1.50	1.42	80	109	110	116
0.002	1.72	1.36	1.33	1.31	97	122	124	126
0.003	1.55	1.41	1.40	1.39	107	117	118	119
0.01	1.54	1.52	1.50	1.23	107	109	110	123

Table 45 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for polyacrylamide (PAA) - CTAB system at different temperatures.

Polymer Concentration %, (w\v) %	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} nm^2**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0	1.21	1.19	1.13	1.10	1.38	1.40	1.47	1.51
0.00001	0.30	0.50	0.80	1.11	5.4	3.3	2.1	1.5
0.0001	0.25	0.57	0.62	0.89	6.6	2.9	2.7	1.9
0.001	0.25	0.50	0.56	0.58	6.7	3.3	3.0	2.7
0.002	0.23	0.28	0.31	0.36	7.3	5.9	5.4	4.6
0.003	0.43	0.49	0.57	0.70	3.8	3.3	2.9	2.4

Table 46 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for P(AA-AAc) 85:15 copolymer - CTAB system at different temperatures.

Polymer Concentration (%, w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^2 hm^2**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	1.29	1.32	1.32	1.31	128	126	126	126
	1.30	1.31	1.29	1.30	127	126	128	126
0.001								
0.002	1.03	0.93	0.97	0.99	161	178	170	168
0.003	1.07	1.05	1.00	0.98	155	158	166	169
0.01	1.03	1.02	1.01	0.99	160	163	168	168

Table 47 : The maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}) for P(AA-AAc) 65:35 copolymer - CTAB system at different temperatures.

Polymer Concentration (%, w/v)	**Γ_{max} X 10^{10} mol cm^{-2}**				**A_{min} X 10^2 nm^2**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
0.0001	0.82	0.79	0.77	0.73	202	210	214	227
0.001	0.93	0.93	0.91	0.88	175	178	182	188
0.002	1.03	1.03	1.00	0.99	160	161	167	167
0.003	1.21	1.18	1.17	1.15	137	140	144	144
0.01	0.96	0.93	0.92	0.92	173	178	181	181

Table 51 : Thermodynamic parameters of adsorption for P(AA-AAc) 65:35 copolymer - Triton X 100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	$-\Delta G^\circ_{ad}$ (kJ mol^{-1})				ΔH°_{ad} (kJ mol^{-1})	ΔS°_{ad} (J mol^{-1} K^{-1})
	30°C	35°C	40°C	45°C		
0.0001	46.6	48.9	51.8	56.6	153.3	660
0.001	46.9	49.9	54.0	56.6	154.0	662
0.002	47.9	49.6	52.1	54.7	91.4	461
0.003	45.1	49.3	52.1	55.2	155.2	665
0.01	52.5	54.4	63.3	66.6	158.7	102

Table 52 : Thermodynamic parameters of adsorption for P(AA-AAc) 50:50 copolymer - Triton X 100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**ΔH°_{ad} (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	50.1	50.9	52.2	55.1	47.9	322
0.001	50.2	51.2	54.1	56.3	78.7	424
0.002	48.7	50.1	53.4	54.7	80.6	426
0.003	51.7	54.6	56.3	57.4	93.7	480
0.01	54.8	55.7	57.6	65.5	154.7	695

Table 53 : Thermodynamic parameters of adsorption for polyacrylic acid (PAAc) - Triton X100 system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**ΔH°_{ad} (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	49.6	51.5	52.9	58.3	118.3	552
0.001	49.5	54.6	57.4	61.5	185.2	776
0.002	56.0	59.4	60.5	61.2	44.4	334
0.003	55.4	56.4	58.4	59.6	33.2	292
0.01	55.0	55.9	56.7	57.6	28.9	174

Table 54 : Thermodynamic parameters of adsorption for polyacrylamide - CTAB system at different polymer concentrations.

Polymer Concentration (%, w/v)	$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})				$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})	ΔS°_{ad} (kJ mol^{-1} K^{-1})
	30°C	35°C	40°C	45°C		
0.0	72.5	73.7	76.0	77.2	27.6	0.330
0.00001	148.2	111.2	84.6	72.3	1682.7	5.084
0.0001	172.9	100.8	100.2	78.6	1873.2	5.668
0.001	165.8	130.7	112.0	101.3	1445.2	4.244
0.002	189.8	168.2	162.2	146.1	1017.9	2.742
0.003	119.9	111.2	104.6	95.3	606.3	1.606

Table 55 : Thermodynamic parameters of adsorption for P(AA-AAc) 85:15 copolymer - CTAB system at different polymer concentrations.

Polymer Concentration (%, w/v)	$-\Delta G^\circ_{ad}$ (kJ mol^{-1})				$-\Delta H^\circ_{ad}$ (kJ mol^{-1})	ΔS°_{ad} (J mol^{-1} K^{-1})
	30°C	35°C	40°C	45°C		
0.0001	64.2	64.7	65.2	65.8	31.2	109
0.001	70.2	70.7	71.4	71.1	38.9	103
0.002	74.4	75.2	76.8	77.2	12.4	205
0.003	73.3	73.7	74.9	75.3	30.5	141
0.01	71.6	72.4	72.8	73.7	31.5	133

Table 56 : Thermodynamic parameters of adsorption for P(AA-AAc) 65:35 copolymer - CTAB system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^{\circ}_{ad}$ (kJ mol^{-1})**				**$-\Delta H^{\circ}_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	80.8	81.2	82.0	82.5	44.9	118
0.001	77.8	79.3	80.2	80.5	23.6	180
0.002	72.0	73.0	73.4	74.5	23.2	161
0.003	68.3	68.9	69.6	71.0	14.3	178
0.01	74.0	75.4	76.2	77.0	13.9	199

Table 57 : Thermodynamic parameters of adsorption for P(AA-AAc) 50:50 copolymer - CTAB system at different polymer concentrations.

Polymer Concentration (%, w/v)	**$-\Delta G^\circ_{ad}$ (kJ mol^{-1})**				**$-\Delta H^\circ_{ad}$ (kJ mol^{-1})**	**ΔS°_{ad} (J mol^{-1} K^{-1})**
	30°C	**35°C**	**40°C**	**45°C**		
0.0001	83.3	84.1	85.5	85.6	33.0	166
0.001	83.2	83.3	83.4	83.5	74.8	271
0.002	90.1	90.6	90.7	91.2	69.5	68
0.003	87.2	88.3	88.6	88.7	75.0	436
0.01	79.8	79.9	79.9	80.0	75.6	138

group helps adsorption to take place and since at higher temperature the surfactant is less hydrated, comparatively less energy is needed for adsorption to take place[227]. The magnitudes of ΔG°_{ad} values for Triton X 100 in presence of PAAc are more negative than PAA. The ΔG°_{ad} values for the copolymers lie in between those of the two homopolymers. The acrylic acid moiety being more predominant in case of the copolymers this kind of behaviour is observed. Similar tendencies are observed for ionic surfactant - polymer systems, though the absolute magnitudes are much lower(Table54-57). The enthalpy and entropy values were calculated by the equation

$$\Delta G^{\circ}_{ad} = \Delta H^{\circ}_{ad} - T\Delta S^{\circ}_{ad}$$

The overall entropy changes in the systems were found to be very high. The adsorption process in case of these polymers with TX100 was found to be endothermic. In case of CTAB, in presence of the copolymers, the adsorption is exothermic suggesting differences in binding patterns of these polymers with ionic and nonionic surfactants.

(v) Viscosity studies :

Water-soluble polymers are widely used to control the rheological properties of an extensive range of aqueous based formulations. The viscosity of polymer solutions is a very important and fundamental property and is essential in many industrial formulations. The intrinsic viscosity $[\eta]$ of the polymer solutions were determined using the Huggins and Kraemer equation[16].

$$\eta_{sp} / C = [\eta] + K' [\eta]^2 C + \ldots\ldots\ldots\ldots$$

$$\ln \eta_r / C = [\eta] - K'' [\eta]^2 C + \ldots\ldots\ldots\ldots$$

where the specific viscosity $\eta_{sp} = \eta_r - 1$ and relative viscosity $\eta_r = \eta_{soln}/\eta_{solv}$. The coefficients K′ and K″ are direct measures of interactions between the macromolecules. K′ - K″ are constants for a given polymer / solvent / temperature system. Intrinsic viscosity $[\eta]$ of the polymers were determined in presence of various surfactant concentration (Fig. 45). Polyacrylamide being a nonionic polymer, it was

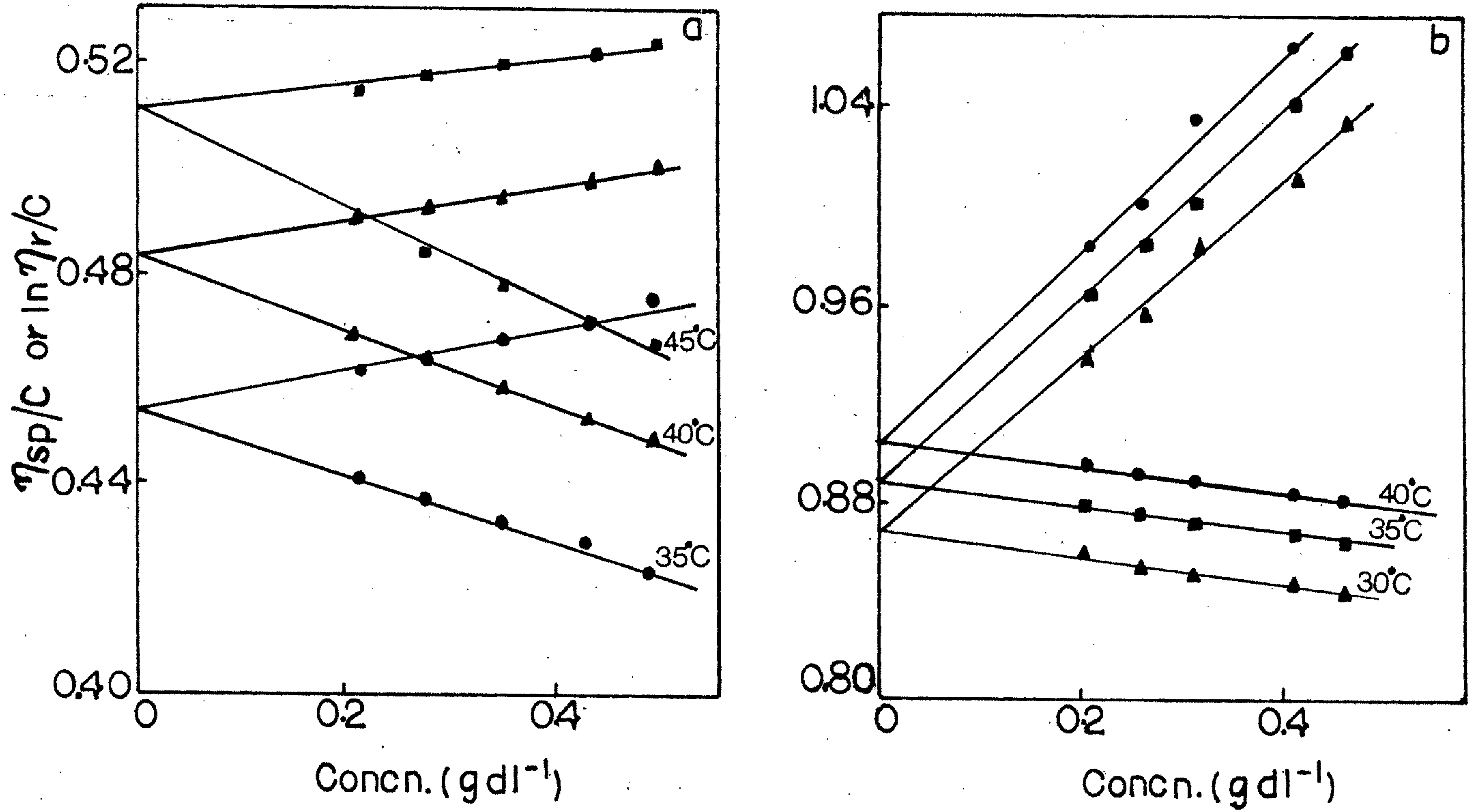

Fig. 45 : Representative plots ln η_r/C or η_{sp}/C vs. concentration for (a) PAAc / 0.005% TX100; (b) P(AA-AAc) 50:50 copolymers in presence of NaCl at different temperatures.

