CHAPTER 7

STUDIES ON SOLUTION PROPERTIES OF POLYMER-NONIONIC SURFACTANT MIXED SYSTEM

SOLUTION PROPERTIES OF POLYMER-NONIONIC SURFACTANT MIXED SYSTEM

7.1 INTRODUCTION AND REVIEW OF PREVIOUS WORKS

Complex water-based fluids containing polymers and surfactants find important practical applications in various domains such as detergency, paints, cosmetics, oil recovery etc. They also play a key role in many biological systems. When surfactants are employed in practice they are almost without exception mixed with various substances either accidentally or intentionally for improving their performances. This is also true for polymers in solution. When a surfactant and a polymer happen to be mixed in aqueous solutions, often significant changes in properties of the individual species appear. These may arise because polymer and the surfactant both belong to the group of substances whose solution property shows marked deviation from regularities. Thus polymer surfactant interactions are not only of a diverse industrial interests but also stimulate academic investigations. The practical importance of polymer-surfactant systems has led to a significant experimental effort to study their behaviour. The interactions between synthetic or natural polymers and surfactants were intensively studied during last few decades. In most cases a strong cooperative association is observed between polyelectrolytes and oppositely charged surfactants and a rather weak interactions are observed between nonionic polymers and ionic surfactants. Interactions between ionic polymers and nonionic surfactants have only been reported in cases where hydrogen bond between polymer and the surfactant is effective[1]. Indeed, a variety of experimental techniques have been utilized to probe the nature of polymer-surfactant interactions including viscosity and conductivity measurements, dialysis, fluorescence spectroscopy, NMR and neutron scattering techniques.[2, 3] Typically hydrophilic nonionic polymers showed no sign of interactions with polyoxyethylated nonionic surfactant.[4] No binding between polyvinyl pyrrolidine (PVP) and TritonX-100 was found, however, mildly hydrophobic nonionic polymers such as propylene oxide and partially hydrolyzed polyvinyl acetate interact with nonionic surfactants.[5] In spite of the above general observations, it was found that nonionic surfactants do interact with polyacrylic acid and other polymers.[6,7] Some of the systems are having solutions

of nonionic polymers and ionic surfactants. These include aqueous solutions of polyethylene oxide (POE) and sodium dodecyl sulphate.[8, 9] Contrary to anionic surfactant, cationic surfactants interact very weakly with POE or PVP and this has been explained by the fact that these surfactants have a very large head group which prevents polymer penetration in their micelles. It has been suggested that the overlap between hydration shells of the polymer and the surfactant head group in the micelles largely determines the effect of the surfactant charge type.[10-12] It was observed that above a critical surfactant concentration, known as critical aggregation concentration (CAC), some ionic surfactants could bind cooperatively to nonionic polymers.[13] The CAC is usually much smaller than critical micelle concentration (cmc), which signals the onset of micelle formation in the corresponding polymer free surfactant solution. In dilute solutions, the polymer-surfactant complex is viewed as composed of a series of spherical micelles with their surfaces covered by polymer segments and connected by strands of the same polymer molecule. Results of NMR studies also provided ample evidence that in these complexes water-soluble polymers do not penetrate into the hydrophobic miceller core, but instead adsorb at the micelle surface and remain in close contact with the surfactant hydrophilic moieties. In addition to the above, neutron scattering studies at the air/water interface show that the water of hydration around the ionic head group extends a short distance down the alkyl chain.[14] Thus aggregate formation of ionic surfactants on hydrophobic polymers is promoted both by hydrophobic interaction of the polymer chain near the head group of ionic surfactant and by increasing the distance between ionic groups compared to a simple micelle. In contrast, nonionic surfactants having weaker repulsion between the head groups show much weaker association.[15] However, association between ethoxylated nonionic surfactants and polyacids has been reported.[17] In these systems, hydrogen bonding between the COOH and the oxygen of the ethylene oxide chain as well as hydrophobic interactions promotes surfactant aggregation on the polymer chain. Association between polyethylene oxide and polyacrylic acid at low pH has been observed and attributed to hydrogen bonding between the polymer and the surfactant.[18,19] Cartalas and coworkers studied the interaction between hydrophobically modified poly (sodium acrylate) and a series of oligoethylene glycol mono dodecyl ether surfactants.[20] The alkyl groups of the modified polymers were found to associate with the surfactant aggregates , which induced dramatic changes in rheology of these systems. It was argued that at least

two different types of gel structures could be recognized in solutions containing hydrophobically modified polymers and surfactant aggregates. Similar viscosity behavior was found when anionic or cationic surfactants were added to hydrophobically modified poly (sodium acrylate) or some other hydrophobically modified polymer aqueous solutions.[21-24] The interaction between ethyl (hydroxyethyl) cellulose and the anionic surfactant sodium dodecyl sulfate has been studied by Lindman and co-workers in dilute aqueous solutions at different temperatures with the aid of viscometry.[25] The delicate interplay between hydrophobic interactions of surfactant and polyelectrolyte is demonstrated through the reduced viscosity data. At surfactant concentration slightly above the CAC the intrinsic viscosity data suggest a sharp collapse of the polymer surfactant aggregates. In presence of moderate amount of surfactant the molecular complexes expand due to amended thermodynamic conditions and enhanced electrostatic repulsion between chains decorated with SDS.

