

CHAPTER 8
SUMMARY AND CONCLUSION

SUMMARY AND CONCLUSION

An introduction covering various aspects of the present research scheme on aqueous polymerization of acrylamide and solution properties of polyacrylamide have been presented in chapter 1 (page 1-15). Usual redox polymerization of acrylamide in aqueous medium yields polymer having not so high molecular weight primarily because of fast termination process via transfer of electron to the oxidant of the redox couple (e.g. metal ions at higher oxidation state) from the growing polymer chain. It has been shown that if the polymerization reaction could be initiated in the interlayer spaces of a mineral phyllosilicate viz., montmorillonite by redox couple involving the trapped metal ions, one may expect a controlled linear termination process because the growing polymer chain may not be able to transfer the electrons to these metal ions in the constrained spaces. This technique may particularly be useful for obtaining very high molecular weight polyacrylamide (PAM). On the other hand, to understand the role of charged groups on factors that govern the efficiency of PAM in its various uses in solution phase especially in the salt rich waters, complete molecular characterization is required. In the case of charged PAM the relative dissociation of the ionic groups and the distribution and alignment of the charged dipoles along the chain are expected to play a decisive role on the final state of conformation of the polymer chain. In view of the above, attempt has been made to increase the chain length of polyacrylamide by loading the potential electron acceptor (metal ions) into the interlayer space of hitherto unexplored phyllosilicate in the above application viz., vermiculite, prior to the reaction. A brief review covering all these aspects viz., polymers of acrylamide, structure of the clay mineral vermiculite, clay-organic interaction, clay-catalyzed polymerization and polymer-solvent interaction have been presented.

Chapter 2 (page 16 -20) describes the scope and object of the present investigation. In recent years, scientists and engineers working on environmental and industrial problems have renewed their interest in water-soluble synthetic polymers because of their very broad range of application. The critical limitation of polyelectrolytes including those derived from hydrolyzed homo-polyacrylamide is the loss of viscosity in presence of mono and /or multivalent electrolytes. Very high molecular weight polyacrylamide has been found to be exceptionally effective

flocculants. It has already been mentioned that if the polymerization is carried out in a constrained space such that the growing polymer chain cannot transfer the electron efficiently to the oxidant of the redox couple an enhanced chain growth results. On the other hand, many present and possible industrial applications of high molecular weight polymer arise from unusual properties they induce to their solutions. The study of their solution property is a prerequisite for the development of this modern domain. The characterization of very high molecular weight polymers raises a number of problems. Therefore, systematic studies arising from the coupling of different experimental techniques are required for the elucidation of diverse theoretical and experimental aspects. In recent years the study of polyelectrolytes has seen a revival stimulated by the use of newly available experimental techniques and the introduction of new theoretical concepts. It is noteworthy that solutions of polyelectrolyte exhibit a behavior that may differ considerably from that of either uncharged macromolecules or low-molar-mass electrolytes.

The experimental technique for the study of polymerization including the methods of preparation and purification of different vermiculite samples viz., hydrogen vermiculite, ferric vermiculite and ceric vermiculite are presented in chapter 3 (page 21 -25). In addition to the above, different experimental techniques viz., viscometry, potentiometry, conductometry and tentiometry (surface tension measurement) for the study of solution properties of ionic and nonionic polyacrylamide are described.

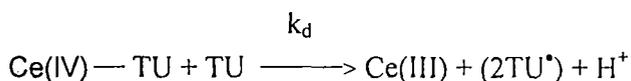
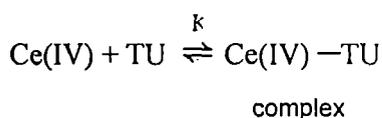
In chapter 4 (page 26 -61), results of the study on the catalytic activity of clay mineral in the present aqueous polymerization process of water-soluble polymers and to prepare polymers having high molecular weight with high rate of formation under ordinary condition are presented. Vermiculite microenvironment has shown a dramatic effect on the polymerization of acrylamide by Ce (IV)/TU combination in aqueous medium via the slow termination due to inability of a growing polymer chain to transfer to the oxidant trapped inside the layered space. A detail study concerning the kinetic and mechanistic aspects has been made for the aqueous polymerization of acrylamide with ceric vermiculite/thiourea initiating system. Kinetic, spectroscopic and other analytical data have been taken into consideration to determine the pathways involved in the reaction. The molecular weights of the polymer are moderately high and ranged from 2.39×10^5 to 1.62×10^6 . The initial rate of polymerization, R_p 's observed are ranged between $(0.79-5.88) \times 10^{-4} \text{ mol.L}^{-1}.\text{s}^{-1}$