easy to compute intrinsic viscosity $[\eta]$ using the above equation. However, the copolymers and PAAc behaved like polyelectrolytes as mentioned earlier. Their solutions in water showed unique dependence on concentration. η_{sp}/C for these polymers in TX100 solutions increases with dilution. Hence, it was difficult to compute intrinsic viscosities of these polymers using the Huggins and Kraemer equations. Therefore, an empirical relation the Fuoss-Strauss[330] equation was used to compute $[\eta]$ for such systems.

$$\eta_{sp} / C = A' / (1 - B'C^{1/2}) \text{ or } \frac{C}{\eta_{sp}} = \frac{1}{A'} + \frac{B'}{A'} C^{1/2}$$

where A' and B' are constants. Straight lines were obtained on plotting $(\eta_{sp}/C)^{-1}$ against $C^{1/2}$. The A' values so obtained are taken as $[\eta]$. Some representative plots for such systems is given in Fig. 46. The large increase in (η_{sp}/C) values as the solution is diluted is probably due to the fact that as the solution is diluted, the polymer molecules no longer fills up all the space and the intervening regions extract some of the mobile ions. Net charges develop in the domains of the polymer molecule causing them to expand. As this process continues with further dilution, the expansive forces increase. At high dilutions the polymer molecules loose most of their mobile ions and are extended virtually to their maximum length (leading to more chain-chain entanglement). This leads to high η_{sp}/C values[321].

The $[\eta]$ values for the polymer systems at different TX100 concentrations are given in Table 58. The copolymers and PAAc show large $[\eta]$ values in presence of different TX100 concentrations. It is a characteristic property of polyelectrolytes to show large $[\eta]$ values. The viscosity of these polymers were carried out in presence of an electrolyte NaCl. Addition of an electrolyte suppresses the loss of the mobile ions, hence the rise in η_{sp}/C at low concentrations was eliminated and conformity with the Huggins and Kraemer equations was restored. From Table 58, it can be seen that for

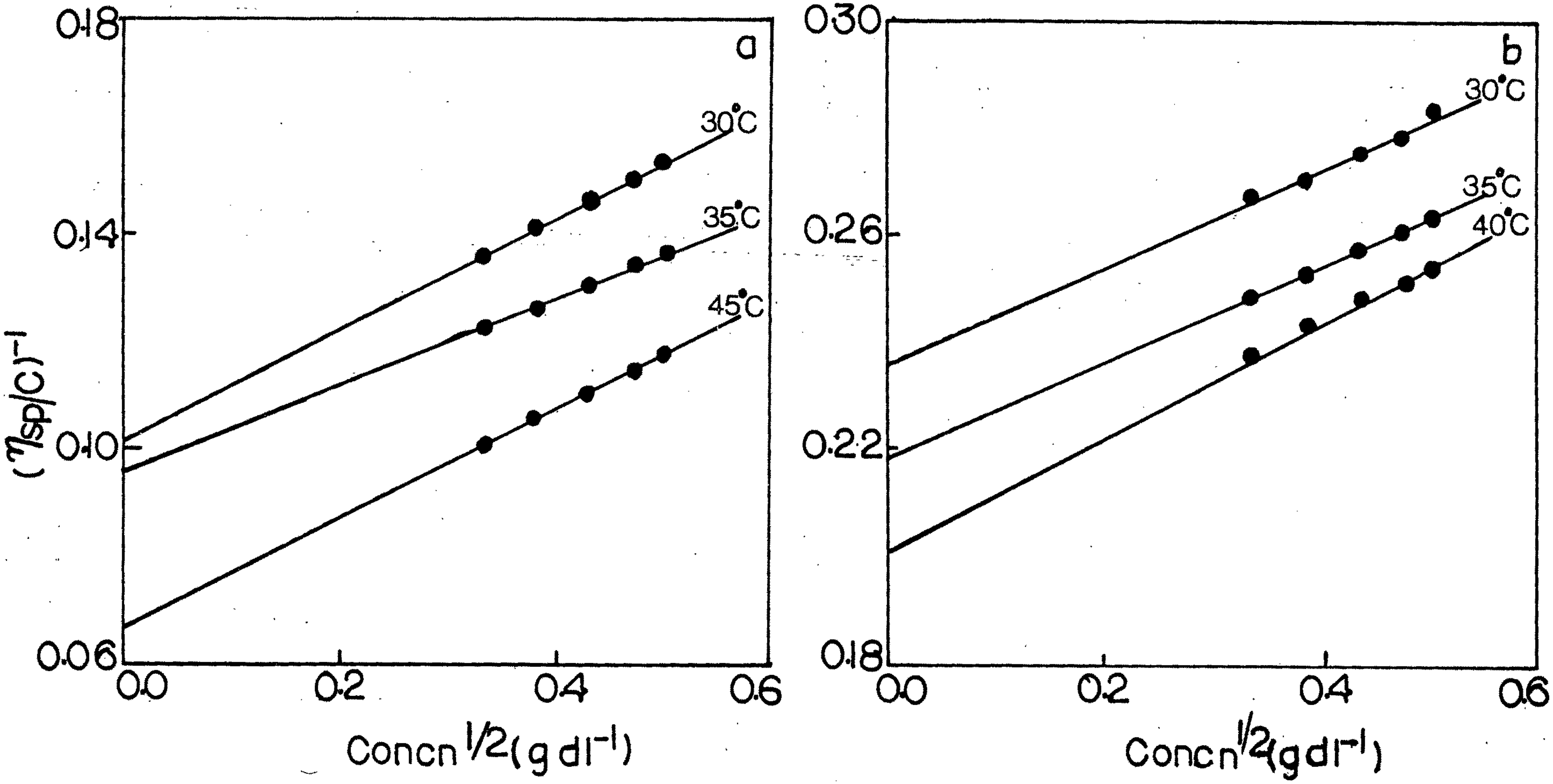

Fig. 46 : Plots of $(\eta_{sp}/C)^{-1}$ vs. $(C)^{1/2}$ for (a) P(AA-AAc) 65:35 copolymer; (b) P(AA-AAc) 50:50 copolymer in presence of 0.005% TX100 at different temperatures.

Table 58 : Intrinsic viscosity [η] (dl/g) of various polymer systems in presence of Triton X100 at different temperatures.

Polymer Systems	Triton X100 Concentration (%, w/v)															
	0.0				0.005				0.015				0.10			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
*S1	--	2.98	2.91	2.62	1.87	1.85	1.78	1.75	1.96	1.89	1.87	1.84	1.94	1.90	1.88	1.83
S2	20.3	26.4	32.6	38.9	10.2	15.1	21.3	27.4	22.5	28.0	33.5	35.2	8.72	26.3	31.3	35.5
S2 + NaCl	2.25	2.26	2.27	2.31	1.65	1.72	1.77	1.84	1.93	1.98	2.02	2.06	2.11	2.14	2.18	2.25
S3	22.4	26.2	31.6	39.8	9.8	10.6	12.5	16.2	10.5	11.8	14.9	18.5	20.8	23.8	32.2	38.5
S3 + NaCl	1.07	1.09	1.15	1.17	1.04	1.22	1.39	1.49	1.22	1.29	1.38	1.48	1.34	1.46	1.55	1.72
S4	6.4	7.1	8.9	11.2	4.2	4.6	5.2	6.0	3.7	4.3	6.4	8.3	4.7	5.9	9.0	10.8
S4 + NaCl	0.90	0.92	0.93	0.99	0.85	0.87	0.88	0.91	0.87	0.89	0.91	0.92	0.87	0.91	0.94	0.97
S5	18.3	23.6	28.4	33.5	12.4	14.3	16.5	21.6	15.2	17.3	20.6	24.2	17.1	20.7	27.5	32.2
S5 + NaCl	0.53	0.65	0.71	0.77	0.43	0.45	0.48	0.51	0.45	0.45	0.54	0.56	0.49	0.52	0.55	0.59

*S1 - PAA; S2 P(AA-AAc) 85:15; S3 P(AA-AAc) 65:35; S4 P(AA-AAc) 50:50; S5 PAAc.

These notations are used in other tables hence forth.

the polyelectrolyte like systems, [η] values drastically reduce in presence of NaCl. For polyacrylamide polymers, [η] decreases with increase in temperature whereas, polyelectrolytes show an increase in [η] with increasing temperature. As mentioned earlier increase in temperature of polymer solution generates two antagonistic effects[324,325]. First an increase in temperature generally leads to an increase in solvent power i.e. solubility increases. This leads to uncoiling of the polymer chains leading to an increase in [η] with temperature. Secondly increase in temperature may lower the rotational barrier thereby enhancing the degree of rotation about the skeletal bond, forcing the molecular chains to assume a more compact coiled configuration. This leads to a decrease in [η] with increase in temperature. The [η] values in presence of the surfactants are lower. This may be an indication that surfactants help to decrease entanglement of polymer chains and assist in a smoother flow.

In case of the CTAB-polymer systems, it was difficult to carry out viscosity studies of the copolymers and PAAc with CTAB in the region of cmc. As mentioned earlier addition of an ionic surfactant to polymers brings polyelectrolytes close to charge neutralization which results in phase seperation[221]. However, further addition of ionic surfactant may resolubilize the precipitate. The properties of a polyelectrolyte play a major role in directing complex formation and microstructure. Hence, we carried out viscosity measurements at higher CTAB concentrations. Moreover, at these CTAB concentrations the polyelectrolyte like behaviour of the copolymers and PAAc was not found. Hence, it was easy to compute intrinsic viscosity [η] by the Huggins and Kraemer[16] equations (Fig. 47). Table 59 gives [η] values of CTAB-polymer systems at different CTAB concentrations. It was found that [η] values for all these systems increase with increase in temperature. This behaviour of CTAB at such high concentrations is akin to a salt. Increase in temperature results in increase in electrostatic repulsions which lead to larger [η] values with increase in temperature.

