

## **Chapter 4**

Interaction of cationic micelles with 1 and 2 naphthols: self fluorescence monitoring of stimuli-responsive viscoelasticity and location of surface activity

## 4.1 Introduction and Review of Previous Work

Stimuli-responsive properties of viscoelastic gels of long wormlike micelles are fascinating and have created a great deal of interest in recent years [1-4]. Most extensively studied system is the cetyltrimethylammonium bromide (CTAB) micelles in presence of a hydrotrope, sodium salicylate (SS). Unlike simple halides, salicylate promotes sphere to wormlike micellar transition at very low concentrations, viz., near the normal critical micelle concentration (cmc, 1 mM) of CTAB. The flexible and elongated wormlike micelles under dilute conditions show complex and unusual rheological phenomena, which include strong viscoelasticity and shear-induced structure (SIS) formation[5-7]. It is particularly interesting that, while a wide variety of wormlike ionic micellar solutions display identical rheological responses, a common element in most of these systems is the presence of salt anions such as SS. Although a few examples are available in the literature where additives other than SS have been used, these molecules have never been considered as high up as the promoter like SS[8]. However, a number of studies on micellar shape transition in cationic, anionic, and zwitterionic surfactant systems induced by polar and nonpolar organic species under comparatively high concentration conditions have been reported in the literature [9-11]. While hydrophobic molecules with either aromatic ring or small polar group have shown better efficiency, no unusual rheological feature was apparent under this condition. The presence of an anionic charge on the promoter molecule has been considered pivotal in achieving low concentration shape transition of cationic micelles via charge screening because it decreases the average area per surfactant head group allowing the packing parameter to exceed the critical value of  $1/3$ [12]. However, other important factors including the role of OH group of the promoter molecule have not attracted much attention, and as such, the puzzling question as to why not only its presence but also its position in the aromatic ring of SS molecule is so vital remains broadly unanswered[13]. Therefore, to understand the role of the OH group precisely, it was tempting to check what would

happen if we use uncharged naphthols where the hydrophobic part is very strong and the anionic charge is absent. In this paper we have studied effect of neutral 1- and 2-naphthols on the shape transition of CTAB and CPB micelles and shown that inter-molecular H bonding between OH groups of micelle embedded naphthol molecules plays a key role in micellar shape transition in absence of any charge screening of head groups and imparts strong viscoelasticity to the dilute aqueous surfactant solution.

## **4.2 Experimental**

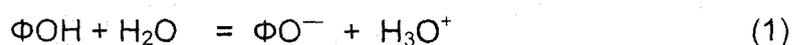
1-Naphthol(puriss) and 2-naphthol(puriss)(Aldrich products) were purified further by vacuum sublimation followed by recrystallization from 1:1 aqueous methanol. CTAB (puriss, Aldrich) and CPB (Aldrich) were used as received. <sup>1</sup>H NMR and Fourier transform infrared (FTIR) were recorded on a Bruker (300 MHz) spectrometer and a Shimadzu (083000) spectrometer, respectively. Steady state fluorescence was measured on a Perkin-Elmer LS-55 luminescence spectrometer. UV absorption spectra were recorded on a Jasco (V-530) spectro-photometer. Shear-induced viscosity was measured on a rota-tional viscometer (Anton-Paar, DV-3P; accuracy (1% and repeatability (0.2%) equipped with temperature controller and with the facility of varying shear rates.