depending on various reaction parameters. The plot of the logarithms of empirical rate constant R_p against the reciprocal of the absolute temperature yields the value of activation energy of the reaction as 29.29 kJ/mol. The ^{13}C spectra showed methylene, methane and carbonyl carbons of head-to-tail polymer of acrylamide. It seems apparent from the ^{13}C spectra that Bernoulli statistics are followed and stereo regularity has not been observed. However, the polymer trapped inside the interlayer spaces of vermiculite, which could not be extracted by washing with water may have such possibility of showing stereoregularity. Attempts are being made to extract these polymers in mild condition for further study. The rate of reaction follows the second order kinetics with respect to the monomer concentration, which is deviated from the homogeneous solution phase reaction condition. The significant changes due to the occurrences of the reaction on the vermiculite surface indicate that mechanism of polymerization is greatly affected by mineral microenvironment. The order of polymerization is found to be 0.5 with respect to metal ion oxidant. The relationship of polymerization rate with TU concentration was obtained from the slope of logarithm R_p versus logarithm [TU] plot and from the plot of the R_p vs. [TU], [TU] exponent of 0.85 was found. This value is also different from that of homogeneous polymerization reaction in which second order kinetics with respect to TU is followed. Ce (IV)-TU couple is an effective initiator for the aqueous polymerization of acrylamide. The polymers formed by this initiating system should carry with TU at the terminal. To rationalize the above findings and to predict the possible mechanism of the above polymerization reactions following assumptions are made:

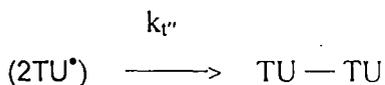
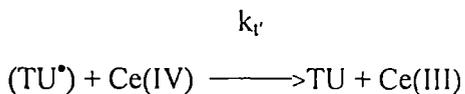
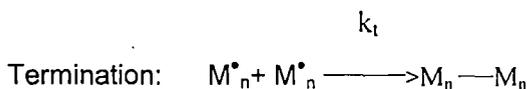
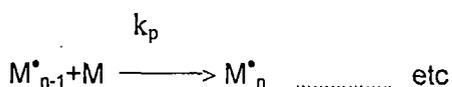
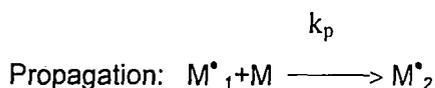
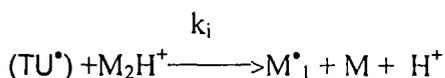
1. Intercalated TU reacts with Ce (IV) ions of the vermiculite layered spaces to form reactive isothiocarbamido primary radical via an intermediate complex. The decomposition of the complex is the rate-determining step.
2. In the constrained interlayer space of vermiculite the monomer molecules remains as pair either through hemi salt formation where two amide molecules share a proton by means of symmetrical hydrogen bond or /and through weak coordination to the exchanged cations.
3. Cage effect is prominent in the vermiculite phase reactions in which the solvent molecules in the constrained space form a potential barrier such that the reactive isothiocarbamido radical cannot diffuse out from the wall of the barrier and favors their recombination.

4. Polymerization locus is the interlayer space of vermiculite. The linear termination of growing polymer chain by Ce (IV) ions is restricted due to the presence of metal ions in the layered space. Initiation, propagation and termination of the polymerization may be shown as follows:

Initiation:



where Ce(III) is ferric ions in vermiculite and (TU*) is caged TU radicals.



Applying steady state condition for different intermediate species, the rate equation under the present condition has been found to be

$$R_p = k_p (k_d k_i K K^1 / k_t' k_t'')^{1/2} K_{TU}^a (K_m^a)^{1/2} (L_0^a)^3 [Ce(IV)]^{1/2} [TU]_s [M]_s^2$$

(where L_0^a , K_m^a , K_{TU}^a are total active sites in unit mass of the mineral and selectivity coefficients of M and TU on vermiculite respectively).

