

CHAPTER 3
EXPERIMENTAL

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3.1 MATERIALS

Acrylamide (AM, reagent grade, Fluka) was purified by recrystallisation from methanol (two times) and dried in vacuum oven at 45° C for two days. Thiourea (TU, E.Merck) was used after recrystallising twice from distilled water (m.p.180°C). N-tertiary butylacrylamide (N-t BAM) (reagent grade, Fluka) was used as received. Triton-X100 (octylphenoxy polyethoxyethanol) was purchased from Fluka (Switzerland) and used without further purification. N, N dimethyl formamide (Merck, India) used for the present study, was stored over P₂O₅ for nearly 10 hours and distilled before use. Low carboxyl content polyacrylamide (LPAM; molecular weight 2.0X10⁵), and high carboxyl content polyacrylamide (HPAM; molecular weight 2.0X10⁵) were purchased from Across Organics (USA) and were used as received. High molecular weight polymers (viscosity average molecular weight 8.9x10⁶, A-type, NPAM) were purchased from Across Organics (USA). Double distilled water has been used throughout.

An aqueous suspension of 25 liter was prepared by stirring continuously 100 gms of the vermiculite (Aldrich) mineral in double distilled water. The suspension was maintained at pH 8.0 by adding NaOH solution. After every 24 hours, 10 cm layer of the suspension (from the top) was siphoned out and each time the original volume was restored by adding water. This process gives sample having particle size less than 2 micron¹. The clay suspension was collected after acidification with HCl to pH nearly 4 and allowing settling at the bottom of the container or by centrifugation. This coagulated clay was washed repeatedly with double distilled water and centrifuged. Free iron oxide was removed by dithionate-citrate method. Organic matters were removed by gently heating at 80° C with 30 % (v/v) H₂O₂ (Merck). H⁺-Vermiculite (HV) was prepared by shaking the stock minerals (3% w/w) in presence of 0.2 (M) HCl for about 6 hours followed by repeated centrifugation (20,000 rpm) and washing with doubled distilled water ². The cation exchange capacity (CEC) of vermiculite was determined by potentiometric titration with standard KOH solution under nitrogen atmosphere and found to be 1.50 meq.g⁻¹. Ce (IV)-vermiculite (CeV) was prepared by shaking HV suspension (3%w/v) in presences of 0.3 (M) cerric ammonium nitrate

$(\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6]$ (reagent grade) at pH 2.5 for 6 h. followed by purification by repeated centrifugation and washing with doubled distilled water until the test of Ce (IV) ion in the supernatant liquid was negative. A separate adsorption experiment of Ce(IV) onto H^+ -vermiculite (HV) showed that maximum exchange capacity of Ce(IV) ion onto the mineral was same (1.50 meq.g^{-1}) as above. The colloid content of clay minerals in each case was determined by evaporating a known volume of suspension to complete dryness. The suspensions were stored at $5\text{-}10^\circ\text{C}$ temperatures.

The water content of vermiculite sample was measured following the method described by Marinsky and coworkers and found to be 10 ml.g^{-1} (ref.3).

The commercial grade nitrogen was passed through a series of bubblers containing Fiesser's solution.⁴ The oxygen free nitrogen was dried by passing through two bubblers containing concentrated sulphuric acid dried.

3.2 POLYMERIZATION

Measured quantities of acrylamide (AM) were taken in well-stoppered Pyrex bottles and polymerization reaction was carried out in dark to avoid any photo-initiated polymerization. Required amount of TU solution were added to the bottles and the mixtures were purged with purified nitrogen for 30 minutes at the experimental temperature. Required amount of dilute HCl solution was added drop wise to maintain pH of the reaction mixture. Polymerization reaction was started by adding deaerated CeV solution to the mixture. The reactions were carried out for desired time with intermittent shaking. Polymerization reactions were stopped by lowering the temperature with chilled water placing the reaction vessel in an ice bath after different time interval to determine degree of conversion as a function of polymerization time. The freezed reaction mixtures were then centrifuged to remove the clay mineral. The polymer was precipitated out by adding excess of acetone (Merck), washed repeatedly with acetone and dried in vacuum at 40°C for 48 hours. Four series of copolymers of acrylamide with *N*-t BAM at various concentrations but with a total monomer concentration of 0.42 M were conducted in aqueous solution at 50°C using Fe (III)-TU redox system in which Fe [III] ions were preloaded in the interlayer space of vermiculite clay mineral. Required amounts of AM and *N*-t BAM (dissolved in miceller pseudo-phase of nonionic surfactant, Triton-X 100(R) because *N*-tert butyl acrylamide is insoluble in water) were taken in a well stopperd Pyrex