## **4.3 Results and Discussion**

### **4.3.1 Microscopic polarity at the location of OH groups of embedded naphthols**

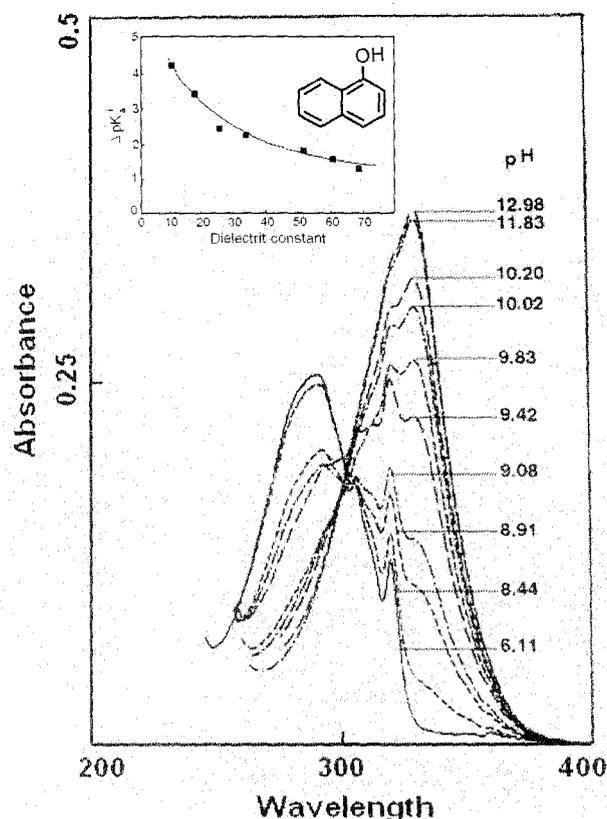
It is believed that while the aromatic ring of naphthols are embedded in micelles the core of which having dielectric constant around 2-7 only, the OH groups are stood out toward water region. NMR study also confirms that the aromatic ring of the naphthol resides near the non-polar core in between tetraalkylammonium head

groups of the surfactants. Although almost all of the previous studies on the hydrotrope induced microstructural transitions of micelles argue that the OH groups are protruded out of the micellar surface and remains close to aqueous layer, no experimental verification has so far been reported. To understand the exact nature of the location of the OH group, the micropolarity of the residence sites is determined. Spectral characteristics, specially fluorescence spectra, are often very sensitive to the environments around the probe molecule. Because of this, fluorescence spectroscopy has become one of the important methods for the study of the structure and dynamics of the microheterogeneous systems. Unfortunately, the excited state proton transfer process (ESPT) of hydroxyaromatic compounds, viz., 1 and 2-naphthols complicates their spectral properties. The absorption spectra are also not sensitive to the environmental conditions in the present system. Moreover, information regarding the microenvironment of aromatic  $\pi$ -electron system which might have been obtained from the study of spectral characteristics, would not be helpful in determining the location of protruded OH groups of naphthol molecules. Therefore  $pK_a$  shift of the acid-base equilibrium of OH group of naphthols in microheterogeneous medium relative to aqueous solution would be the ideal route for getting such information precisely. This shift in  $pK_a$  in a cationic micelle like CTAB relative to aqueous solution may be due to the surface potential of the micelle and the polarity variation at the micellar interface from that of the bulk (in absence of any specific interaction). The theoretical background of the analysis of data pertaining to the interfacial acid-base equilibrium of naphthol molecules has been well documented for other similar probes[14, 15]. While determining  $pK_a$  values of the present system, let us assume that the acid-base equilibrium of the OH group of naphthols is described by



Where  $\Phi\text{O}^-$ ,  $\Phi\text{OH}$  and  $\text{H}_3\text{O}^+$  are deprotonated and protonated (neutral) forms of the naphthols and the proton respectively. For the naphthol indicators in aqueous

micellar solution, the apparent  $pK_a$  values were obtained from the change in the ultraviolet absorption spectra as a



**Figure 4.1:** UV absorption spectra of 1-Naphthol (0.5 mM) in 5.0 mM CTAB at varying pH.

function of bulk aqueous pH by means of the following Handerson-Hasselbach equation (which considers only concentration terms at low concentration conditions) as follows ( equation 2):