Section B of chapter 4 (page 42-50) deals with the studies on copolymerization of AM with N-t-BAM. Microstructures and reactivity ratios of the copolymers are also determined. Observed data indicate that the copolymerization follow the conventional copolymerization kinetics under a prerequisite that the reactivity of a polymer radical is only determined by the terminal monomer unit. Values of r_1 and r_2 have been found to be 0.43 and 0.32 respectively for Fineman-Ross method and 0.62 and 0.26 for Kelen-Tüdös method. On reversing the indices of the monomer the values of the reactivity ratios changes from 0.43 to 1.56 (r_1) and 0.32 to 0.44 (r_2). For the AM-N-t BAM copolymers mean sequence length of AM vary between 18.61 and 2.83 at molar ratio of 94.79/5.21 to 81.99/18.01 respectively. For those molar ratio compositions, the values of mean sequence length of N-t-BAM were 1.01 and 1.075 respectively.

In section C of chapter 4 (page 51-54) a general discussion of the foregoing study is presented. The experimental results on the adsorption of AM and TU onto vermiculite also discussed. Low charge vermiculite may have interlayer expansion characteristic, which bear closer resemblance to those of high charge montmorillonite than to those shown by other vermiculite of high charge. The isotherm for Ce (IV) ion adsorption onto vermiculite exhibit L-type nature, which suggests strong sorbate-sorbent interaction. The maximum saturation corresponds to 0.97 meq/g of the mineral. Unlike AM, TU leads to the monolayer formation only and maximum capacity is found to be 1.52 mmol/g, which is consistent with that of the monolayer of the AM.

In the section A (page 62- 76) of chapter 5, the results of the investigation on unperturbed dimension, interaction parameter and related aspects of unhydrolyzed polyacrylamide in water-DMF mixtures have been described. In the previous chapter (chapter 4), we have reported the technique by which the molecular weight of PAM may be increased by trapping the initiator component in the interlayer space of vermiculite. This method has been adopted to prepare polymers of high molecular weights for the solution property studies as presented in this section of the present chapter. The increase in molecular dimension from monomer to oligomer, from

oligomer to usual length polymer and from later one to pleistomer is accompanied by the appearance of new properties. The intrinsic viscosities of the polymer have been measured for different fractions of the polymer and also in different compositions (water/ DMF) of the cosolvent mixture. From the relation between $[\eta]$ and M , the unperturbed dimension and molecular expansion factor have been measured. The Huggins constant value in each case was also determined in order to have ideas on the influence of cosolvent system on the aggregation of the polymer. While DMF is a poor solvent for PAM, water – DMF mixture acts as a cosolvent in certain proportions. It is observed that there is a maximum in $[\eta]$ vs. ϕ_{DMF} plot at the solvent composition $\phi_{\text{DMF}} = 0.2$ for PAM type C (low molecular weight) at all the studied temperatures. For PAM type-B (medium molecular weight) at 50°C and for PAM type-A (high molecular weight) at 30°C there is a maxima at $\phi_{\text{DMF}} = 0.3$ and there is a minimum at 50°C for type-A and at 40°C for type-B at $\phi_{\text{DMF}} = 0.2$. Small values of K_H indicate better cosolvency at this solvent composition and temperature. Very high values of K_H for PAM type-B are the indication of strong aggregation for polymer molecules at all temperatures studied. The changes in molecular dimension of unhydrolyzed PAM in water-DMF system are manifested in the varied molecular expansion parameters as a result of interaction with two-component liquid. Values of $[\eta]$ and V_E show that higher the molecular weight of the polymer smaller is the concentration of DMF required for developing cosolvency effect. Solutions of all three polymers of different molecular weights generate two antagonistic effects with the increase in temperature. As a result, there has been no visible effect of temperature on $[\eta]$. Temperature coefficient (K') values of unperturbed dimension indicate polymer molecules to possess a low energy configuration up to $\phi_{\text{DMF}} = 0.3$ and a high energy more compact configuration thereafter. Unperturbed dimension (K_θ), actual end to end distance ($\alpha_n K_\theta$), characteristic ratio ($C\alpha$) and the steric factor (σ) assume their highest values at $\phi_{\text{DMF}} = 0.4$ and are decreased with temperature. But α_n , which represents the long-range interaction, assumes its lowest value at this solvent composition and increases with temperature. Shape factor values of unhydrolyzed PAM molecules are very close to 2.5 and are not affected by solvent composition, molecular weight and the temperature of the study indicating a near spherical configuration.