It is very interesting to check if this behavior could occur also with other polymer/surfactant systems. For this reason present work on the interaction of flexible polymers (anionic and nonionic PAM) and nonionic surfactant (Triton-X-100) has been undertaken. The polymers are of high molecular weight nonionic polyacrylamide and anionic (bearing 8.2 and 72 mole% acid) polyacrylamide. The objective of the present work is thus to gain insight into the factors that control the viscosity behavior in dilute solution of nonionic and anionic polyacrylamide under various conditions of temperature and surfactant addition. On the other hand, the variation of CAC and polymer saturation point (PSP) as a function of polymer concentration are of interest because it allows monitoring the complex formation between the polymer and the surfactant as well as provide at least qualitative idea regarding the stoichiometry of such complexes. In view of this a study has also been undertaken on the variation of CAC and PSP of Triton-X-100 as a function of concentration and the nature of the added polymer (NPAM, HPAM, LPAM) with the help of surface tension measurement. In addition to this, thermodynamics of the interaction has also been studied by monitoring the above changes as a function of temperature.

7. 2 RESULTS AND DISCUSSION

VISCOSITY

The intrinsic viscosity $[\eta]$ is a measure of the hydrodynamic volume in solution since

$$[\eta] \propto S^3/M \qquad\qquad 1$$

where S is the radius of gyration and M is the molecular weight of the polymer. Intrinsic viscosity $[\eta]$ data of NPAM, LPAM and HPAM in presence of various concentrations of surfactant (0.001-0.1%) at different temperatures are presented in table-7.1 - 7.3. Dramatic drop of $[\eta]$ at the initial addition of surfactant for all the polymers is observed. A drop in $[\eta]$ during the formation of polymer-surfactant complex has been reported earlier for nonionic ethyl (hydroxyethyl) cellulose in presence of SDS.[25-26] The marked drop of intrinsic viscosity may be attributed to a strong contraction of polymer-surfactant entities at the onset of surfactant binding to polymer. Above critical aggregation concentration (CAC) micelles begin to form inside the macromolecule, accompanied by collapse of the polymer chain as a result of cooperative binding of surfactant molecule. In a recent theoretical study it was suggested that in a flexible polymer-surfactant system the critical aggregation concentration (CAC) is associated with a considerable change in polymer statistics and polymer-surfactant interactions lead to an effective reduction in the second virial coefficient of the polymer.[27] As a result of this, the polymer is assumed to undergo partial collapse at the CAC. Furthermore, in another theoretical study of binding of small molecules to semiflexible polymers, it was argued that bound molecules might modify the local characteristics of polymer conformations e.g. change its local stiffness.[28] In a recent viscosity study on the dilute aqueous solution of hydrophobically modified (hydroxylpropyl) guar polymer in the presence of TX-100 an abrupt drop in $[\eta]$ was observed at surfactant concentration close to its critical micellization concentration (cmc).[29] This effect was explained in terms of intense intramolecular hydrophobic association junctions. It is interesting to note that drop in the $[\eta]$ is true for all the polymers under the present study and the intrinsic viscosity minima lies in the CAC range of the surfactant (CAC is measured tensiometrically, shown in table 7.12. It was argued previously that nonionic surfactant could bind cooperatively with ionic polymers only. But present investigation indicates that nonionic polymers also can bind cooperatively with nonionic surfactant. At higher

Table 7.1 Intrinsic viscosities (dl.g⁻¹) of NPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (°C)	0.00	0.001	0.01	0.100
30	16.31	14	15.93	16.12
35	16.51	14	16.11	16.43
40	16.49	14.6	16.90	16.47
45	16.43	14.6	16.76	16.44
50	16.39	14.6	21.38	16.40
55	16.38	14.7	16.87	16.38
60	16.35	14.2	18.12	16.12

Table 7.2 Intrinsic viscosities (dl.g⁻¹) of HPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (°C)	0.00	0.001	0.01	0.100
30	43.92	35.18	41.43	44.43
35	40.45	35.96	37.48	44.81
40	44.01	36.93	41.20	45.70
45	45.34	37.07	42.25	46.44
50	46.04	40.43	43.59	47.01
55	47.24	39.15	42.79	48.24
60	47.63	39.30	43.63	49.22

surfactant concentration, (0.01 and 0.1 %, w/v), it is seen that [η] rises at all the experimental temperatures and the conformational expansion as observed is most probably a result of enhanced excluded volume effect due to improved thermodynamic condition (table 7.1-7.3).

