STUDIES OF INTERACTION OF WATER-SOLUBLE POLYMERS WITH DIFFERENT SURFACTANTS

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The present work described in this thesis is focussed on polymer-surfactant interactions. The first part lays emphasis on the polymer synthesis and characterization of the water soluble polymers. These polymers are homopolymers polyacrylamide (PAA), polyacrylic acid (PAAc) and their copolymers in different monomer feed ratios. The physicochemical properties of these polymers along with surfactant are studied. The knowledge of the physicochemical studies of polymer-surfactant interactions play an important role in determining the industrial end products. The different physicochemical methods involved in these studies were surface tension, conductance, viscosity measurements, cloud point determinations, steady state fluorescence quenching and small angle neutron scattering measurements.

The synthesis of 'tailor made' polymers, to meet specific requirements, has gained importance in recent past. These water soluble polymers were synthesized by the free-radical solution polymerization technique. The polymers are PAA, PAAc and their copolymers in different monomer feed ratios of 85:15, 65:35 and 50:50 (w/v). They were characterized by spectroscopic techniques like IR, NMR, thermal methods like DSC, TGA and also by viscosity measurements. Knowledge of the successive addition of monomer units both in case of homo and copolymers, configurational and conformational structure of chains, sequence distribution can be obtained by spectroscopic characterization.

The IR spectra showed characteristic absorptions which agreed well with those reported in literature. The IR spectrum of PAA showed absorption bands at 1650 cm^{-1} due to the C=O bond of the carbonamide group. The other groups showed characteristic absorption bands at the respective wavelengths. IR spectra of PAAc showed absorption band due to the O-H bond present in the -COOH group in the range of 3300-3500 cm^{-1}. The IR spectra of copolymers P(AA-AAc) show absorption bands typical of constituent monomeric units and their relative intensities depending on composition.

Further evidence for the two monomers incorporated is given by NMR spectroscopy. Both the ^{13}C-NMR and ^{1}H NMR spectra are complimentary to each other. In case of the copolymers, an extra peak due to the incorporation of the methine carbon (-CHCOOH) was observed at δ=63.97 ppm. The intensity of this peak increased with the increase in AAc content.

The experimental feed ratios of various monomers as well as the composition of the resulting copolymers were obtained from the elemental analysis data. From the elemental analysis data, the reactivity ratios were estimated for the copolymers, using the Finemann-Ross and Kelen-Tudos methods. The reactivity ratios for monomer-1 (acrylamide) and monomer-2 (acrylic acid) were determined by the Finemann-Ross method using equation :

$$\frac{X}{Y}(Y-1) = r_1 \frac{X^2}{Y} - r_2$$

On plotting X (Y-1) / Y against X^2/Y, a straight line was obtained whose slope was r_1 and intercept yielded r_2. $X = M_1/M_2$ and $Y=\Phi_1/\Phi_2$ where M_1 and M_2 are the mole fraction of acrylamide and acrylic acid in the feed. Φ_1 and Φ_2 are mole fractions of acrylamide and acrylic acid. The Kelen-Tudos method uses the equation in the copolymer :

$$\theta = r_1 \xi - \frac{r_2(1-\xi)}{\varepsilon}$$

ξ and ε are mathematical function obtained from the relations of G and F. The values obtained by Finemann-Ross method for r_1 and r_2 are 0.463 and 1.092 for acrylamide and acrylic acid. The corresponding r_1 and r_2 values by the Kelen-Tudos method are 0.427 and 0.945 respectively.

Using information on the reactivity ratios, the statistical distribution of the monomer sequences M_1-M_1, M_2-M_2 and M_1-M_2 were calculated. Mean sequence lengths χ_{AA} and χ_{AAc} were also calculated for the copolymer systems by using these relations :

$$\chi_{AA} = 1 + r_1 [\phi_1] / [\phi_2]$$

$$\chi_{AAc} = 1 + r_2 [\phi_2] / [\phi_1]$$

For the series of AA-AAc copolymers studied, χ_{AA} varied from 1.33 at 0.44/0.56 mole ratios of AA/AAc in the copolymer to 2.4 with a 0.76/0.24 mole ratios. The calculated mole ratios indicate an alternating tendency.

Thermogravimetric analysis (TGA) were done for these polymers. Thermograms of the copolymers fall in between the homopolymers implying that thermal stability of copolymers is between the homopolymers. Two stage decomposition was observed in all cases excepting PAA. PAA showed a three staged decomposition. The activation energy associated with each stage of decomposition were evaluated by well-known methods like Broido, van Krevelen - these methods used a single stage heating rate. The Ozawa and the Reich methods used thermograms recorded at multiple heating rates to calculate activation energy.

