CHAPTER - 2

MATERIALS AND METHODS

2.1 Preview

2.2 Materials

2.3 Experimental Methods For

- i) Synthesis of Polymers
- ii) Characterization of Polymers

Physicochemical Methods

- i) Surface Tension Measurements
- ii) Interfacial Tension Measurements
- iii) Conductance Measurements
- iv) Viscosity Measurements
- v) Cloud Point Determinations
- vi) Fluorescence Spectroscopy
- vii) SANS Measurements

2.1 Preview

In this chapter different materials used for the studies, the experimental procedures used for polymer synthesis and different methodologies adapted for their characterization are given. This chapter also describes the various physico-chemical methods used for studying polymer-surfactant interactions.

2.2 Materials

Acrylamide (Mitsubishi Chemicals Ltd.) and acrylic acid (National Chemicals, Baroda) were used for polymerization without any prior purification. Hydrogen peroxide (Glaxo, India, 30% w/v) and potassium persulfate (Merck, India) were used as received. The solvents used for the studies were freshly distilled prior to use.

The salts used for the studies, sodium nitrate, sodium chloride, magnesium nitrate, were Anal R grade from Merck, India. They were dried at about 150°C for more than two h and cooled in a dessicator before being used.

The surfactants used for the studies were Cetyl trimethyl ammonium bromide (CTAB), octylpolyethoxy ethanol (TX 100). CTAB (Trizma Chemicals, India) was recrystallized from acetone : methanol (75 : 25, v/v) mixture and dried before use. TX-100 was procured from Fluka Chemie, Buchs, Switzerland. No minimum was observed in the surface tension - log concentration profile for both CTAB and TX 100. The critical micelle concentration (cmc) of CTAB was found to be 0.933 mM at 30°C (Lit. reports of 0.90 mM)[211,261]. For TX 100 the cmc value obtained at 30°C was 0.234 mM[52,262].

Pyrene (Fluka, Switzerland) was used as received. Cetyl pyridinium chloride (CPyCl) was obtained from Loba Chemie, India and was twice recrystallized from benzene. Triply distilled water was used for preparing all solutions.

2.3 Experimental Methods

i) Polymer Synthesis :

Polymerization of acrylamide, acrylic acid and their copolymers in various feed ratios was carried out by the free radical solution polymerization technique[263]. Polyacrylamide (PAA) was synthesized by taking 20% (w/v) of acrylamide in water in presence of 10 ml H_2O_2 (3%, w/v). The whole set up constituted of a three necked flask, equipped with a stirrer, water condenser, and a nitrogen inlet. The flask was maintained at a desired temperature in a thermostated water bath. The reaction mixture was stirred at 82°C for a period of one half hour. The reaction mixture after polymerization was poured into excess of methanol to precipitate out polyacrylamide. The product obtained was washed with methanol and finally dried in vacuo before characterization.

Synthesis of polyacrylic acid (PAAc) was carried out using potassium persulfate as the initiator, 40 g of acrylic acid in 160 ml of water was taken in a three necked flask. The reaction set up was maintained as before. The reaction was carried out at 80°C for a period of 2 h. The reaction mass was poured into excess of acetone to precipitate out the product. It was washed with excess of acetone. The product obtained was again dissolved in solvent water and the product was dried by freeze drying technique. This method was used for drying in order to avoid cross linking of the polymer. In this manner, the product obtained was water soluble polyacrylic acid.

Copolymerization of acrylamide and acrylic acid was carried out in different feed ratios of the two monomers[264]. The ratios chosen for the studies were 50:50, 65:35, 85:15 (w/w) of acrylamide and acrylic acid respectively. The recipe for the synthesis of copolymer 85:15 (w/w) of acrylamide and acrylic acid (AA-AAc) was as follows : 17 g of acrylamide, 3 g of acrylic acid, 0.14 g of $K_2S_2O_8$ as the initiator were taken in 180 ml of water. The reaction was carried out under nitrogen atmosphere at 68°C for a period of 2.5 h. The reaction set up was the same as for the synthesis of the homopolymers. The polymeric product was obtained by reprecipitation in methanol.