Table 7.3 Intrinsic viscosities (dl.g^{-1}) of LPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (°C)	Surfactant concentration (%)			
	0.00	0.001	0.01	0.100
30	26.7	15.5	20.0	23.14
35	25.9	19.1	20.3	23.15
40	27.3	19.0	21.5	23.54
45	27.1	18.5	20.8	23.64
50	29.7	19.7	21.7	24.00
55	31.6	20.6	22.0	24.12
60	33.5	20.7	22.9	23.19

Table 7.4 Voluminosity (dl.g^{-1}) of NPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (°C)	Surfactant concentration (%)			
	0.00	0.001	0.01	0.100
30	8.51	5.12	5.25	5.33
35	8.61	5.19	5.33	5.37
40	8.69	5.25	5.39	5.42
45	8.72	5.25	5.41	5.45
50	8.78	5.31	5.49	5.54
55	8.81	5.32	5.50	5.56
60	8.93	5.31	5.99	8.56

Therefore, at concentrations higher than CAC the system can be considered to consist of necklace type of configuration.[31] According to necklace model suggested by K. Shirahama polymer chains are wrapped around the surfactant aggregates with their hydrophobic segment penetrating into the Stern layer of the aggregates by displacing water molecules.[32]

Viscosity values of aqueous solution of different types of PAM (NPAM, LPAM and HPAM) were used to determine the volume related parameter (V_E), shape factor

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(v) and molecular expansion factors (α) (ref. 33) of the polymer in presence of different concentrations of the surfactant adopting the methods discussed in chapter 5. Values of V_E (table 7.4 - 7.6) for the polymers are found to decrease at the initial addition of surfactant; subsequent addition of surfactant results in an increase in the value of the volume related parameter. This is, however, expected considering the observed variation of [η] with the concentration of surfactant because both are basically a measure of the hydrodynamic volume of the polymer chain. The value of v has been shown to be 2.5 for spherical particles. From table 7.7- 7.9 it is observed that for HPAM, LPAM and NPAM the values of v in most cases deviate from 2.5 at all temperatures and surfactant concentrations under investigation. This result suggests that the shape of the polymer molecules is other than spherical in presence of nonionic surfactant. In this context it may be noted that the shape of the above polymers molecules are found to be spherical in aqueous and aqueous-organic mixtures in the presence or in absence of salts. The change in the shape of the polymer molecules in presence of nonionic surfactant is, however, not surprising. It has already been suggested that the bound ions or molecules may significantly modify the local stiffness of the polymer chain resulting in the restructuring of the overall shape. Moreover, according to the necklace model polymer chain are wrapped around the surfactant aggregates with their hydrophobic segments penetrating with the Stern layer.[32]

Table 7.5 Voluminosity (dl.g^{-1}) of LPAM in presence of various concentrations of surfactant at different temperatures.

Temperature	Surfactant concentration (%)			
(^{0}C)	0.00	0.001	0.01	0.10
30	7.81	7.24	7.19	7.15
35	7.83	7.26	7.15	7.13
40	7.87	7.33	7.14	7.12
45	7.81	7.26	7.08	7.07
50	7.88	7.35	7.20	7.11
55	7.90	7.40	7.21	7.14
60	7.93	8.15	7.20	7.18

Table 7.6 Voluminosity $(dl.g^{-1})$ of HPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (°C)	Surfactant concentration (%)			
	0.00	0.001	0.01	0.100
30	8.8	8.65	8.66	8.66
35	8.84	8.68	8.69	8.69
40	8.89	8.72	8.74	8.74
45	8.81	8.71	8.72	8.72
50	8.93	8.82	8.83	8.83
55	8.89	8.84	8.86	8.87
60	8.91	8.85	8.89	13.36

Table 7.7 Shape factor of NPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (°C)	Surfactant concentration (%)			
	0.00	0.001	0.01	0.100
30	1.92	2.72	3.03	3.00
35	1.92	2.75	3.02	3.06
40	1.89	2.78	3.13	3.03
45	1.89	2.78	2.98	3.01
50	1.86	2.75	3.89	2.96
55	1.86	2.76	3.06	2.94
60	1.83	2.67	3.02	1.91

The expansion factors (α), determined following the methods already described in chapter 5, are presented in the table 7.10. For all the above polymers, it is found that on the initial addition of surfactants the end-to-end distance decreases but on further addition of surfactant the end-to-end distance increases. This is expected from their intrinsic viscosity data also. The initial addition of surfactant causes wrapping of the surfactant molecules by the polymer segments to take place

and further addition of surfactant molecules (micelles) force the chains to expand. Such results were also observed in case of SDS-poly (vinyl pyrrolidone) system previously.[34]

Table 7.8 Shape factor of LPAM in presence of various concentrations of surfactant at different temperatures.

Temperature (^{0}C)	Surfactant concentration (%)			
	0.00	0.001	0.01	0.100
30	3.42	2.14	2.78	3.23
35	3.30	2.63	2.83	3.24
40	3.47	2.59	3.01	3.30
45	3.46	2.54	2.93	3.34
50	3.77	2.68	3.01	3.37
55	4.00	2.78	3.05	3.37
60	4.22	2.53	3.18	3.22

Table 7.9 Shape factor of HPAM in presence of various concentrations of surfactant and at different temperatures.