Differential scanning calorimetry (DSC) was another method to monitor the effect of heat changes on a polymer sample. The values of glass transition temperature, Tg, obtained for PAA was 84.8°C and the onset of softening temperature was ~ 190°C. DSC of PAAc showed a TG at 110°C and enthalpy change associated with it as 60.5 Jg^{-1}. Copolymers showed an enhancement in Tg values due to specific interactions between acrylamide and acrylic acid moieties.

Viscosity studies were carried out. Molecular weight for the homopolymers were computed by using the Mark-Houwink-Sakurda equation

$$|\eta| = KM^{\alpha}$$

where K and α are constant for a given polymer / solvent system. The intrinsic viscosity $[\eta]$ was calculated for the polymer solutions, using the Huggins and Kraemer equation

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

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

where K' and K'' are constants for a given polymer / solvent / temperature system. However, in case of the copolymers and PAAc, $[\eta]$ values could not be calculated using the above equation. In these cases, η_{sp}/C increases with increase in dilution and hence $[\eta]$ values could not be calculated. However, such systems were handled by using the empirical relation given by Fuoss and Strauss

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

Straight lines obtained on plotting $(\eta_{sp}/C)^{-1}$ against $C^{1/2}$ gives $[\eta]$ values from the intercept. The viscosity measurements were carried out in presence of electrolytes like $NaNO_3$ and $Al(NO_3)_3$. Addition of an electrolyte to these copolymers and PAAc restores conformity with the Huggins and Kraemer equation. Other parameters like K'-K'', voluminosity V_E, shape factor ν and activation parameters at infinite dilutions were calculated. K'-K'' values are generally 0.5 for a good solvent systems. The values obtained are ~ 0.5 for most of the systems. The shape factor values are also found to be ~ 2.5 suggesting spherical conformations in solutions. However, the polyelectrolyte like systems showed large $[\eta]$ values as expected.

The polymer-surfactant interactions were studied using these polymers with nonionic surfactant Triton X100 and cationic surfactant Cetyl trimethyl ammonium bromide (CTAB). The physicochemical studies included surface tension, conductance, viscosity, cloud point, determinations of micellar aggregation number N_{agg} of TX100 in presence of these polymers and some SANS measurements. Surface tension measurements were done in case of TX100, whereas both surface tension and conductance measurements were carried out for CTAB-polymer system. There was no variation of conductance with TX100 concentration in polymer-TX100 systems. Two critical concentrations were obtained by both these methods. The first break point is called the critical aggregation concentration (cac) and the second break point is the polymer saturation point (psp). The cac and psp values are in general lower and higher respectively than the cmc of pure surfactant. However, in case of PAA-TX100 systems both the cac and psp values are found to be below the cmc of TX100. As the acrylic acid moiety increases in these polymers, the psp values increase. In PAAc-TX100 systems, the psp values are higher than cmc of pure TX100. The cac values are found to be independent of polymer concentration and temperature for a particular polymer. The psp values for PAA-TX100 decrease with increasing temperature similar to the behaviour of nonionic surfactant complex. However, in case of the copolymers and PAAc the psp values increase with increasing temperature and polymer concentration. Since more number of polymer sites are available for binding with increase in polymer concentration the psp values increase. The lower psp value to that of cmc (in PAA-TX100) indicates that the normal micelle formation starts even before the polymer gets saturated with the surfactant.

In the CTAB-polymer systems, both the surface tension and conductance measurements gave cac and psp values. However, these studies were not possible with PAAc. In case of a oppositely charged polyelectrolyte-surfactant complex, there is a possibility of charge neutralization, which results in phase separation. In case of PAA-CTAB systems the psp values decrease with increase in temperature. The presence of a nonionic polymer probably decrease the ion repulsion with increase in temperature hence psp decreases. While for the copolymers-CTAB systems, the psp values increase with increase in temperature. The cac values for these systems are also independent of temperature and polymer concentration. However, the cac values obtained by the surface tension are lower in case of all the systems.