The polymeric product was further purified by removal of respective homopolymers. The homopolymer PAAc was soluble in dioxane. The product obtained on reprecipitation was treated with dioxane to remove PAAc. The product hence obtained was dissolved in methanol-water mixture (50:50, v/v). The homopolymer PAA remained insoluble in this mixture and was filtered out. The copolymer which remained soluble in water-methanol mixture was poured into an excess of methanol to reprecipitate the copolymer, which was thoroughly washed with methanol and finally dried invacuo before characterization[265].

The reaction conditions were exactly the same for the copolymers having acrylamide and acrylic acid in the feed ratios 50:50 (w/w) and 65:35 (w/w). The reaction mixture was heated at 68°C for a period of 2.5 h under N_2 atmosphere. The polymeric product obtained was also purified to remove the respective homopolymers. The purification procedure was the same as of the other copolymers.

ii) Characterization of Polymers :

Characterization of the polymers was done by IR, NMR, elemental analysis, Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

IR spectra of homopolymers and copolymers were done by preparing films. The films were prepared by dissolving the polymers in water and pouring them over a pool of mercury. The films were obtained by vacuum evaporation of the solvent. IR-spectra of the films was recorded on a Shimadzu IR-408 spectrophotometer.

The NMR of the polymer solutions in D_2O was recorded on a varian XL, 300 MHz for PMR and 75 MHz for ^{13}C NMR at RSIC, IIT, Mumbai. Elemental analysis was carried out on a FISONS, EA, 1108, C,H,N analyzer. TGA - thermograms were recorded on a Shimadzu thermal analyser DT-30B. The TGA recordings were done in presence of air, at different heating rates of 10, 15, 20 K min^{-1}. DSC of the polymer samples were recorded on a Mettler ME-4000 at Sun Pharmaceuticals R & D Centre, Baroda.

Physicochemical Studies :

i) Surface Tension : Critical micelle concentration (cmc) was obtained by the surface tension method using the du Nouy ring tensiometer (S.C.Dey and Company, Calcutta, India). Measurements were done by using a ring made of platinum-iridium alloy. The different temperatures used for the studies were 30, 35, 40, 45°C. The temperature was maintained constant by circulating thermostated water through a jacketed vessel containing water or the polymer solutions. Various polymer concentrations were used for the studies. The surface tension (γ) decreases with increasing surfactant concentration. The concentration of the surfactant was varied by adding aliquots of concentrated stock solution to a known volume of solution in the jacketed vessel by means of a microsyringe. The ring was cleaned between each measurement of surface tension. The measured surface tension values are plotted as a function of logarithm of surfactant concentration (log C)[266]. The two break points, critical aggregation concentration (cac) and polymer saturation point (psp) are obtained from surface tension γ-log concentration plots (γ vs. log C) for the surfactant in presence of polymers.

ii) Interfacial Tension : Interfacial tension (IFT) measurements were done on a spinning drop tensiometer (model 500, University of Texas, Austin). The capillary tube was filled with a liquid having higher density and a small drop of liquid of lower density was introduced with the help of a microsyringe. Here the surfactant in cyclohexane formed the droplet and the polymer containing aqueous phase formed the continuous phase. After filling, the capillary was tightly capped and fixed on the rotor. The temperature was set at the required value controlled by a heating device. The speed of the rotor was adjusted in such a way that the length of the elongated droplet was four times to its diameter. Reading was taken after the drops were allowed to equilibriate for a period of 0.5 h. Time for one revolution or speed (S) was noted from the digital counter. Diameter (D) was noted with the help of the travelling microscope. IFT between the two phases are related with the diameter (D), time for one revolution (ρ) and difference of density of two phases (σ)

$$\mathbf{IFT = 0.521 \times 10^6 \frac{\Delta\sigma D^3}{\rho^2}}$$

where 0.521 is the correction factor which is characteristic of the instrument taking the refractive index of water i.e. 1.33 into consideration. The experiment was repeated by changing the speed of revolution and the readings were reproducible[267].