Temperature (^{0}C)	Surfactant concentration (%)			
	0.00	0.001	0.01	0.100
30	4.99	4.06	4.78	5.01
35	4.57	4.14	4.31	5.15
40	4.95	4.23	4.71	5.22
45	5.14	4.25	4.84	5.32
50	5.15	4.58	4.93	5.32
55	5.31	4.43	4.83	5.43
60	5.34	4.44	4.90	3.68

Viscosity data are used to evaluate activation parameters of viscous flow using Frenkel-Eyring equation as follows (detail in chapter 5). Linear variation is observed in the plot of ln (ηV/Nh) against T^{-1} with correlation coefficient of 0.96 or higher for all the systems studied. Some representative plots (Frenkel-Eyring) are shown in figure 7.1 - 7.3.
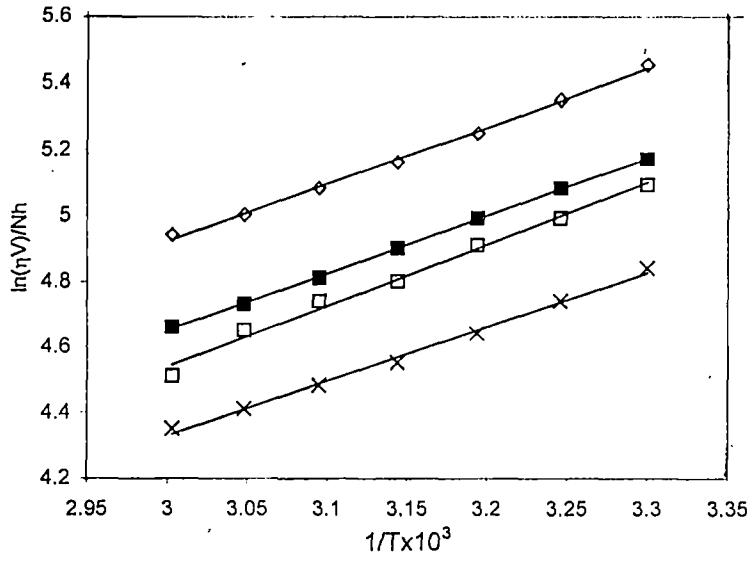
Figure:7.1 :F.E.Plot for LPAM.

◇ 0.007gm/cc,Tx=0.1%   ■ 0.0035gm/ccTx=0.1%

□ 0.0035gm/cc,Tx=0.01%   × 0.00178gm/cc.Tx=0.01%

◇ 0.007gm/cc,Tx=0.1%

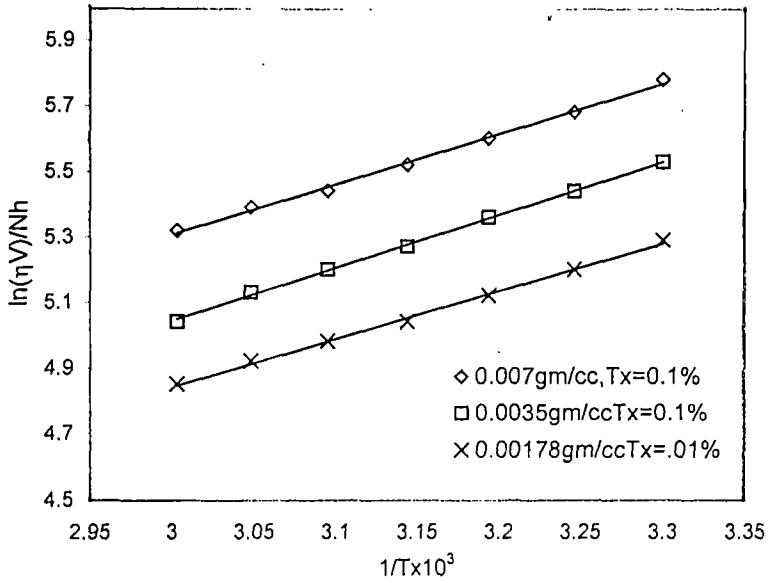□ 0.0035gm/ccTx=0.1%

× 0.00178gm/ccTx=.01%

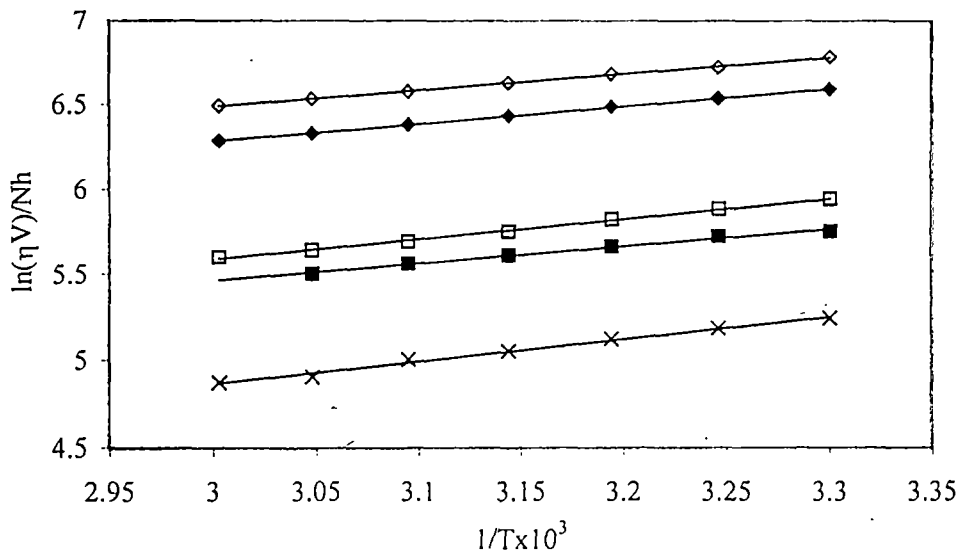*Figure:7.2* :Plot of ln(ηV/Nh) vs T^{-1} for HPAM in presence of different concentrations of Tx-100.