By using the cac and psp values various thermodynamic parameters associated with micellization in presence of polymers were evaluated. The free energy changes ΔG°_{psp}, enthalpy ΔH°_{psp} and entropy ΔS°_{psp} were calculated using the equation

$$\Delta G^{\circ}_{psp} = RT \ln C_{psp} \text{ (for TX100)}$$

and in case of ionic surfactant system, the following equation was used

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

the C_{psp} values taken in the mole fraction scale. The ΔG°_{psp} values for all the systems become more negative with increase in temperature suggesting micellization is more spontaneous and favoured in presence of polymers. In case of CTAB, the 'α' term which is the degree of ionization is calculated from the ratio of the slopes between cac and psp and above psp. The α values were around 50-75% which agreed well with values for other systems like PEO-SDS or PVP-SDS. The ΔS°_{psp} and ΔH°_{psp} values were obtained from the ΔG°_{psp} vs T plots. The entropy values for the PAA-TX100 systems are very high, however, due to the presence of charges in case of the polyelectrolytes the magnitudes of entropy values decrease. Similarly for the polymers-CTAB systems the magnitude of ΔS°_{psp} values are much lower. Moreover, the extent of randomness in case of the copolymer-CTAB systems is much lower. In case of the polymers-TX100 complex formation, it should be noted that micellization in presence of PAA is endothermic whereas micellization in presence of the copolymers and PAAc is exothermic. Exothermicity and endothermicity are specific to the nature of surfactant and additive. For the PAA-CTAB systems the enthalpy values are negative at low concentrations of the polymer. However values become positive at higher polymer concentrations. On the other hand in case of the copolymers-CTAB large negative enthalpy values suggest micellization to be exothermic. For all these systems an enthalpy-entropy compensation was observed suggesting that at isostructural temperatures i.e. 310 K for polymers-TX100 and 374 K for polymers-CTAB systems the micellization is independent of any structural changes in the system and depends upon enthalpic factors.

The ΔG°_{ps} values indicate strength of interaction between surfactant and polymer at cac. It can be noted from the ΔG°_{ps} values that these values for PAA-TX100 systems are more negative compared to the copolymers and PAAc which indicate differences in binding pattern of PAA with TX100 and other polymers studied with TX100. Even in case of the CTAB-polymer systems, the ΔG°_{ps} values of the copolymers are different from that of the homopolymer PAA. The Gibbs free energy of transfer of the surfactant monomer from aqueous micellar solution to the aqueous polymer solution was given by

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

In most of these systems, the free energy of transfer of the surfactant monomer, towards the polymer-surfactant micelle is more negative, suggesting addition of polymer leads to spontaneous micelle formation. The micelle stabilization is more pronounced in case of PAA, probably because of being more hydrophilic compared to other polymers.

Interfacial parameters like Γ_{max} which is the measure of surfactant adsorbed at the air/water interface and A_{min} which is the minimum area per molecule were evaluated from the surface tension data

$$\Gamma = -\frac{1}{2.303\ RT}\ d\gamma / d\log C$$

In case of the PAA-TX100 systems the Γ_{max} values show similar behaviour as nonionic surfactants and the Γ_{max} values increase with increase in temperature whereas in case of the copolymers and PAAc systems (in presence of TX100) increase in temperature hinders adsorption at the liquid / air interface. The surface excess quantity is lower as polymer concentration is increased indicating that surfactants prefer relatively more water-polymer matrix than the water-air interface. In case of the polymers and CTAB systems, the PAA moiety shows different behaviour compared to the copolymers. The Γ_{max} values increase with increase in temperature in PAA-CTAB system whereas for the copolymers-CTAB system, the

Γ_{max} values are found to decrease in general but no regularity is observed. From the surface excess quantity it was possible to calculate A_{min}, the minimum area per molecule, from the relation

$$A_{min} = 10^{14} / N\ \Gamma_{max}\ nm^2$$

In the PAA-TX100 system, the A_{min} values decrease with increase in temperature suggesting a closely packed surface, whereas in case of the copolymers and PAAc with TX100 the A_{min} values are found to increase with increase in temperature suggesting a loosely packed surface. Similarly in case of the CTAB-PAA systems also, the increase in temperature leads to higher A_{min} values whereas in case of CTAB-copolymers systems, with increase in temperature, the A_{min} values do not vary much.

The thermodynamic parameters of adsorption at the air / liquid interface are calculated both in presence and absence of polymers. The ΔG°_{ad} values were calculated by the relation

$$\Delta G^{\circ}_{ad} = \Delta G^{\circ}_{psp} - N\Pi_{psp} A_{psp}$$

where Π_{psp} and A_{psp} are the surface pressure and area per molecule respectively at the polymer saturation point.

In all the cases the ΔG°_{ad} values are found to be more negative compared to ΔG°_{m} or ΔG°_{psp} values indicating adsorption at the air \ water interface to be a relatively more spontaneous process than micelle formation. In all the cases the ΔG°_{ad} values become more negative with increase in temperature suggesting dehydration of the hydrophilic group is required for the adsorption to take place and at a higher temperature surfactant is less hydrated, lesser energy is needed for adsorption. However, in case of PAA-CTAB systems the ΔG°_{ad} values become less negative with increase in temperature suggesting that adsorption takes place less easily with increase in temperature. All these studies, and the parameters evolved indicate differences in binding patterns of PAA with the surfactants and the other polymers with surfactants.