$$pK_a^{obs} = pH - \log \left[ \frac{[\Phi O^-]}{[\Phi OH]} \right] \quad (2)$$

provided that the quantity  $[\Phi O^-] / [\Phi OH]$  is determined by  $(A - A_{\Phi OH}) / (A_{\Phi O^-} - A)$  where  $A$ ,  $A_{\Phi OH}$  and  $A_{\Phi O^-}$  are the absorbances of naphthols at experimental pH and low and high pH's respectively. The near uv spectra of 1-naphthol as a function of the bulk aqueous pH in CTAB micelle solution are shown in Figure 4.1 (unfortunately, the spectral profile of 2-naphthol is insensitive towards bulk aqueous pH and, therefore, can not be studied). For the acid-base equilibrium of the

interfacially located organic molecule, the  $pK_a^{obs}$  be now separated into two components viz., an electrostatic component and a non-electrostatic environmental component. This is formalised in relation 3,

$$pK_a^{obs} = pK_a^0 - e \Psi_0 / 2.303kT \quad (3)$$

where,  $pK_a^0$  is the apparent  $pK_a$  value if surface potential of the micelle,  $\Psi_0$ , is null. Information can be obtained about the acid-base equilibrium at the surfactant-water interfaces by comparing  $pK_a^0$  values of naphthols in the aqueous micellar systems with the  $pK_a$  values for naphthols in the aqueous-organic mixtures, e.g., dioxane-water mixtures. The apparent  $pK_a$  in organic-aqueous mixture,  $pK_a^m$ , is defined in the following relation (equation 4).

$$pK_a^m = B + \log U_H^0 - \log [\Phi O^-] / [\Phi OH] - \log \gamma_{\Phi O^-}^m / \gamma_{\Phi OH}^m \quad (4)$$

where,  $\gamma^m$ 's are activity coefficient terms in the medium, B is the pH meter reading and  $\log U_H^0$  is the correction factor to be applied to pH meter reading to measure the actual hydrogen ion concentration in organic-aqueous mixtures. The  $pK_a^0$  values relate to a system where the conjugate acid-base species reside in an interfacial microenvironment but the bulk aqueous solution pH is measured. Hence, the comparison between  $pK_a$  values in dioxane-water mixtures and  $pK_a^0$  values in micelle systems should take into account the primary medium effect on the proton. In other words,  $pK_a^0$  values need to compare to  $pK_a^i$  values rather than  $pK_a^m$ 's where,

$$pK_a^i = pK_a^m + {}_mY_{H^+} \quad (5)$$

and  ${}_mY_{H^+}$  denotes the primary medium effect on the proton. It is usual to assume that the mean primary medium effect on HCl,  ${}_mY_{\pm}$ , approximates to  ${}_mY_{H^+}$ . The  $\log U_H^0$  and  ${}_mY_{\pm}$  values given in references 14, 15 were employed to derive  $pK_a^i$  values in dioxane-water mixtures. These  $pK_a^i$  ( $\Delta pK_a^i = pK_a^i - pK_a^w$ ) values as a function of medium dielectric constant are shown in Figure 4 (inset). The  $pK_a^0$  values of 1-naphthol in CTAB micelles are determined with the aid of eqn.3 and the known value of surface potential of CTAB micelles of +141 mV[14]. The effective dielectric constant ( $D_{eff}$ ) values are obtained by comparing  $\Delta pK_a^0$ 's ( Table 1 ) of 1-naphthol

in micellar surface with that of  $\Delta pK_a^i$  values in 1,4-dioxane-water mixtures (Figure 4; inset). It may be noted that  $D_{\text{eff}}$  values are measured on the basis of several assumptions: (i) both the protonated and deprotonated forms of the naphthol indicator are quantitatively partitioned into the micellar phase at least at high surfactant: naphthol ratio (ii) the activity coefficient term (  $\log \gamma_{\Phi O^-}^i / \gamma_{\Phi OH}^i$  ) is negligibly small so that  $\Delta pK_a^0$  values are directly comparable with the  $\Delta pK_a^i$  behaviour in different solvent dielectric constant bulk media (iii) although the OH groups of naphthol are protruded from the micellar surface, the acid-base equilibrium is still under the influence of micellar surface potential and (iv) it is evident that much like 1,4 dioxane-naphthol system, the interfacial water of CTAB micelles form H-bonds with micelle embedded naphthols (discussed later), which act as H-donor in both the above cases. No serious error in the evaluation of  $D_{\text{eff}}$  due to presence of this H-bond is thus anticipated because such effect, if any, would be compensated by the similar interaction present in the reference system ( naphthols in dioxane-water)