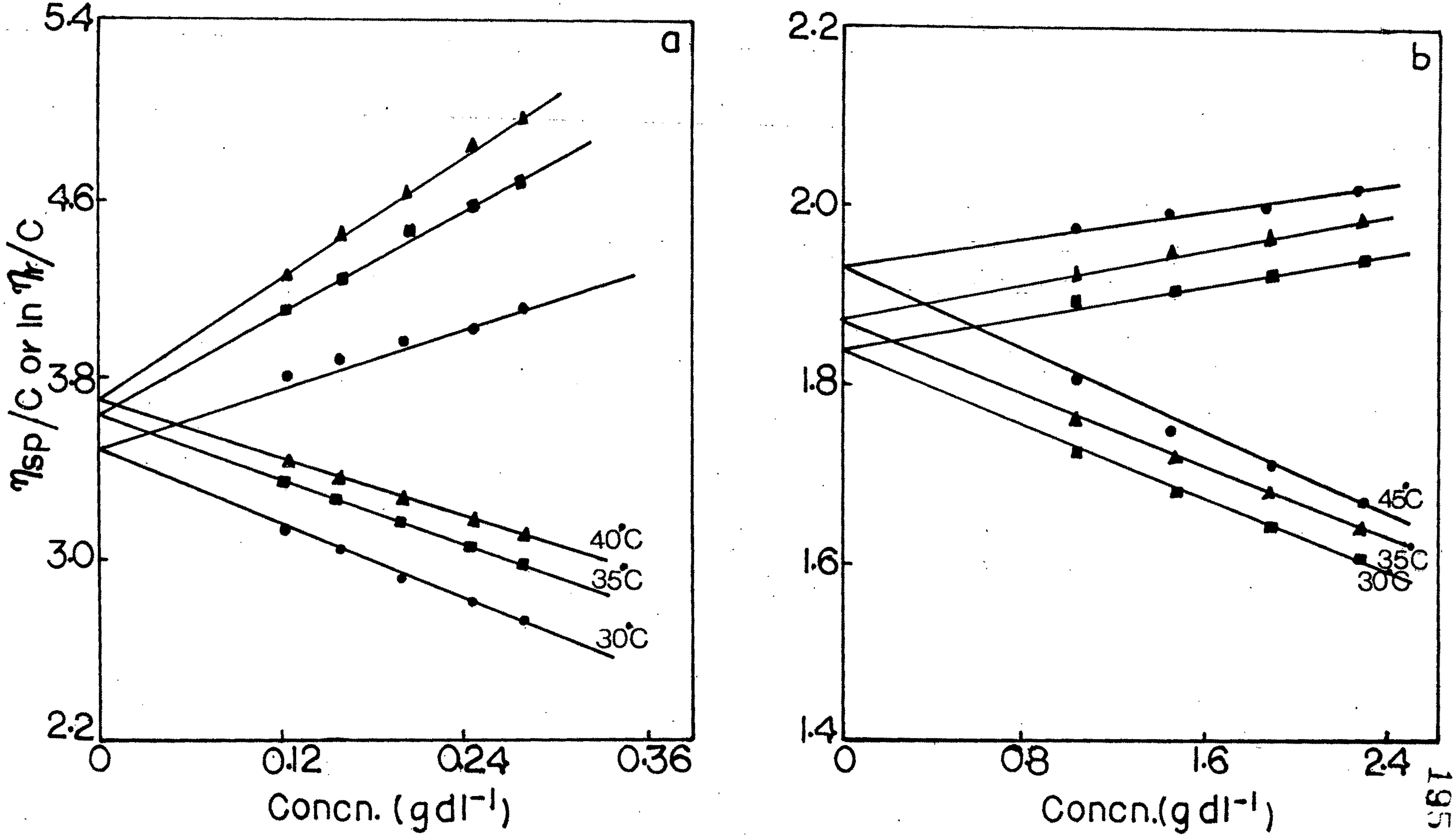

Fig. 47 : Representative plots of ln η_r/C or η_{sp}/C vs. concentration for (a) PAAc / 1.0% CTAB; (b) PAA / 1.0% CTAB at different temperatures.

Table 59 : Intrinsic viscosity [η] (dl/g) of various polymer systems in presence of CTAB at different temperatures.

Polymer Systems	**CTAB Concentration (%, w/v)**											
	0.75				**1.0**				**1. 5**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
S1	1.87	1.89	1.90	1.93	1.84	1.87	1.93	1.97	1.80	1.84	1.88	1.94
S2	2.32	2.37	2.42	2.45	1.97	2.03	2.09	2.16	1.84	1.89	1.93	1.97
S3	2.60	2.67	2.74	2.80	2.30	2.34	2.35	2.38	1.90	2.08	2.28	2.32
S4	3.62	3.73	3.75	3.80	3.28	3.30	3.33	3.36	2.90	2.94	3.06	3.08
S5	3.77	3.81	3.85	3.93	3.54	3.64	3.71	3.81	3.32	3.39	3.44	3.46

The relative viscosity η_r at different concentrations was used for calculations of voluminosity V_E of a polymer solution at a given temperature. The voluminosity values give the volume of the solvated molecule in solution. V_E is obtained by plotting Y_1 against concentration (C g dl^{-1}) where[322-323]

$$Y_1 = (\eta_r^{0.5} - 1) / C\,(1.35 \times \eta_r^{0.5} - 0.1)$$

The straight line obtained is extrapolated to C=O and the intercept yielded V_E. Figs. 48 and 49 gives representative plots for polymers TX100 and polymers-CTAB system. The shape factor ν was then calculated from the equation

$$[\eta] = \nu\, V_E\,.$$

The shape factor and V_E values for the TX100 polymer systems for different concentrations are given in Tables 60 and 61. The magnitude of V_E values change with changes in $[\eta]$. However, ν - the shape factor values for the systems which showed conformity with Huggins and Kraemer equation, were found to be around ~ 2.5. The values are independent of temperature and suggest spherical conformations of macromolecules in solution[331]. However, for the polyelectrolytic systems, the shape factor values are much larger than ~ 2.5 suggesting conformations other than spherical in solutions. In case of CTAB-polymer systems, the ν values are ~ 2.5 suggesting spherical conformations in solutions (Tables 62 and 63).

The $[\eta]$ values of polymers in presence of surfactant and in water were used to calculate the ratios of expansion factor δ/δ_o for the polymer chains in surfactant solutions.

From the theory of polymers it is known that[270]

$$|\eta| = \Phi\,(r_o^2/M)^{3/2}\, M^{1/2}\, \delta^3 = KM^{1/2}\, \delta^3$$

where Φ is a universal constant = 2.84×10^{21} (independent of polymer, temperature and solvent).

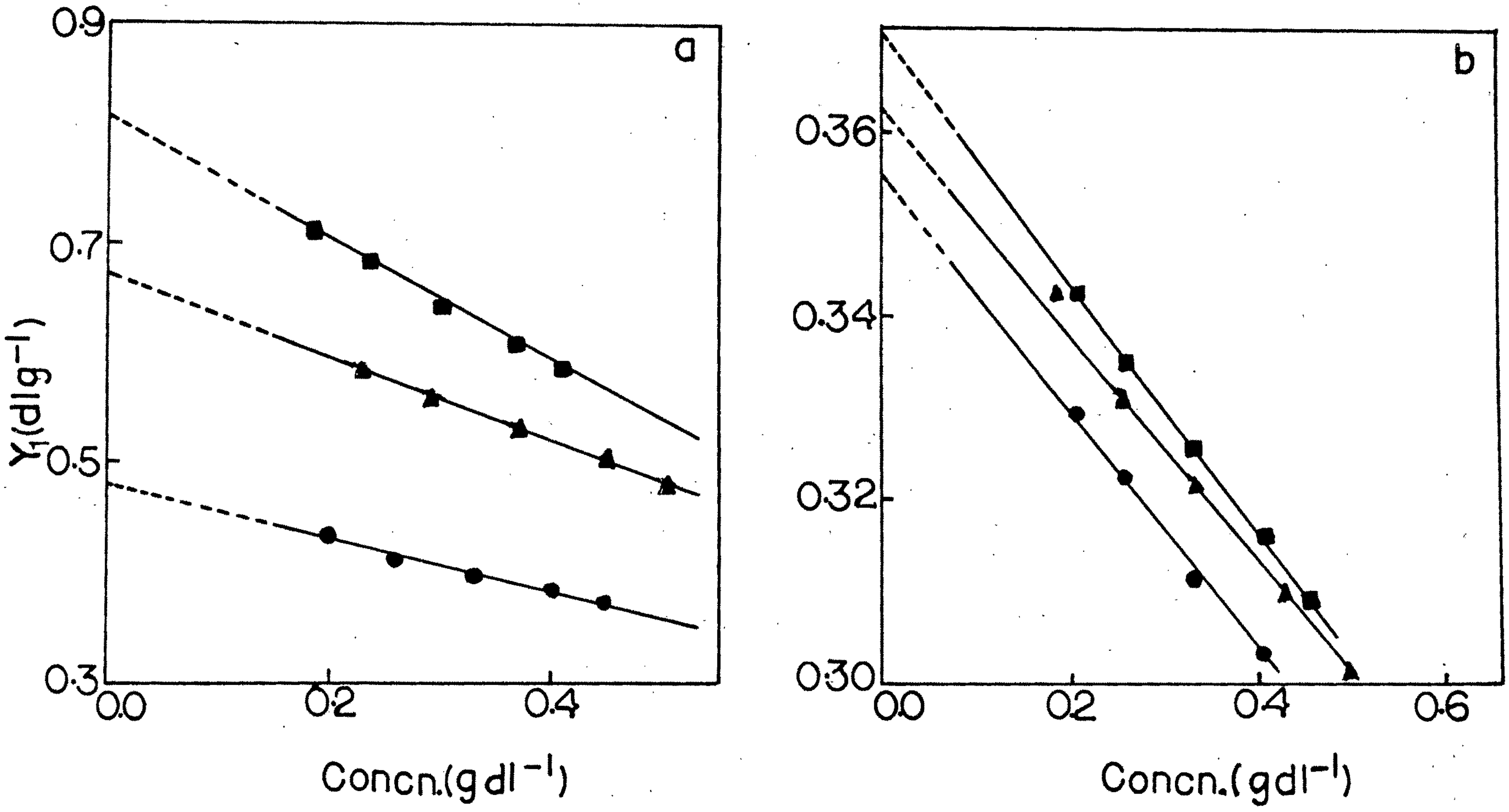

Fig. 48 : Plot of Y_1 vs. concentration $(g\,dl^{-1})$ for (a) ● P(AA-AAc) 85:15 / 0.1% TX100. ▲ P(AA-AAc) 65:35 / 0.05% TX100; ■ P(AA-AAc) 85:15 / 0.005% TX100 in presence of NaCl; (b) ● P(AA-AAc) 50:50 / 0.1% TX100 at ● 30°C; ▲ 35°C; ■ 40°C.