iii) Conductance : Conductance measurements were carried out using a Mullard conductivity bridge[268]. A dip type cell was used having a cell constant of 0.6645 cm^{-1}. Polymer solutions of known concentrations were kept in a thermostated water bath at required temperature. Concentration of surfactant was varied by adding aliquots of concentrated stock solution with the help of a microsyringe. Plots of specific conductance versus surfactant concentration give break points from which cac and psp were obtained. The temperatures studied were 30, 35, 40 and 45°C.

iv) Viscosity : Viscosity of the polymer solutions were determined using a four armed Ubbelohde viscometer maintained at constant temperature in a thermostated water bath. Viscosity average molecular weight was determined by the Mark-Houwink-Sakurda[269] equations for the homopolymers polyacrylamide and polyacrylic acid.

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

where K and α values for PAA in water are 6.31 x 10^5 and 0.80 respectively. For PAAc in 0.1 M NaCl the K and α values are 15.47 x 10^5 and 0.90 respectively[270].

Intrinsic viscosity, $[\eta]$ of the polymers in absence and presence of the surfactants was computed by well-known procedures[16].

v) Cloud point determinations : Cloud point of 1% TX 100 solutions were carried out in presence of different polymer concentrations. Cloud point was determined by visually noting the temperature at which turbidity was observed[271]. The temperature at which turbidity disappeared on cooling was also noted. The average of the two was taken as the cloud point of the system. Heating and cooling was regulated to 0.5°C / min around the cloud point.

vi) Fluorescence spectroscopy : Fluorescence spectroscopy is one of the favourite methods for the measurement of micellar aggregation numbers. A Shimadzu RF-500 spectrofluorimeter was used for the measurements. Pyrene was used as a probe and Cetyl pyridinium chloride (CPyCl) was used as a quencher. The excitation and emission wavelengths were 335 and 385 nm respectively.

The whole procedure is based on the quenching of emission from a fluorescent probe (F) in this case pyrene by a quencher Q i.e. CPyCl, added in increasing amounts to a solution containing known amounts of surfactant and F. In presence of polymers also the same mechanism is followed at fixed polymer concentrations. Both the probe and quencher are chosen to have high affinity for the micelles and in data analysis one assumes a Poisson distribution of F and Q among the micelles. This methodology was originally developed by Turro and Yekta[161] for ionic micelles and have been extended to polymer - surfactant aggregates[272].

vii) Small angle neutron scattering (SANS) measurement : The SANS experiments were carried out on a mixed system of polymer and surfactants. The surfactants used were SDS and CTAB. The polymer used was PAA which was synthesized as mentioned earlier. All the solutions in neutron scattering experiments were prepared in D_2O (at least 99.5 atom % D, pure). The presence of D_2O provides a good contrast between a micelle and the solvent in a SANS experiment. Neutron scattering experiments were performed on a 7.0 m (source - detector distance) SANS instrument at the CIRUS reactor[273], BARC, Trombay, Mumbai. The sample- to- detector distance was 1.8 m. The spectrometer made use of a BeO filtered beam and had a resolution ($\Delta Q/Q$) of about 15% at $Q = 0.05\text{Å}^{-1}$. The angular distribution was recorded using an one dimensional position sensitive detector (PSD)[274]. The position sensitive detector allows the data to be recorded over the full Q range $Q = 4\Pi \sin ½ \phi/\lambda$ where λ is the wavelength of incident neutrons and ϕ is the scattering angle. The wavelength λ = 0.52 nm. The SANS data was normalized to absolute scale by comparing the data against those from a standard sample Porasil A-11.The solutions were held in a 0.5 cm path length UV grade quartz sample holder with tight fitting teflon stoppers. The sample temperature was maintained at 30 ± 0.1°C. The surfactant solutions used were of 100 mM. Concentration of polymer was 1.0% (w/v).