**Table 4.1.** Results of pH titration of 1-naphthol in aqueous and aqueous CTAB micellar solution at 25°C.

Conc.of CTAB/mM					
(Conc. of 1-HN= 0.5mM)	$pK_a^w$	$pK_a^{obs}$	$\Delta pK_a^{obs}$	$pK_a^0$	$\Delta pK_a^0$
20		8.623	0.765	11.007	1.619
50	9.388	8.679	0.709	11.063	1.675
100		8.914	0.474	11.298	1.910

**Table 4.2 .**  $D_{\text{eff}}$  values of OH group location of micellar interface

Conc. of CTAB/mM (Conc. of 1-HN = 0.5mM)	$D_{\text{eff}}$
20	$51 \pm 3$
50	$49 \pm 3$
100	$45 \pm 2$

Table 4.2 shows that  $D_{\text{eff}}$  at the interface of CTAB micelles, as measured by the  $pK_a$  shift of interfacially located naphthols, vary from  $51 \pm 3$  to  $45 \pm 2$  as a function of CTAB concentration from 20mM to 100mM (concentration of naphthol being 0.5mM throughout). This result indicates that naphthols are increasingly partitioned in micelles as the CTAB concentration is increased. Utilising the solvatochromic visible absorption band maximum  $E_T(30)$ ,  $D_{\text{eff}}$  estimates of 28-33 were obtained previously for CTAB micelles[16]. Therefore, in comparison to the previously determined micropolarity of CTAB micellar surface ( $D_{\text{eff}} \sim 30$ ), the present value of 45 (under condition when most of the naphthol molecules are partitioned in micelles) is substantially high. This is an interesting observation. This clearly indicates that the OH groups are directed away from the surface of the micelles and are located around more polar region. Assuming a polarity gradient to exist with the distance from the micellar surface, one can have a rough idea of the location of the OH groups in the Stern layer. A recent application of numerical Poisson-Boltzman methods to the determination of the electrostatic potential and counter ion distribution around polyelectrolyte such as DNA may be relevant in this respect [17]. In this case the situation had prompted to choose a dielectric constant "field", where low dielectric values exist near 30 at the polyelectrolyte surface and increasing away to the values near 78.5 in bulk water. A rough estimation following the above work, which takes on a cylindrical polyelectrolyte (e.g.,DNA) surface of radius 10A as the

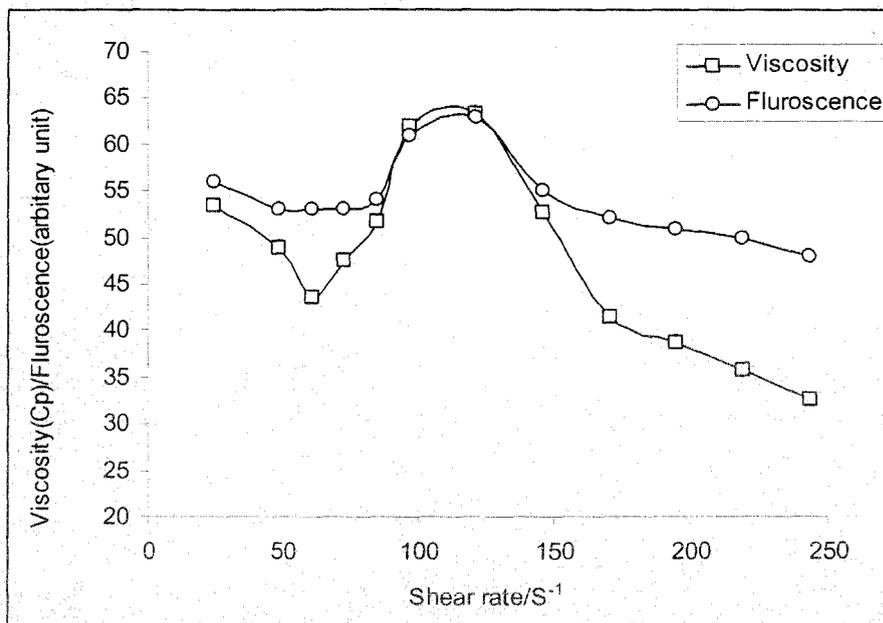
low dielectric region, shows that the present  $D_{\text{eff}}$  value of 45 (compared to  $\sim 30$  at the micellar surface) could be rationalised assuming OH group of naphthol to be protruded away from the CTAB micellar surface through nearly 1Å distance toward the Stern layer[17].