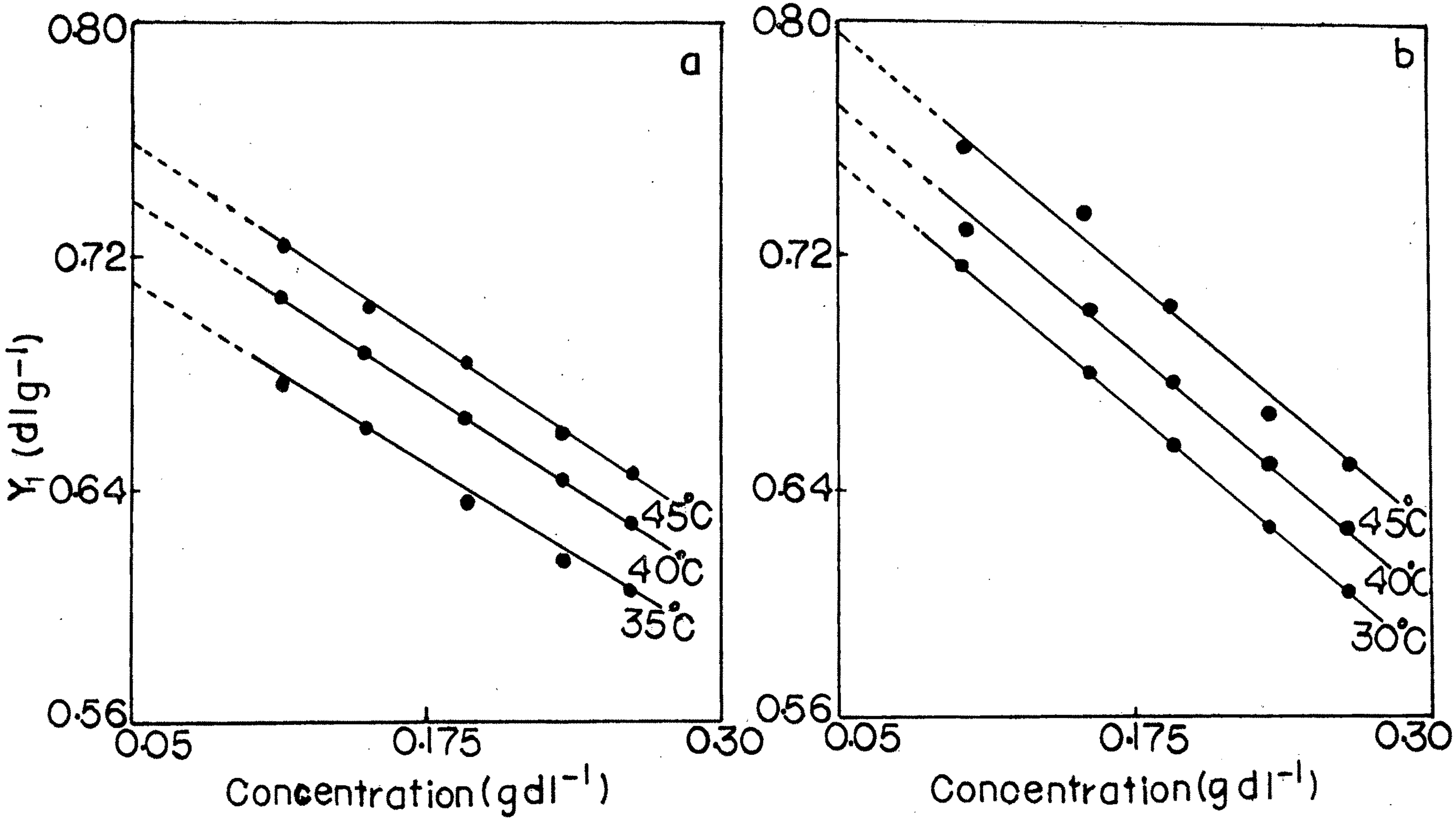

Fig. 49 : Plot of Y_1 vs. concentration (g dl^{-1}) for (a) P(AA-AAc) 85:15 copolymer / 1.5% CTAB; (b) P(AA-AAc) 65:35 copolymer / 1.5% CTAB at different temperatures.

Table 60 : Voluminosity (V_E) and shape factor (ν) values for various polymer systems in presence of different concentration of TX100.

Polymer Systems	Triton X100 Concentration %,w\v															
	0.0								0.005							
	V_E				ν				V_E				ν			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
S1	--	1.16	1.17	1.04	--	2.6	2.5	2.4	0.72	0.67	0.68	0.68	2.6	2.5	2.6	2.6
S2	2.75	2.92	3.28	3.71	7.4	8.2	9.3	9.7	2.42	2.6	2.71	2.95	5.8	5.8	6.0	6.4
S2 + NaCl	0.86	0.87	0.87	0.90	2.6	2.6	2.6	2.6	0.64	0.66	0.69	0.72	2.6	2.6	2.5	2.6
S3	2.71	2.97	3.21	3.40	8.3	8.5	9.8	9.9	2.30	2.45	2.64	2.77	4.3	4.4	4.9	5.3
S3 + NaCl	0.42	0.43	0.45	0.46	2.5	2.5	2.6	2.5	0.40	0.47	0.54	0.57	2.6	2.5	2.6	2.6
S4	2.0	2.23	2.47	2.64	3.2	3.4	3.6	3.7	1.35	1.42	1.49	1.52	3.1	3.1	3.4	3.5
S4 + NaCl	0.35	0.36	0.37	0.38	2.5	2.5	2.52	2.5	0.34	0.36	0.37	0.38	2.5	2.5	2.5	2.5
S5	3.63	4.10	4.54	4.82	5.3	6.7	7.3	8.2	2.38	2.58	2.66	2.71	5.2	5.5	5.7	5.8
S5 + NaCl	0.20	0.26	0.28	0.30	2.5	2.5	2.55	2.57	0.17	0.18	0.19	0.20	2.5	2.5	2.5	2.5

Table 61 : Voluminosity (V_E) and shape factor (ν) values for various polymer systems in presence of different TX100 concentration.

Polymer Systems	**Triton X100 Concentration**															
	0.0								**0.005 (%, w/v)**							
	V_E				ν				V_E				ν			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
S1	0.75	0.74	0.72	0.72	2.61	2.54	2.56	2.55	0.74	0.73	0.73	0.69	2.62	2.56	2.57	2.64
S2	3.50	3.63	3.72	3.75	6.41	8.40	9.1	9.4	2.0	3.26	3.35	3.42	4.34	6.12	9.20	10.4
S2 + NaCl	0.74	0.76	0.77	0.79	2.61	2.61	2.60	2.60	0.81	0.80	0.81	0.87	2.6	2.66	2.61	2.6
S3	2.20	2.74	3.04	3.33	4.78	4.31	4.89	5.55	3.23	3.56	3.64	3.79	6.4	6.68	8.84	10.16
S3 + NaCl	0.48	0.51	0.58	0.53	2.52	2.52	2.58	2.55	0.52	0.56	0.60	0.66	2.60	2.60	2.57	2.61
S4	1.2	1.32	1.4	1.7	3.08	3.26	3.3	3.4	1.4	1.56	2.05	2.34	3.21	3.70	4.38	5.25
S4 + NaCl	0.34	0.36	0.38	0.40	2.50	2.51	2.50	2.52	0.34	0.36	0.37	0.38	2.55	2.54	2.54	2.54
S5	2.61	2.88	3.17	3.46	5.28	6.00	6.5	7.00	3.1	3.42	3.8	4.23	5.53	6.05	7.29	7.60
S5 + NaCl	0.18	0.21	0.22	0.23	2.51	2.52	2.51	2.50	0.19	0.21	0.22	0.24	2.50	2.50	2.52	2.51

Table 62 : Voluminosity (V_E) values for polymers at different CTAB concentrations.

Polymer Systems	**CTAB Concentration %,w\v**											
	0.75				**1.0**				**1.5**			
	30°C	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**	**30°C**	**35°C**	**40°C**	**45°C**
S1	0.76	0.75	0.75	0.76	0.70	0.73	0.75	0.76	0.71	0.74	0.74	0.76
S2	0.90	0.92	0.93	0.94	0.77	0.80	0.80	0.84	0.72	0.74	0.77	0.78
S3	0.99	1.00	1.04	1.05	0.92	0.92	0.92	0.87	0.76	0.78	0.87	0.85
S4	1.33	1.33	1.35	1.35	1.23	1.25	1.24	1.22	1.10	1.13	1.13	1.16
S5	1.37	1.38	1.38	1.39	1.29	1.39	1.40	1.45	1.25	1.23	1.31	1.32

Table 63 : Shape factor (ν) values for polymers at different CTAB concentrations.

Polymer Systems	CTAB Concentration % ,w\v											
	0.75				1.0				1.5			
	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C	30°C	35°C	40°C	45°C
S1	2.5	2.5	2.5	2.5	2.6	2.5	2.5	2.5	2.5	2.5	2.5	2.5
S2	2.5	2.6	2.6	2.6	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
S3	2.5	2.6	2.6	2.6	2.5	2.5	2.5	2.6	2.5	2.5	2.5	2.6
S4	2.7	2.8	2.7	2.8	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
S5	2.7	2.7	2.8	2.8	2.7	2.6	2.6	2.6	2.6	2.6	2.6	2.6

$(r_o^2)^{1/2}$ = root mean square end to end unpreturbed distance of the polymer coil, independent of solvent and temperature.

M = molecular weight of the polymer

δ = expansion factor of the polymer

$$\therefore |\eta| / |\eta|_o = (\delta/\delta_o)^3$$

where $|\eta|_o$ is the intrinsic viscosity of polymer in water and $|\eta|$ is the intrinsic viscosity in surfactant solution.

Table 64 gives the expansion factor ratios of the polymers in TX100 both in presence and absence of NaCl. The values explain that when the concentration of TX100 is low the macromolecules remain contracted, but as the concentration of TX100 increases, it gets adsorbed on the polymer and the end to end distance increases resulting in the expansion of the macromolecular chain. The initial addition of surfactants results in wrapping of the molecules by the polymer segments and further addition results in expansion of polymer coils due to repulsion among surfactant molecules or micelles forcing the polymer chains to expand. Such results were observed for SDS-PVP system[354].The schematic representation is shown in Fig. 50.

However, in case of CTAB-polymer systems (Table 65) especially in case of the copolymers, PAAc and CTAB, that initial addition of surfactant results in wrapping up of the polymer chains and further addition of the surfactant not much changes were observed. This is probably due to the fact that these polymers behave like polyelectrolytes and show expanded chain conformations in water. However addition of surfactant which behaves like a salt lowers [η] values to a great extent. So an initial addition of the surfactant large δ/δ_0 values are observed but on further addition of surfactant not much changes in the expansion factor ratios were observed. In case of PAA-CTAB systems, the macromolecule PAA remains contracted, but as concentration of CTAB increases, due to repulsions of the head group, the macromolecule expands and hence the expansion factor ratios increase.

Table 64 : Expansion factor ratios for the polymers in presence of different TX100 concentrations.