Figure:7.3 :F.E.Plot for NPAM in presence of different
concentration of surfactant at various concentration of polymer.

◇ 0.0036gm/cc,Tx=0.1%   □ 0.00178gm/cc,Tx=0.1%
✕ 0.0009gm/cc,Tx=0.01%   ◆ 0.0036gm/cc,Tx=0
■ 0.00178gm/cc,tx=0

Table 7.10 Expansion factors for polymers in presence of different concentrations of surfactant.

Temp.^{0}C	NPAM			LPAM			HPAM		
	α_1	α_2	α_3	α_1	α_2	α_3	α_1	α_2	α_3
30	0.95	0.99	0.98	0.98	0.99	0.99	0.99	0.99	0.99
35	0.95	0.99	0.98	0.98	0.99	0.99	0.99	0.99	0.99
40	0.96	1.00	0.98	0.98	1.00	0.99	0.99	1.00	0.99
45	0.96	1.00	0.98	0.98	1.00	0.99	0.99	1.00	0.99
50	0.96	1.09	0.98	0.98	1.0	0.99	0.99	1.00	0.99
55	0.96	1.01	0.98	0.98	1.00	0.99	0.99	1.00	0.99
60	0.95	1.03	0.98	0.98	1.01	0.99	0.99	1.00	0.99

$\Delta H^{\#}_{vis}$ and $\Delta S^{\#}_{vis}$ values at different polymer concentrations and solvent compositions for hydrolyzed and nonhydrolyzed PAM's are determined. These values were extrapolated to zero polymer concentrations to estimate ΔH_{vis}^0 and ΔS_{vis}^0 values, which are shown in the table 7.11. Positive values of ΔH_{vis}^0 and ΔS^0_{vis} were obtained for all the systems. The slope of the plot of ΔH^0_{vis} vs. ΔS_{vis}^0 for all the systems together yields the value of structural temperature of the system. This parameter is found to be 28.2^{0}C. It may be noted that at this temperature free energy of activation for the viscous flow becomes independent of the entropic forces and solely depends on enthalpic forces.[35, 36] It is interesting to note that the structural temperature value obtained in the present case is very close to that observed previously (e.g. 305K) for similar polymer but with different degree of hydrolysis.[37]

Table 7.11 Viscosity activation parameters of the polymers in presence of various concentrations of Tx-100. ΔH_{vis}^0, ΔS_{vis}^0 in kJ.mol^{-1} and J.mol^{-1}.K^{-1} respectively.

Tx-100	NPAM		LPAM		HPAM	
(%)	ΔH_{vis}^0	ΔS_{vis}^0	ΔH_{vis}^0	ΔS_{vis}^0	ΔH_{vis}^0	ΔS_{vis}^0
0.001	11.93	30.51	13.30	23.74	15.19	28.99
0.010	12.40	29.90	14.24	25.54	12.50	27.89
0.100	11.38	25.54	14.30	23.71	13.11	25.65