The intrinsic viscosity measurements of these polymers were carried out in presence of different surfactant concentrations. $[\eta]$ values were calculated by the Huggins and Kraemer equations as mentioned earlier. However, for the copolymers and PAAc which behaved like polyelectrolytes, $[\eta]$ values were calculated by the empirical relation given by Fuoss and Strauss. The copolymers and PAAc behaved like polyelectrolytes in presence of nonionic TX100. However, in presence of CTAB - these systems abstained from polyelectrolytic behaviour. Addition of CTAB - in the region of cmc results in the precipitation of the polymer however on further addition of CTAB solubilization occured and at such high concentrations CTAB behaved akin to a salt and restored the conformity of these polymers with the Huggins and Kraemer equation. The polyelectrolyte like systems have large $[\eta]$ values. In case of the polymers - TX100 systems, the intrinsic viscosity measurements were done in presence of NaCl. The addition of NaCl reduces $[\eta]$ values drastically. In case of the ionic surfactant CTAB-polymer systems, the $[\eta]$ values increase with temperature. Increase in temperature results in ion-ion repulsions hence increase in $[\eta]$ values with temperature.

The $[\eta]$ values in presence and absence of polymers were used to calculate the expansion factor ratios. For the polymers-TX100 systems, the expansion factor ratios on initial addition of surfactant - the macromolecules remain contracted but on further addition of surfactant the end-to-end distance increases, resulting in expansion of the macromolecular chain. However, in case of the CTAB-polymer system, the initial addition of surfactant lead to an increase in end-to-end distance and further addition of surfactant, not much changes in the expansion factor ratios occur.

The relative viscosity η_r data was used to calculate the shape factor and voluminosity values.

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

The shape factor ν was then calculated from the equation

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

The shape factor value gives an idea about the macromolecules in solution. The shape factor values of PAA in TX100, the copolymers and PAAc in presence of NaCl were found to be ~ 2.5 suggesting spherical conformations in solution. These values are independent of temperature. However, for the polyelectrolytic systems, the ν values are much larger. In case of polymers-CTAB systems all the ν values are around ~ 2.5 suggesting spherical conformations.

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

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

The $\Delta G^{\neq\circ}_{vis}$, $\Delta H^{\neq\circ}_{vis}$ and $\Delta S^{\neq\circ}_{vis}$ values were calculated at infinite dilution. The $\Delta G^{\neq\circ}_{vis}$ values remained constant for most of the systems studied. The $\Delta H^{\neq\circ}_{vis}$ and $\Delta S^{\neq\circ}_{vis}$ values varied with polymer and surfactant concentrations. Both these systems showed a $\Delta H^{\neq\circ}_{vis}$ - $\Delta S^{\neq\circ}_{vis}$ compensation at the isostructural temperatures of 304 K and 305 K respectively for polymer-TX100 and polymer-CTAB systems. At these temperatures it is assumed that the free energy of activation for the viscous flow becomes independent of the entropic forces and solely depends on enthalpic forces.

Cloud points of 1% TX100 effectively decreases in presence of higher PAA concentrations. This is because of the removal of water by the polymers and thereby helping the TX100 micelles to come near each other and effectively decreasing the cloud point. However, PAAc and 50:50 w/w P(AA-AAc) copolymer show some elevation in the cloud point at certain concentrations. The polyelectrolyte like behaviour of these copolymers induce ion-dipole or dipole-dipole interactions with water molecules and probably act as a bridge between PS-micellar complexes. The cloud point being the result of intermicellar interaction, higher temperature is needed to remove bridging water molecules.

The micellar aggregation number N_{agg} of TX100 was found to be lower in presence of the polymers. The N_{agg} in presence of homopolymers was lower than in presence of the copolymers. The lower aggregation number of surfactant in presence of polymers is an evidence of interaction taking place between them. The higher aggregation number in presence of the copolymers than homopolymers may be due to extended chain conformations in case of the copolymers.

The SANS measurements, showed that the scattering intensity from PAA (1%, w/v) was very low. The position of Q_m in the scattering intensity vs Q profile of CTAB or SDS does not change much in presence of the polymers. Various relations were used to calculate the n from the relative position of Q_m. The n values of surfactants do not change much in presence of PAA, that is because the PAA is not able to bring much change in the scattering profile SDS and CTAB.