Polymer Systems	30°C			35°C			40°C			45°C		
	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3
S1	-	1.01	1.0	0.85	1.01	1.01	0.85	1.02	1.01	0.87	1.02	1.00
S2	0.80	1.30	1.00	0.83	1.23	1.00	0.87	1.17	1.00	0.94	1.10	1.00
S2+NaCl	0.90	1.05	1.03	0.91	1.05	1.03	0.97	1.04	1.02	0.93	1.04	1.03
S3	0.76	1.02	1.26	0.74	1.04	1.26	0.73	1.06	1.30	0.74	1.05	1.28
S3+NaCl	1.00	1.05	1.03	1.04	1.02	1.04	1.07	1.00	1.01	1.08	1.05	1.05
S4	0.90	1.01	1.00	0.87	1.01	1.01	0.84	1.01	1.01	0.81	1.00	1.02
S4+NaCl	0.98	1.00	0.98	0.98	1.00	1.01	0.98	1.01	1.01	0.97	1.00	1.01
S5	0.88	1.07	1.04	0.85	1.07	1.07	0.83	1.10	1.10	0.86	1.04	1.10
S5+NaCl	0.93	1.01	1.03	0.28	1.05	1.01	0.88	1.1	1.10	0.87	1.03	1.02

$\delta_1 = \delta_{0.005} / \delta_0$; $\delta_2 = \delta_{0.015} / \delta_{0.005}$; $\delta_3 = \delta_{0.10} / \delta_{0.015}$

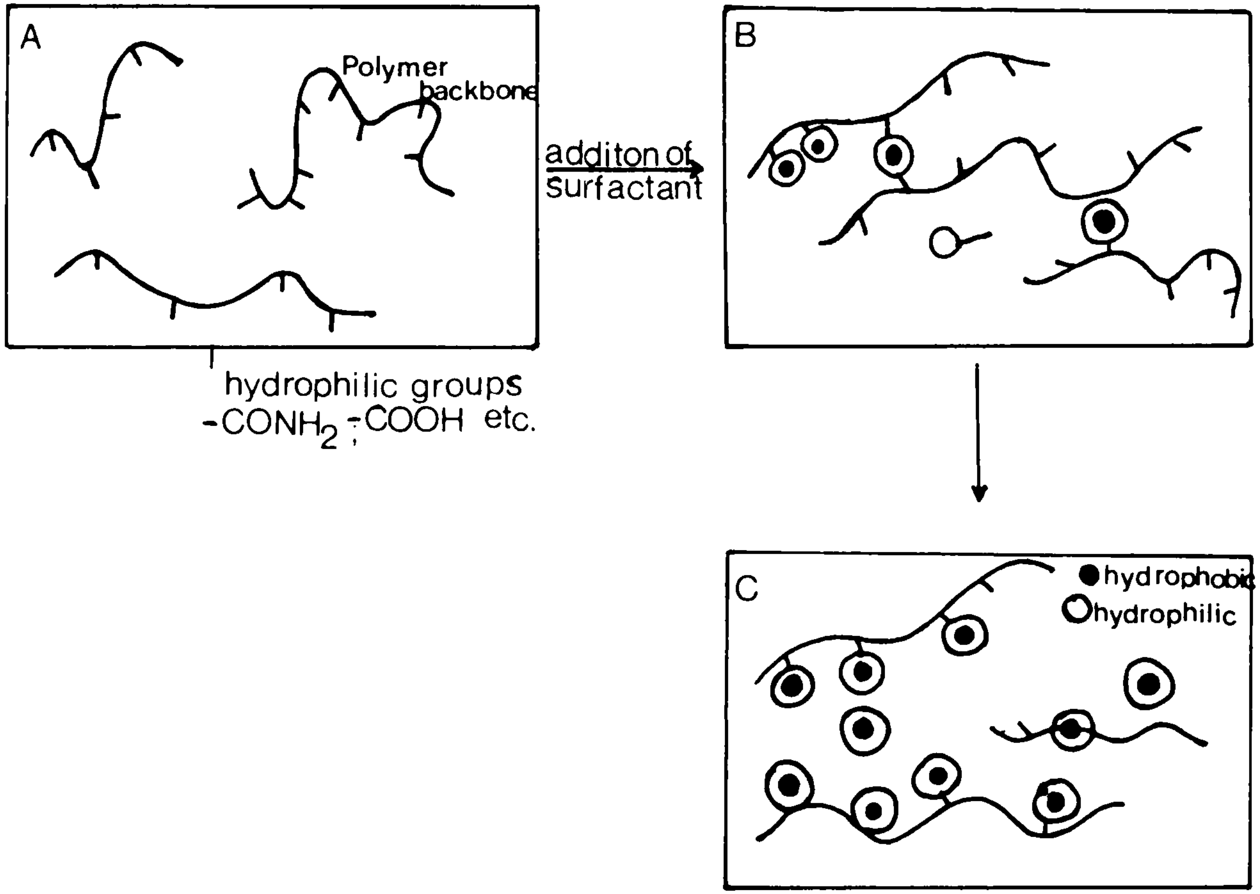

Fig. 50 : Pictorial representation of polymer - chains wrapping surfactant molecules (following Ulf Olofsson et al., *Langmuir*, **10**, 1421, 1994).

Table 65 : Expansion factor ratios for the polymers in presence of different CTAB concentrations.

Polymer Systems	30°C			35°C			40°C			45°C		
	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3	δ_1	δ_2	δ_3
S1	-	1.02	1.01	1.16	1.00	1.02	1.15	1.0	1.0	1.10	1.0	1.0
S2	2.21	1.05	1.02	2.23	1.06	1.02	2.38	1.05	1.03	2.51	1.04	1.03
S3	2.05	1.04	1.03	2.14	1.05	1.04	2.25	1.05	1.01	2.42	1.04	1.0
S4	1.21	1.03	1.04	1.24	1.03	1.03	1.34	1.04	1.03	1.43	1.04	1.02
S5	1.70	1.03	1.03	1.84	1.02	1.02	1.95	1.01	1.02	2.05	1.00	1.03

$\delta_1 = \delta_{0.75} \backslash \delta_0$; $\delta_2 = \delta_{1.0} \backslash \delta_{0.75}$; $\delta_3 = \delta_{1.5} \backslash \delta_{1.0}$

Various activation parameters for the viscous flow were evaluated from the viscosity data using the Frenkel-Eyring[324] equation.

$$\eta = Nh/V \exp \Delta G^{\neq}_{vis} / RT$$

where V is the molar volume, N is the Avogadro number, h is the Plancks constant, R the gas constant, T the temperature and $\Delta G^{\neq}_{vis}$ is the free energy for the viscous flow. The above equation can be rewritten as

$$\ln (\eta V/Nh) = \Delta G^{\neq}_{vis} / RT = \Delta H^{\neq}_{vis} / RT - \Delta S^{\neq}_{vis} / R$$

where $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ are the enthalpy and entropy for the viscous flow, ln (ηV/Nh) when plotted against the reciprocal of temperature yields a linear graph (Fig. 51,52) with the slope and intercept yielding $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ respectively. As mentioned in chapter-3, the ηV/Nh is a unitless quantity. On plotting $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ values against concentration of polymer and extrapolating it to C=O, $\Delta H^{\neq o}_{vis}$ and $\Delta S^{\neq o}_{vis}$ values are obtained. $\Delta G^{\neq o}_{vis}$ values are then computed by the thermodynamic relation :

$$\Delta G^{\neq o}_{vis} = \Delta H^{\neq o}_{vis} - T\Delta S^{\neq o}_{vis}$$

All the activation parameters obtained at infinite dilution for the TX100 polymer systems are given in Table 66. The $\Delta G^{\neq o}_{vis}$ values remain constant for all the systems studied. Even for the CTAB-polymer (Table 67) the magnitude of $\Delta G^{\neq o}_{vis}$ values remain the same. However, the $\Delta H^{\neq o}_{vis}$ and $\Delta S^{\neq o}_{vis}$ values vary from system to system. Again on plotting $\Delta H^{\neq o}_{vis}$ and $\Delta S^{\neq o}_{vis}$ values for all systems, a linear plot was obtained. The slope of the plot for polymer-TX100, and polymer-CTAB systems were 305 K and 304 K respectively. At this temperature, it is assumed that the free energy of activation for the viscous flow becomes independent of entropic forces and solely depends on enthalpic factors.

(vi) Cloud point measurements :

Cloud points (CP) are the characteristics of nonionic surfactant systems, and are the manifestations of the solvation / desolvation phenomenon of nonionic surfactant solutions. The desolvation of the hydrophilic groups of the surfactant leads to the formation of cloud point in surfactant solution. A number of workers have carried out

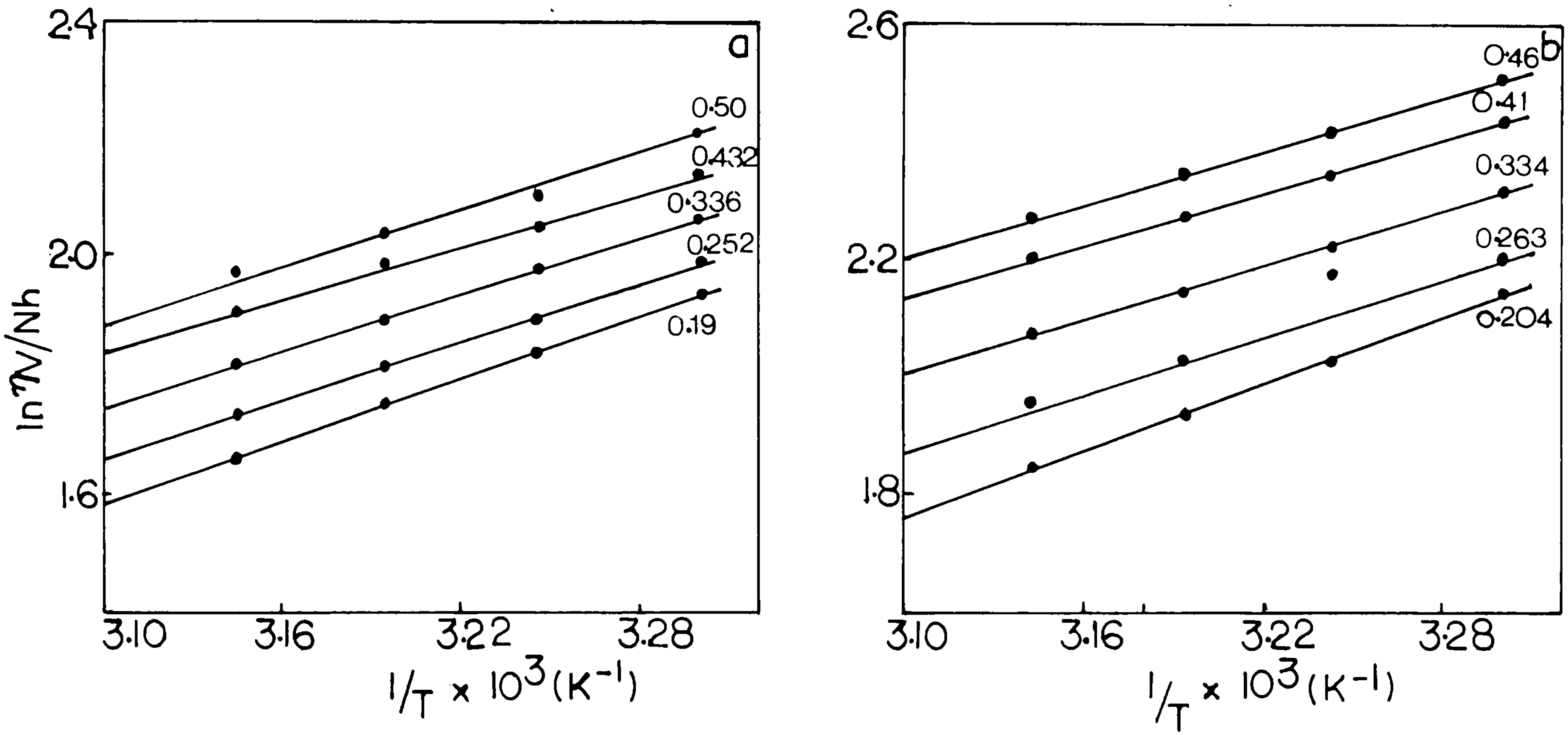

Fig. 51 : Plot of ln ηV/Nh vs. 1/T for (a) P(AA-AAc) 65:35 copolymer / 0.005% TX100: (b) P(AA-AAc) 50:50 copolymer / 0.015% TX100 in presence of NaCl at various polymer concentrations.