SURFACE TENSION

To understand the nature of interaction between polymers and the surfactants in bulk aqueous solution, as well as at interfaces is of great importance. Indeed, a variety of experimental techniques have been utilized to probe the nature of polymer-surfactant interaction. Surface tension measurement study is one such important technique, which is especially useful in this area. Figures 7.4 – 7.6 are representative plots of surface tension vs. logarithm of concentration of TX-100 (log [Tx100]) for NPAM, LPAM and HPAM respectively. Each of these plots exhibit two transition points. Three regions of surfactant concentration representing the distinct stages of surfactant-polymer interactions in aqueous solution are observed. In the first region, which is located at lower concentration region of the surfactant, the surface tension decreases gradually till the first break point comes. Before the first break point, surfactant molecules bind cooperatively to polymers. This break point is known as critical aggregation concentration (CAC) [38]. The CAC values are found to be much smaller than cmc, which indicates the onset of micelle formation in the corresponding polymer free surfactant solution due to locally accumulated high concentration of the bound surfactants. This cooperative binding result in the formation of polymer surfactant complexes in solution .The binding of the surfactant to polymer begins at CAC and it continues till the second transition, called the critical micellization concentration of the polymer surfactant complex or the polymer saturation point (PSP) reaches. In general, the binding of surfactant to the polymers is similar to micellization and the CAC values are lower and PSP is higher than the cmc of surfactant in water. The cmc values, thermodynamic parameters and interfacial adsorption parameters for pure TritonX100 are taken from literature.[37] The CAC values are more independent of temperature than PSP. Further, CAC is independent of polymer concentration. The cmc decreases with temperature initially (0.234 mM at 30°C and 0.195 mM at 45°C) and then increases passing through a minimum. It was suggested that when the surfactant is present in excess and as the concentration of micelles are relatively high, the micelle/water and the air/water interfaces compete progressively for the polymer. Thus surface tension values eventually attain same values as that of pure surfactant. But for the present system the surface tension values are somewhat different from the pure surfactant solutions at polymer saturation point and at higher concentrations. Therefore, it may be suggested that complete transfer of polymer does not occur from air/water interface. The air/water
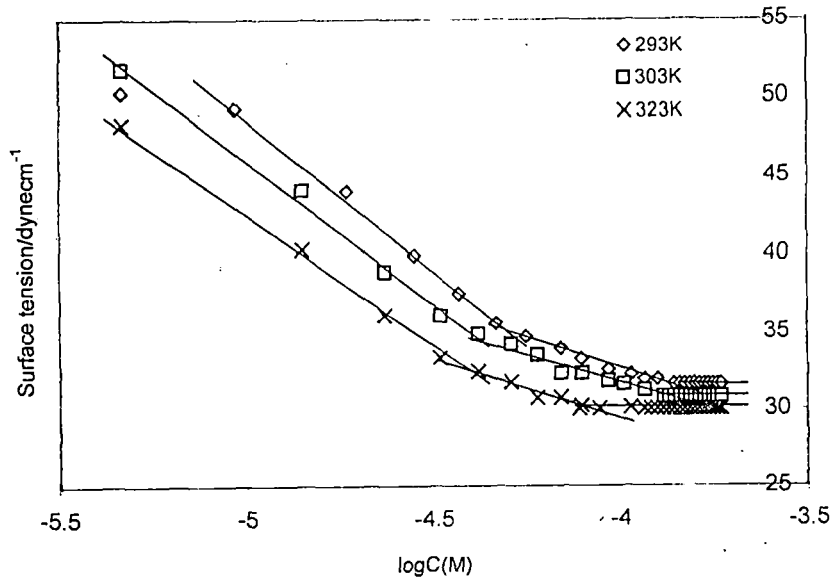
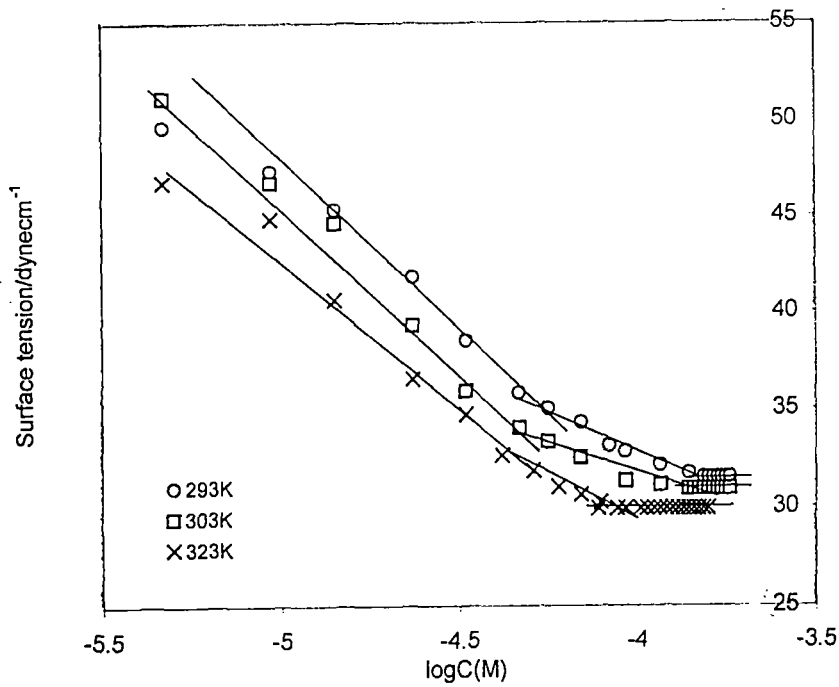*Figure:7.4*:Surface tension vs. -logC plot for Tx-100 in presence of 0.009% LPAM at different temperatures.