In the section B (page 77 - 88) of chapter 5, the results of the investigation on unperturbed dimension, interaction parameter and related aspects of hydrolyzed polyacrylamide in water-DMF mixtures have been described. The intrinsic viscosities $[\eta]$'s of anionic and nonionic polyacrylamide (PAM) were measured in water-dimethyl formamide mixtures at various temperatures. Non-polyelectrolyte behavior of low carboxyl content polyacrylamide (LPAM) was observed in mixed solvent system. The plots of $[\eta]$ vs. solvent composition (ϕ_{DMF}) in mixed solvents passes through a minimum for high carboxyl content (HPAM) and LPAM but through a maximum for nonionic PAM (NPAM). Observed minima may be attributed to the loss of polymer sites available to interact with solvent via H-bonding interaction between neighboring amide and acid groups. The observed maximum for NPAM is possibly due to the most powerful cosolvent effect. Existence of two antagonistic effects is indicated in $[\eta]$ values of NPAM at various temperatures. Huggins constant (K_H) values also show a significant variation of cosolvency as a function of solvent composition. Activation parameters of viscous flow were calculated using Frenkel-Eyring equation. The volume related parameter and the shape factor were also computed. Shape factor data indicate that polymer molecules are more or less rigid spheres and are not affected by temperature and composition of solvent.

Chapter 6 (page 95- 109) reports the results of physicochemical studies on dilute solution properties of high carboxyl content (HPAM) and low carboxyl content polyacrylamide (LPAM) in aqueous solution as a function of concentration, pH, added salt and the temperature. From the reported results it is clear that the conformational properties of carboxyl content polyacrylamide, which is generally used in secondary oil recovery, are strongly dependent on pH and the concentration of added salt. These polymer solutions exhibit that the viscosity decreases with increasing concentration of added salt and increases with pH. Because polyacrylamide are generally used in neutral media, it is of interest to choose hydrolyzed samples that have much higher viscosities than unhydrolyzed polyacrylamide due to the presence of ionic charges. Under salt free conditions the use of highly hydrolyzed samples is preferable because the chains would be more extended. The results on viscosity experiments of LPAM suggest that chain expansion due to intramolecular electrostatic repulsion may not necessarily be essential to cause a marked increase in viscosity at low polymer concentration, since intramolecular repulsion is small for LPAM. This is contradictory to one of the most fundamental concepts in

polyelectrolyte solution. Although the results seem to be clear, there is still a possibility that some polymer chains have larger number of ionic groups in random ionomers, which would lead to some chain expansion due to mutual repulsion of like charges and an increase in viscosity results.

To gain insight into the factors that control the viscosity behavior of dilute solution of nonionic and anionic polyacrylamide under various conditions of temperature and surfactant addition, some experiments are performed and the results of those experiments are presented in chapter 7 (page 110-126). Previously, it was argued 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 surfactant concentrations, (0.01 and 0.1 %), it is seen that $[\eta]$ 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. The results of the investigation suggest that the shape of 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 spherical in aqueous and aqueous-organic mixtures in the presence or in absence of salt. It is also found that on the initial addition of surfactants the end-to-end distance decreases but further addition of surfactant results in the increase in the end-to-end distance. Three regions of surfactant concentration representing the distinct stages of surfactant-polymer interactions in aqueous solution are observed in the plot of surface tension vs. concentration of nonionic surfactant. In the first region, which is located at lower concentration region of surfactant, the surface tension decreases gradually till the first break point comes. Before the first break point surfactant molecules bind cooperatively to polymers. Generally, critical micellization concentration (cmc) of a nonionic surfactant decreases with an increase in temperature due to changes in water structure and water surfactant interaction. In presence NPAM and LPAM (8.2 mol% charge) overall variation of polymer saturation point (PSP) is determined by various interactions in polymer-TX-100-water system. Here, behavior of LPAM is somewhat similar to that of NPAM. However, for HPAM (72 mol% charge) the polyelectrolyte nature of the polymer is responsible for higher PSP values. Moreover, as the polymer concentration increases more binding sites are available for the surfactant to interact,

hence PSP values go on increasing. It is surprising to note that at 50°C temperature PSP values are minimum for all the polymers in the whole range of concentration.