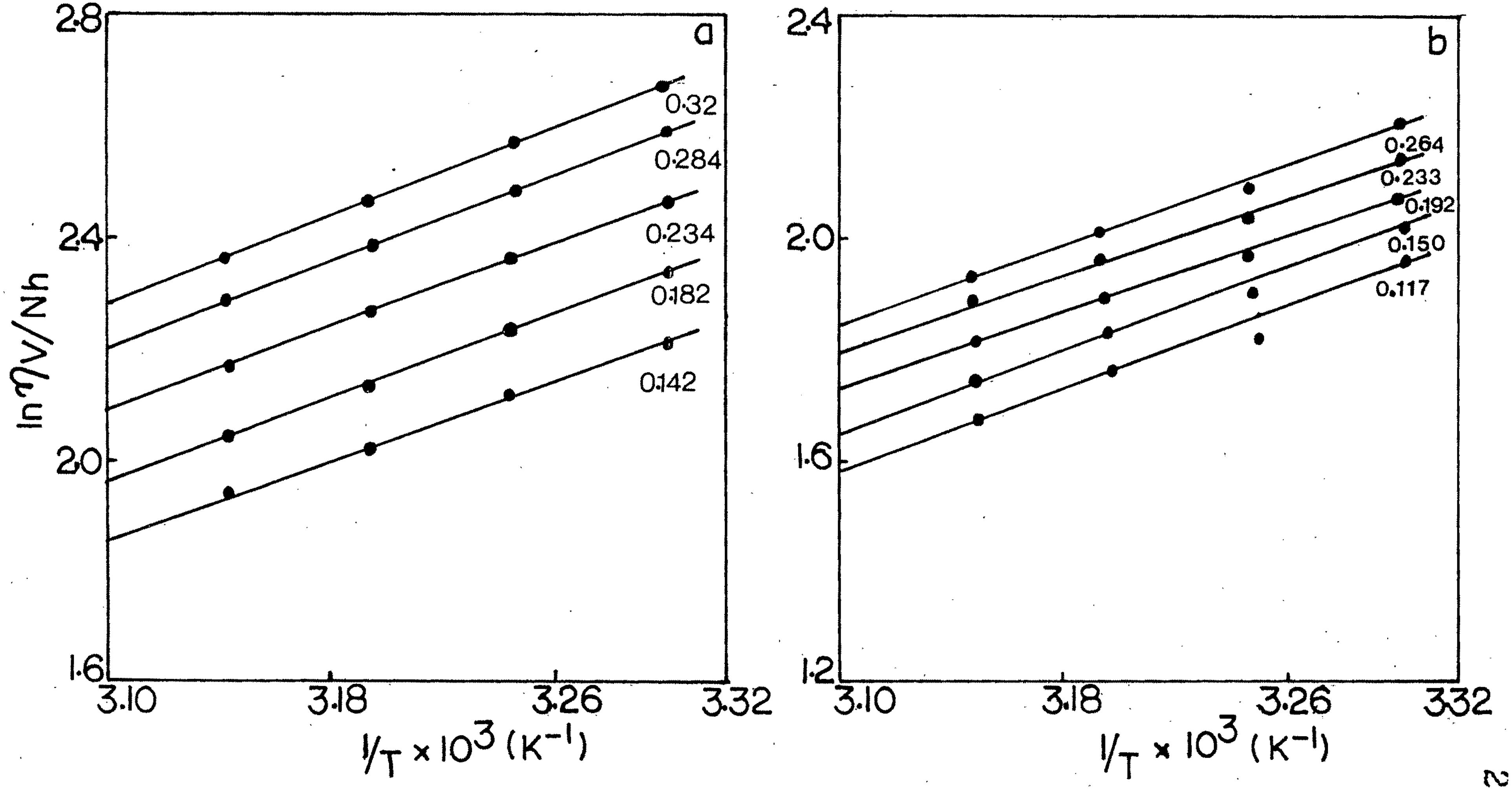

Fig. 52 : Plots of ηV/Nh vs. 1/T for (a) PAAc / 0.75% CTAB; (b) P(AA-AAc) 85:15 / 1.5% CTAB at different polymer concentrations.

Table 66 : Viscosity activation parameters at infinite dilution for the polymers at different TX-100 concentrations.

Polymer Systems	Triton X 100 Concentration %,w\v											
	0.0			0.005			0.015			0.1		
	$\Delta G^{\#,\circ}_{vis}$	$\Delta H^{\#,\circ}_{vis}$	$\Delta S^{\#,\circ}_{vis}$	$\Delta G^{\#,\circ}_{vis}$	$\Delta H^{\#,\circ}_{vis}$	$\Delta S^{\#,\circ}_{vis}$	$\Delta G^{\#,\circ}_{vis}$	$\Delta H^{\#,\circ}_{vis}$	$\Delta S^{\#,\circ}_{vis}$	$\Delta G^{\#,\circ}_{vis}$	$\Delta H^{\#,\circ}_{vis}$	$\Delta S^{\#,\circ}_{vis}$
S1	4.5	15.9	38.0	3.1	15.8	41.4	5.3	18.8	43.8	4.3	18.3	45.5
S2	4.5	16.8	40.0	4.5	16.8	39.9	4.5	17.6	42.5	4.6	17.3	41.4
S2+NaCl	4.4	16.0	37.8	4.4	16.0	37.8	4.4	15.9	37.4	5.5	15.8	33.4
S3	4.5	16.8	40	4.5	16.8	39.9	4.4	16.0	37.6	4.5	17.6	42.5
S3+NaCl	4.33	15.3	35.6	4.3	15.3	35.6	4.3	15.7	36.9	4.3	15.3	35.6
S4	4.6	12.3	25.0	4.6	12.3	24.9	4.6	8.8	13.6	4.7	21.9	56.0
S4+NaCl	4.2	15.5	36.6	4.2	15.5	36.6	4.5	15.5	36.8	4.2	15.8	37.5
S5	4.4	14.8	50	4.4	19.8	49.9	4.4	19.4	48.6	4.5	19.6	49.0
S5+NaCl	4.7	21.9	56.0	4.7	21.9	56.0	4.6	8.8	13.6	4.6	12.3	24.9

$\Delta G^{\neq\circ vis}$ and $\Delta H^{\neq\circ vis}$ in kJmol $^{-1}$; $\Delta S^{\neq\circ vis}$ in Jmol $^{-1}$K^{-1}

Table 67 : Viscosity activation energy parameters at infinite dilution for the polymers at different CTAB concentrations.

Polymer Systems	**CTAB Concentration %,w\v**								
	0.75			**1.0**			**1.5**		
	$\Delta G^{\neq\circ}_{vis}$	$\Delta H^{\neq\circ}_{vis}$	$\Delta S^{\neq\circ}_{vis}$	$\Delta G^{\neq\circ}_{vis}$	$\Delta H^{\neq\circ}_{vis}$	$\Delta S^{\neq\circ}_{vis}$	$\Delta G^{\neq\circ}_{vis}$	$\Delta H^{\neq\circ}_{vis}$	$\Delta S^{\neq\circ}_{vis}$
S1	4.3	16.5	39.7	4.3	15.4	36.1	4.8	15.9	36.2
S2	4.4	17.5	42.4	4.2	14.3	32.7	4.3	15.2	35.5
S3	4.0	14.9	35.3	4.3	21.3	55.0	4.3	16.2	38.5
S4	4.5	15.1	34.6	4.5	14.3	31.6	4.4	11.9	24.2
S5	4.6	14.4	31.7	4.4	16.4	38.8	4.4	15.6	36.5

$\Delta G^{\neq\circ}_{vis}$ and $\Delta H^{\neq\circ}_{vis}$ in kJ mol^{-1}; $\Delta S^{\neq\circ}_{vis}$ in J mol^{-1} K^{-1}

cloud point studies of TX100 in presence of additives. Valaulikar and Manohar[355] have shown that at very small concentration of NaCl the CP of TX100 does not change much. Small amounts of ionic surfactant increase the CP of TX100. The present studies were carried out on 1% Triton X100 using various polymer at different concentrations as the additives. Low polymer concentrations (all the polymers) did not have much effect on CP of TX100 i.e. it remained around 65.5°C. Cloud point of 1% TX100 solution is 66.0°C. However, in presence of higher concentrations of PAA (Fig. 53), the cloud point is very low. At even higher concentrations of PAA i.e. 8% (w/v) solution the phase separation occurs at room temperature itself. PAA lowers the cloud point effectively. This is because of the removal of water by the polymers which helps the TX100 micelles to come near each other and effectively decreases the cloud point. However, PAAc and the 50:50 P(AA-AAc) ratio of the copolymer show some elevation of the cloud point. We believe that the polyelectrolyte like nature of these polymers induce ion-dipole or dipole-dipole interaction with water molecules and these water molecules are probably act as a bridge between different PS-micellar complexes[356]. The cloud point being a result of intermicellar interaction[357], higher temperature is needed to remove the bridging water molecules. Hence, the higher cloud point in presence of these polymers.