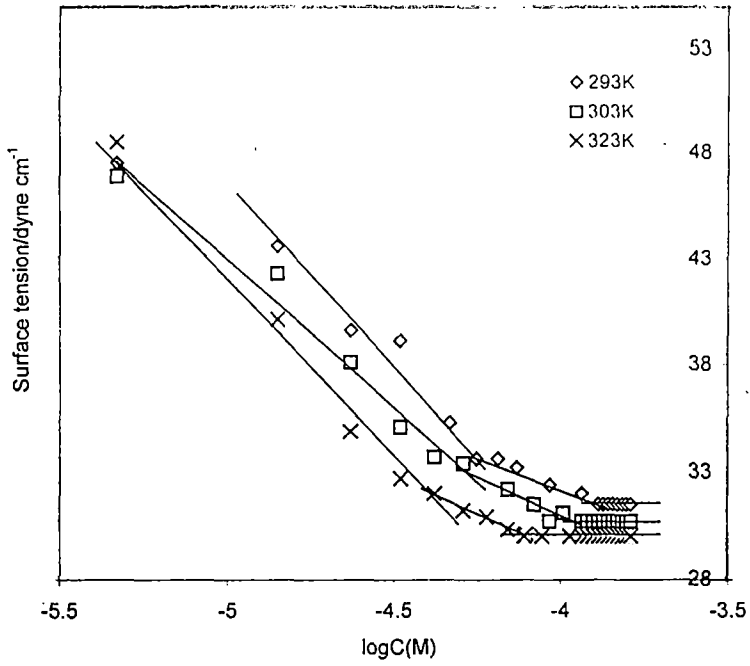*Figure:7.5*:Surface tension vs. -logC plot for Tx-100 in presence of 0.05%HPAM at different temperatures.

Figure :7.6: Surface tension vs. -logC plot for Tx-100 in presence of 0.009 %NPAM at different temperatures.

interface is thus saturated with polymer-surfactant and also normal micelle formation starts even before polymer gets saturated with surfactant.[37] The CAC values of TX-100 in presence of the polymers at four different temperatures are shown in Table 7.12. CAC values are found to decrease with an increase in temperature except in a few at low concentration of the polymer. This trend of variation of CAC values with temperature is similar for all the polymers and is almost independent of the polymer concentration. It is interesting to note that as the carboxyl content of the polymer increases from LPAM (8.2mol %) to HPAM (72 mol %) CAC values also increases. At high polymer concentration and at low temperature, NPAM having higher molecular weight than LPAM and HPAM, yield CAC values, which are higher than that of hydrolyzed PAM's. There are two possible driving forces for polymer surfactant interaction (1) the tendency of polymer to be adsorbed at the micelle - water interface and (2) specific attraction between polymer segments and surfactant heads.[39] For most of the nonionic polymers, specific interaction with ionic or nonionic surfactant heads are usually weak, so that the dominant factor promoting polymer-surfactant complexation is the propensity of the polymer to be adsorbed at a micelle - water interface. Naturally, the trend of change of CAC with polymer concentration for the hydrolyzed (LPAM and HPAM) and unhydrolyzed PAM (NPAM) will be different. Moreover, the molecular weight and the concentration of the polymers influence significantly the polarity along the polymer chain in association with surfactant; high molecular weights polymers always having lower in the polarity, leading to low CAC's, whereas concentration give rise to a somewhat unexpected change. The PSP values for all the above systems at various temperatures are presented in Table7. 14.

Table 7.12 Critical aggregation Concentration (CAC) X10^{5}M of TritonX-100 in presence of different concentrations of anionic and nonionic polyacrylamide at various temperatures (^{0}C).

Polymer↓	0.0025% PAM				0.009% PAM				0.05% PAM			
Temp.→	20	30	40	50	20	30	40	50	20	30	40	50
NPAM	4.0	5.0	4.2	4.2	5.5	4.6	4.6	4.8	6.0	5.3	4.7	4.2
LPAM	4.5	4.5	4.2	4.5	4.5	4.0	4.1	3.9	5.1	4.3	4.4	4.6
HPAM	5.6	4.6	4.8	4.8	5.0	4.8	4.7	4.0	5.6	4.5	4.5	4.8

Table **7.13** Free energy(ΔG_{ps}^0 in kJmol^{-1}) due to polymer surfactant interaction in presence of different concentrations of polymer at various temperatures(^{0}C).

Polymer↓	Polymer concentration (%)											
	0.0025				0.009				0.05			
Temp.→	20	30	40	50	20	30	40	50	20	30	40	50
NPAM	4.39	3.89	4.26	4.04	3.62	4.11	4.02	3.68	3.41	3.75	3.97	4.04
LPAM	4.11	4.16	4.26	3.85	4.11	4.46	4.32	4.23	3.80	4.28	4.14	3.79
HPAM	3.57	4.11	3.91	3.68	3.85	4.00	3.96	4.17	3.57	4.16	4.08	3.68

Table **7.14** Polymer Saturation Point (PSP, mM) of Tx-100 in presence of different concentrations of anionic and nonionic polyacrylamide at various temperatures(^{0}C).