bottle. Appropriate amount of TU solutions were added to the bottles and the mixtures were purged with purified nitrogen gas for thirty minutes at the experimental temperature. Dilute HCl was used to adjust pH, which was necessary to ensure the formation of adequate amount of amido-sulphenyl primary radicals to initiate the copolymerization reaction.⁵ In another set of bottles, known amount of aqueous FeV suspension was degassed and finally added to the former bottles under nitrogen atmosphere to initiate the polymerization reactions. After different time intervals the reaction stopped by lowering the temperature with chilled water placing the reaction vessel in an ice bath. FeV suspensions were separated by centrifugation of the reaction mixture at 20,000 rpm. Low molecular weight polymers (viscosity average molecular weight 2.3×10^5 , C-type) were prepared via redox polymerization of 0.4M acrylamide monomer initiated by Fe (III)/TU redox system at 50°C and pH 1.98 (1.5×10^{-3} M FeCl₃ and 0.04 M TU). To obtain medium molecular weight polymers (viscosity average molecular weight 1.6×10^6 , B-type) 0.4M monomer and 0.06M TU in aqueous suspension of ferric vermiculite (Fe(III)-V) were used at 60°C temperature and at pH=1.98.

The reaction mixtures were centrifuged (20,000 r.p.m.) to remove clay vermiculite after the completion of the reaction. The polymer was precipitated out by adding excess of acetone to the supernatants, washed repeatedly with acetone and dried at 40°C for 48 hours under vacuum. The centrifuged clay mineral was also washed and dried at 60°C for 48 hours under vacuum. The dried samples of polymer as well as mineral weighed to determine the polymer yield and non-extractable polymers in the clay minerals respectively.

3.3 VISCOSITY MEASUREMENTS

Two types of viscometers were used to measure the relative viscosities of the polymer solutions. One is Ubbelohde type suspended level viscometer and another is modified Ostwald type viscometer. First one was used to measure viscosities of polymer solutions prepared in the mixtures of solvents and the later one was used to measure the relative viscosities at various shear rates ranging from few tens per second to few thousands per second for polymer solutions prepared in aqueous solutions in presence and in the absence of added salt. In both cases viscometers were placed in thermostated water bath at appropriate temperature, controlled within the range of $\pm 0.1^\circ\text{C}$ and a digital stopwatch with accuracy ± 0.1 sec measured the

flow time. Solvent flow times were larger than 120 seconds so that the kinetic energy corrections are not necessary⁶. Required quantities of dry polymer were dissolved in 0.2(M), 0.1(M), 0.05(M), 0.025(M), and 0.0125(M) aqueous NaCl solutions to study the effects of salt on solution viscosity. Care was taken to avoid excessive shear during dissolution of the polymer. The dissolution process was generally complete within 1-2 days. These solutions were further diluted to the required concentrations. Desired pH of the solutions was adjusted by using dilute HCl or NaOH solutions. Viscosities were measured after 15 days of completion of dissolution to avoid the effect of aging. The molecular weight of the synthesized polymers was determined by viscosity measurement in aqueous 0.1 (M) NaCl solutions at 30°C using a suspended level Ubbelohde Viscometer and a Mark-Houwink relationship.^{7,8}

$$[\eta] = 9.33 \times 10^{-3} M^{-0.75} \text{ cm}^3 / \text{g}.$$

1

3.4 POTENTIOMETRIC AND CONDUCTOMETRIC MEASUREMENTS

Measurements of pH were made using Systronics (pH system 361, India) pH-mV meter. The meter was standardized using two-point calibration method. Conductance measurements were carried out on Systronics conductivity meter-306 using a dip type cell with a cell constant 1.15 cm⁻¹. The cell was calibrated by standard KCl solutions. The measurements were made in a container maintained at desired temperature.

3.5 ELEMENTAL ANALYSIS

For the determination of copolymer composition elemental analysis for carbon and nitrogen of AM-*N*-t BAM copolymers were conducted by CDRI, Lucknow, India. The copolymer compositions were calculated based on C/N weight % ratios because of the variability of absolute values due to the hygroscopic nature of the copolymer. Elemental analysis was conducted at polymer conversion levels, low and high, to assess drift in the copolymer.

3.6 MEASUREMENT OF SURFACE TENSION

Surface tension of TritonX-100 solutions and solutions of polymer surfactants mixtures were measured using the ring method with a Kruss balance (Germany) at four different temperatures (20^o,30^o,40^o,50^oC). The ring was cleaned between two measurements of surface tension. The solutions were thermostated by circulating

water at desired temperature. Sets of measurements were made by adding small aliquots of concentrated surfactant solutions at constant polymer concentration. Each measurement took 20-40 minutes to reach the equilibrium.

3.7 SORPTION OF TU AND AM ONTO VERMICULITE

10ml portion of a 0.5% suspension of clay was placed in a number of Pyrex bottles and different amounts of either thiourea or acrylamide were added followed by pH adjustment at 2.0 by dilute HCl solution. The total volume of the suspension was made upto 15 ml in each case by adding the requisite amount of water and was shaken at 30°C for 4 hours to attain equilibrium. The supernatant solutions were then centrifuged (20,000 r.p.m.) and analyzed. The electronic absorption spectra were recorded with double beam UV-VIS spectrophotometer (Shimadzu, model-240, Japan) at 235 nm and 195 nm for TU or AM respectively. The temperature was maintained within $\pm 0.1^\circ\text{C}$. Double distilled water was used as solvent.

3.8 REFERENCES

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