(vii) Steady state fluorescence quenching :

This method of determination of micellar aggregation number was originally developed by Turro and Yekta[161]. The following experimental conditions must be achieved; (i) the fractions of the fluorescent probe (F) and the quencher (Q) dissolved in water are negligible; (ii) F and Q do not form ground state complexes; (iii) Q is a very efficient quencher of F; (iv) Q has a negligible absorption at the wavelength of excitation over the entire range of concentrations employed and (v) the micellar aggregates are not too large ($N_{agg} < 100$). One assumes instantaneous quenching of F by Q, so that the extent of decrease of fluorescent intensity provides a measure of the number of micelles containing F and Q. Both F and Q are chosen to have a high affinity for the micelles and in data analysis one assumes a Poisson distribution of F

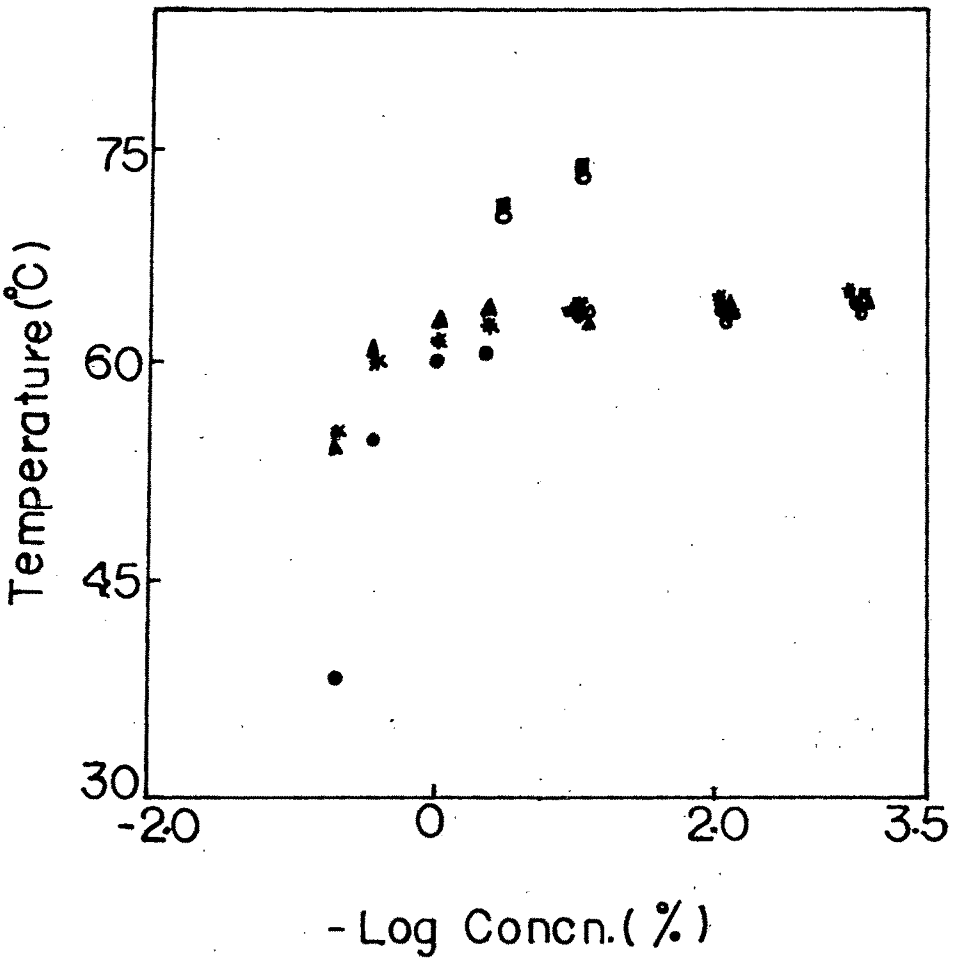

Fig. 53 : Plots of cloud point of 1% (w/v) TX100 in presence of different polymers. ● PAA; ✱ 85:15 P(AA-AAc); ▲ 65:35 P(AA-AAc); ■ 50:50 P(AA-AAc); ○ PAAc.

and Q among the micelles. Under these circumstances the emission intensity I, of the probe in the presence of quencher Q is related to (Q_T) where Q_T is the total quencher concentration, I_o is the fluorescent intensity in the absence of quencher. M is the total micelle concentration.

$$I = I_0 \exp\left[\frac{[Q_T]}{[M]}\right]$$

The micelle concentration is given by the following relation, where N_{agg} is the aggregation number, [S] the total surfactant concentration and cmc the critical micellar concentration.

$$[M] = \frac{[S] - cmc}{N_{agg}}$$

Combining the above 2 equations

$$\ln I_0/I = \frac{[Q_T]}{[M]} = \frac{N_{agg}\ [Q_T]}{[S] - cmc}$$

Thus, the slope of a plot of ln (I_0/I) as a function of quencher concentration allows the determination of N_{agg}. Aggregation numbers for TX100 were determined in presence of these polymers as per the method mentioned above. Fig. 54 represents aggregation number values in presence of increasing percentage of PAA in the feed. The aggregation number of TX100 in presence of polymers decreases, which is a clear indication of PS interaction[92]. Zana et al.[358] have shown that ethyl hydroxy ethyl cellulose (EHEC) interacts with cationic surfactants, such as CTAX (X = Cl, Br). They demonstrated that the polymer-bound micelles have a larger degree of ionization and a lower aggregation number than free micelles. In our systems the three copolymers have higher aggregation numbers compared to the homopolymers may be attributed to the extended chain conformations in the copolymers hence more binding sites, hence an increase in aggregation number. As mentioned earlier also, polymer chains are wrapped around the surfactant aggregates, with their hydrophobic segments penetrating into the Stern layer of the aggregates by displacing the water molecule.

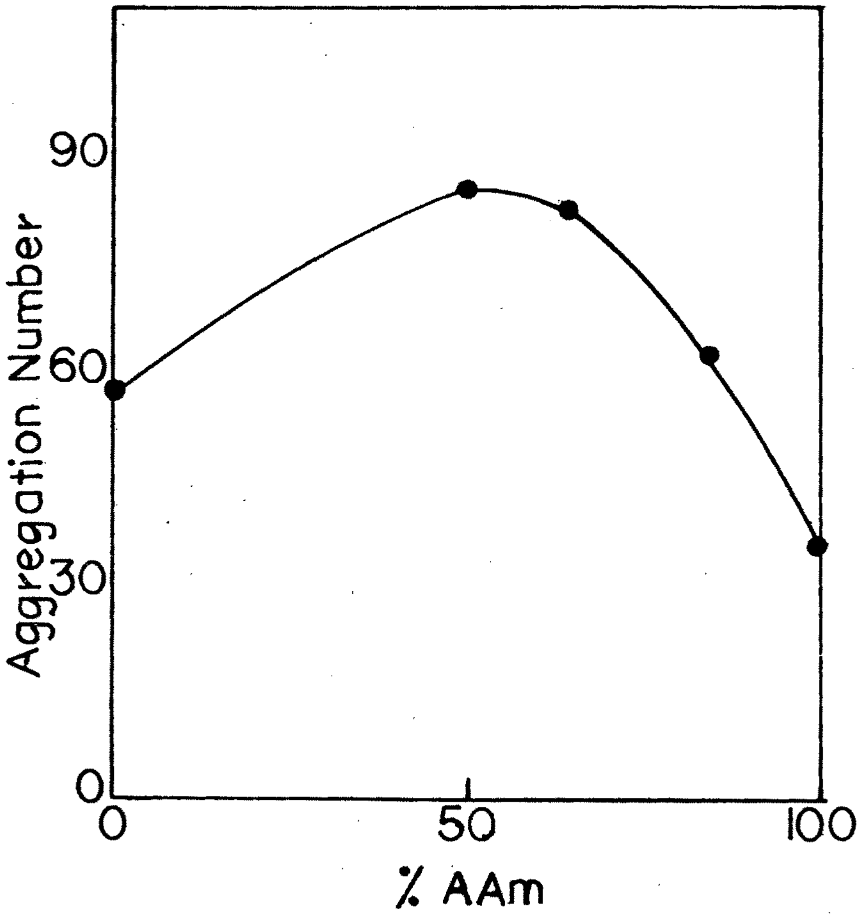

Fig. 54 : Plot of aggregation numbers against % composition of acrylamide in the polymers, at 0.005% (w/v) polymer concentration.

(viii) Small angle neutron scattering studies (SANS):

SANS is an ideal technique for studying the structure (shape and size) of the colloidal particles on a length scale of ~ 10-100 Å. The instrument at Cirus[274] reactor measures particle sizes of the range 20 ~ 150 Å. The small angle neutron scattering experiments have become very useful techniques due to the specific properties of neutrons since they are (i) neutral and are able to examine materials in bulk; (ii) have energy similar to energy of atoms in solids and therefore capable of investigating atomic movements; (iii) they scatter differently from 'H' and 'D' and hence the contrast variation is possible. The strength of SANS in the study of hydrogenous materials lies in the fact that contrast between the particle and solvent can be easily varied[359]. The scattering amplitude of hydrogen is negative (- 0.3723) and that for deuterium is positive (0.67), it is thus possible to have a good contrast between the molecules and the solvent, by deuterating either the molecule or the solvent.

Few workers have carried out SANS measurements of P-S systems[178]. The polymer used was PEO with SDS. They used deuterated SDS to have contrast variation. The complex of SDS-PEO is formed, the polymer web which has size range of 200 to 1000 Å and surfactant micelles with radii of 20 Å[178]. Through these interactions the polymer web adapts itself to the spacings of the micellar array where the micelles are collected at short intervals along the polymer chains, hence forms necklace like structure.

In the present studies measurements were carried out for PAA with CTAB and SDS. SDS and CTAB show good scattering intensities, however the signals obtained by PAA were weak i.e. it showed very low scattering intensity (Fig. 55). In the presence of PAA also not much change in the scattering intensities are observed for the surfactants (Fig. 56,57).The calculation of the aggregation number based only on the peak position is discussed[360] . This method follows the approach given by Chen[361] et al. They showed that the inter particle distance D between the micelles is given by

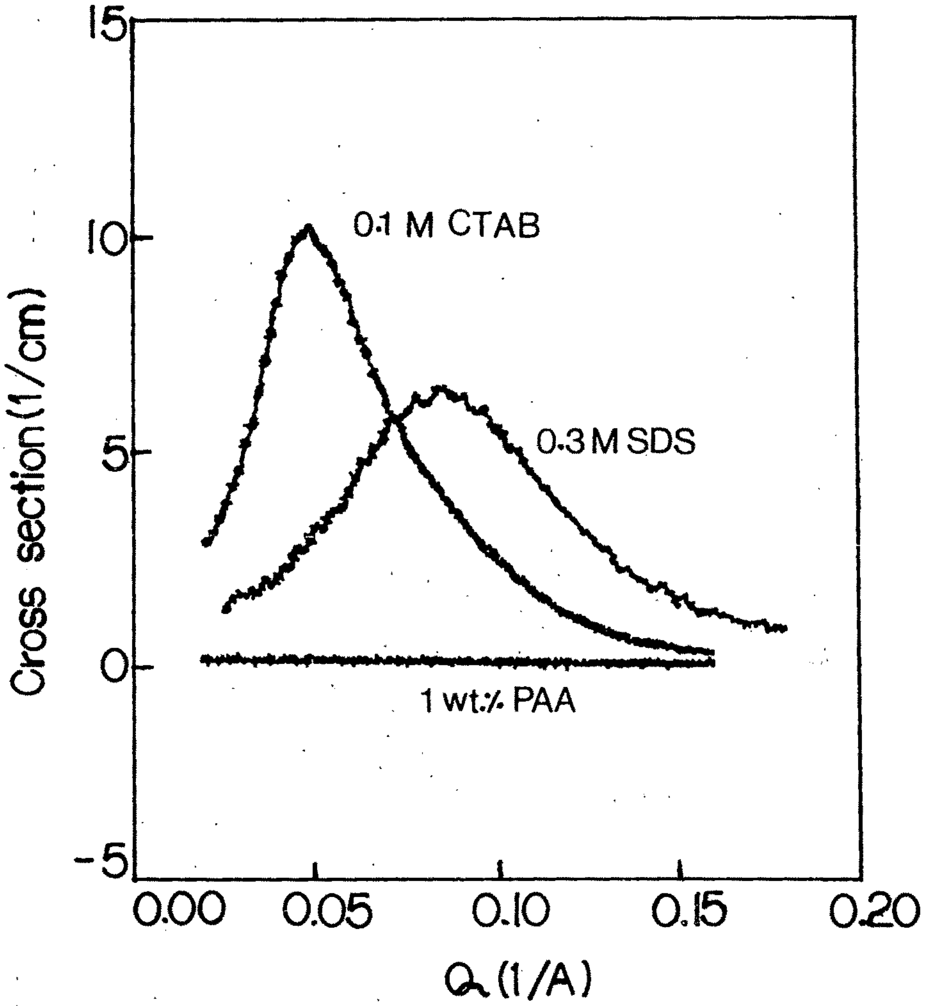

Fig. 55 : Scattering intensity profile for 0.1M CTAB, 0.3M SDS and 1 wt% PAA.