Polymer↓	Polymer concentration (%)											
	0.0025				0.009				0.05			
Temp.→	20	30	40	50	20	30	40	50	20	30	40	50
NPAM	0.106	0.103	0.102	0.088	0.114	0.105	0.100	0.077	0.112	0.105	0.092	0.068
LPAM	0.120	0.114	0.105	0.072	0.127	0.119	0.107	0.077	0.129	0.124	0.109	0.081
HPAM	0.111	0.118	0.122	0.093	0.116	0.122	0.128	0.096	0.114	0.132	0.133	0.097

It is seen that for NPAM and LPAM, PSP decreases with the increase in temperature but completely opposite trend is observed for HPAM (upto 40^{0}C). Lower values of PSP than cmc indicate that polymer facilitates micelle formation even before it gets saturated. Generally, cmc of a nonionic surfactant decreases with an increase in temperature due to changes in water structure and water surfactant interaction. In presence of NPAM and LPAM (8.2 mol% charge), the overall variation of PSP is determined by various interactions in the polymer-TX 100-water system. In this respect, the behavior of LPAM is somewhat similar to that of NPAM. However, for

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HPAM (72 mol% Charge) the polyelectrolyte nature of the polymer is responsible for higher PSP values. Moreover, as the polymer concentration increases more binding

Table 7.15 Thermodynamic Parameters (ΔG^0_{PSP}[1] , ΔH^0_{PSP}[2] and ΔS^0_{PSP}[3] in kJ.mol^{-1} ,kJ.mol^{-1} and J.mol^{-1}.K^{-1}respectively) associated with polymer saturation point at various temperatures (^{0}C) in presence of different concentrations of Tx-100.

Temp.	Polymer	Polymer concentration (%)								
		0.0025			0.009			0.05		
		-[1]	[2]	[3]	-[1]	[2]	[3]	-[1]	[2]	[3]
	NPAM	32.08	1.35	105	31.90	4.71	93	31.94	6.92	85
20	LPAM	31.78	4.78	92	31.64	6.14	87	31.60	5.99	87
	HPAM	31.97	-3.35	120	31.86	-3.50	120	31.90	-5.49	127
	NPAM	33.25	1.45	114	33.20	5.04	126	33.20	7.40	134
30	LPAM	32.99	5.11	125	32.88	6.56	130	32.78	6.41	129
	HPAM	32.90	-3.58	96	32.86	-3.74	96	32.62	-5.88	88
	NPAM	34.37	1.55	115	34.42	5.37	127	34.63	7.90	136
40	LPAM	34.29	5.46	127	34.25	7.00	131	34.19	6.84	131
	HPAM	33.90	-3.83	96	32.82	-3.99	92	33.68	-6.27	87

sites are available for the surfactant to interact, hence PSP values goes on increasing. It is surprising to note that at 50^{0}C temperature PSP values are minimum for all the polymers in the whole range of concentration.

The free energy of micellization (ΔG^0_m) in the absence of polymer and the free energy of aggregation (ΔG^0_{agg}) in the presence of polymer for a nonionic surfactant can be calculated using the following equations,[40]

$$\Delta G^0_m = RT \ln cmc \qquad\qquad 2$$

and the corresponding quantity at CAC is

$$\Delta G^0_{agg} = RT \ln CAC \qquad\qquad 3$$

Now,

$$\Delta G^0_{agg} = \Delta G^0_m + \Delta G^0_{ps} \qquad\qquad 4$$

Therefore,

$$\Delta G^0_{ps} = \Delta G^0_{agg} - \Delta G^0_m = RT \ln(CAC/cmc) \qquad\qquad 5$$

This quantity (ΔG^0_{ps}) is a measure of the strength of interaction between the surfactant and the polymer. ΔG^0_{ps} values of the present systems are tabulated in table 7.13. The difference in the nature of interaction between the polymers with the surfactant is apparent from the values of ΔG^0_{ps}. These values are more negative for NPAM than that of LPAM or HPAM. Here again the effect of chain length (molecular weight) on the binding pattern of surfactant on the polymer is noticed. Similar results were also observed in the cases of SDS and TTAB in presence of polyacrylic acid and hydrophobically modified polyacrylic acid.[40] Thermodynamic parameters for micelle formation are computed using the following relations

$$\Delta G^0_{PSP} = RT \ln PSP \qquad\qquad 6$$

$$\Delta G^0_{PSP} = \Delta H^0_{PSP} - T\Delta S^0_{PSP} \qquad\qquad 7$$

Table 7.15 shows the values of standard free energy (ΔG^0_{PSP}), enthalpy (ΔH^0_{PSP}) and entropy (ΔS^0_{PSP}) changes at $20^0, 30^0, 40^0$ and 50^0C. The free energy becomes more negative with the increase in temperature. This indicates that the formation of the polymer-saturated micelle is relatively more spontaneous. The micellization in the presence of NPAM and LPAM is endothermic whereas in presence of HPAM it is exothermic. At higher concentrations of polymer, the entropy change value decreases from uncharged to high carboxyl content polyacrylamide. This indicates that the polyelectrolyte nature of LPAM and HPAM yield higher values of thermodynamic parameters. In the case of nonionic surfactant, the entropy gain made by the destruction of structured water shell is commonly credited as the driving force for the process. Moreover, with an increase in temperature the entropic gain is greater than the enthalpic gain and hence the free energy becomes more negative. As the temperature increases dehydration of oxyethylene group occurs and there are more numbers of nonpolar conformation available which provide an entropic driving force for the conformational changes to occur.

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