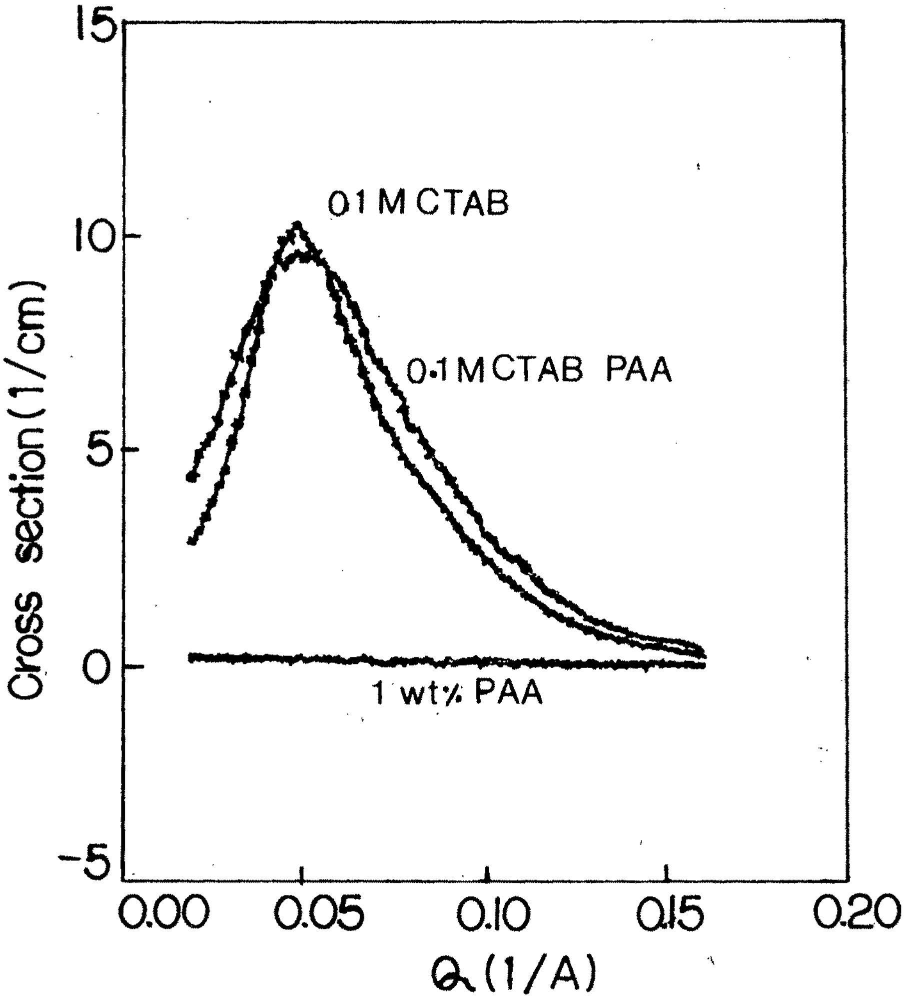

Fig. 56 : Scattering intensity profile for 0.1M CTAB in presence of 1 wt% PAA.

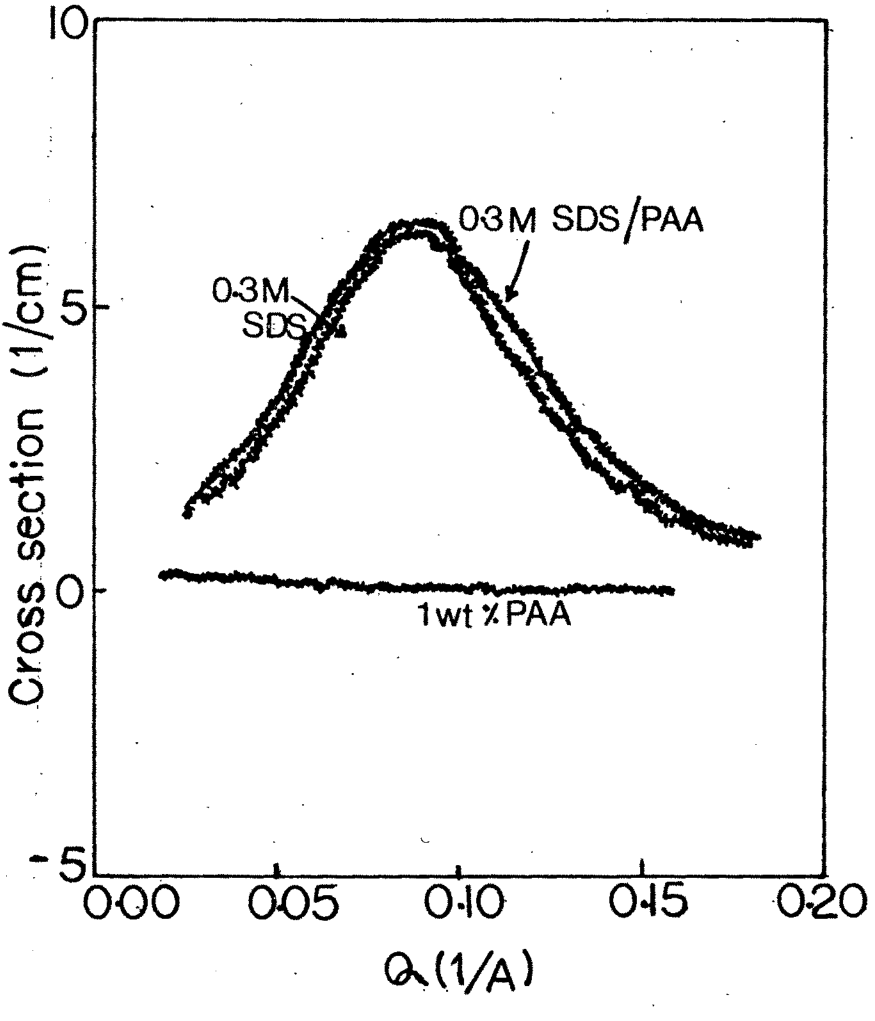

Fig. 57 : Scattering intensity profile for 0.3M SDS in presence of 1 wt% PAA.

$$\mathbf{D = 1/\sqrt{2}\,(4000\,n/\,N_A\,C)^{1/3}\,10^8\,Å}$$

where n is the mean aggregation number and N_A is the Avogadro number.When the expression assumes that micelles are arranged in a face-centre cubic (FCC) lattice. Then the peak position for such situation is related to D by the relation

$$\mathbf{Q_mD = 6^{1/2}\,\pi\; = 7.695}$$

Thus the aggregation number can be calculated from the knowledge of the peak position Q_m.

Assuming a simple cubic packing (SC) in the micellar solution, the aggregation number n was calculated using the relation

$$\mathbf{Q_m = 2 \times 4^{1/3}\pi\,(N_AC\,/\,4000\,n)^{1/3} \times 10^{-8}\,Å^{-1}}$$

Another empirical relation given by Wu[362] et al. for calculation of n

$$\mathbf{Q_m\,D = 6.8559 + 0.0094D}$$

n is calculated using the above three models namely FCC, SC packing and the empirical relation. The aggregation number of SDS obtained by the FCC equation was 80, from the SC structure 62 and empirical relation was 80. In presence of PAA the n do not change much, since the relative position of Q_m do not change to a great extent. The n for CTAB were from FCC 160; SC 123 and empirical relation was 159. In presence of PAA the values were 155, 119 and 151 respectively. The n values do not change much in presence of polymers, since the scattering intensities of CTAB and SDS do not vary much in presence of PAA.

CONCLUSIONS

The surface tension and conductance measurements both show two critical concentrations for the PS systems. The first break is the critical aggregation concentration and the second one is the polymer saturation point. The PAA-TX100 behave similar to a nonionic surfactant complex whereas the copolymers and PAAc have different binding patterns with TX100. The conductance as well as surface tension measurements were carried out for polymer-CTAB systems. For PAAc and

CTAB, being polyelectrolyte - surfactant of opposite charges, it was difficult to carry out studies in the micelle formation region due to phase separations.

The thermodynamic parameters were evaluated at psp. The ΔG°_{psp} becomes more negative with increase in temperature indicating spontaneous micelle formation both in presence and absence of polymers. The PAA-TX100 show large entropy values, however due to the polyelectrolytic nature of the copolymers and PAAc the randomness decreases in those systems. The CTAB systems in presence and absence of polymers show negative enthalpy values. However, the magnitude of enthalpy in case of PAA-CTAB is less negative and at higher concentrations of PAA, it becomes positive. ΔH°_{psp}-ΔS°_{psp} compensation was observed, for all the solvent systems with an isostructural temperature of ~ 300 K. Changes in Γ_{max} and A_{min} values again indicate differences in binding patterns of PAA and other polymers with TX100.

Viscosity studies indicate that PAAc and the copolymers are polyelectrolytic. However, the polyelectrolytic nature is curbed in presence of NaCl. Also at higher concentrations of CTAB, this kind of polyelectrolytic nature is not seen. The expansion factor ratios for polymer-TX100 systems indicate that end-to-end distance first decreases, on addition of surfactant, further addition of surfactant results in increase of end-to-end distance. However, in case of CTAB-polymers systems the end-to-end distances continued to increase though the rate of increase is not much at higher concentrations of CTAB.

Aggregation number of TX100 decreases sharply in presence of homopolymers though higher aggregation number is obtained in presence of the copolymers indicating extended chain conformations in their case. Cloud point values of 1% TX100 decreases sharply in presence of high concentrations of PAA. The SANS experiments gave n values by means of different empirical relations. The n does not vary much in presence of the polymers due to poor scattering intensity from the polymers.