### 4.3.2 Shear-Induced Viscosity and Fluorescence Intensity

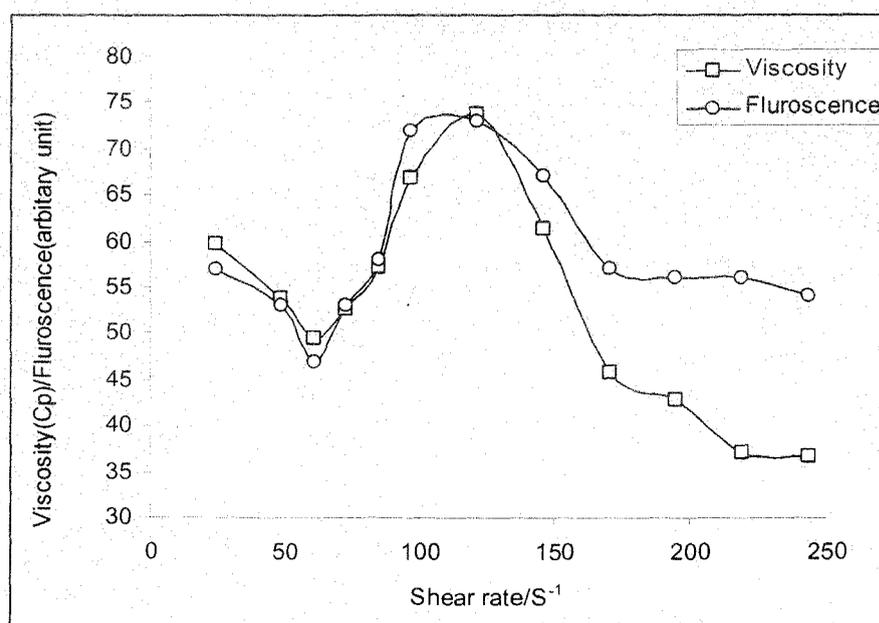
Aqueous CTAB, CPB or OTAB (2-10 mM) and 1- or 2-naphthol (2-10 mM in 2-5% methanol, naphthols being sparingly soluble in water) solutions show viscosities similar to those of water. But as soon as these solutions are mixed together at room temperature, a thick gel-type fluid with high viscoelasticity is developed. Since viscoelasticity tends to disappear in high methanol concentrations, experimental solutions are prepared routinely by transferring the required amount of naphthol solutions (in pure methanol) in the experiment vial first, and then the alcohol was evaporated off completely before the addition of aqueous surfactant solution. Much like the CTAB-SS system, CTAB-naphthols, OTAB-naphthols and CPB-naphthols also display maximum viscoelasticity at a 1:1 molar ratio of surfactant and the promoter. The argument that an excess or deficiency of charge on the micelles due to adsorption of hydrotrope anions (e.g., SS) would shorten the micellar life time and size is not apparently true for the present system because under the present experimental condition of solution pH ( 6.5), the naphthols are mostly protonated, i.e., uncharged ( $pK_a$ 's > 9.0). Therefore, it seems apparent that the symmetrical distribution of surfactant and the promoter molecules leading to highly compact spherical micelles facilitates an optimum surface curvature to attain in presence of H bonding (discussed later), and this results in the sphere to rod transition easily. For further experiments, naphthol to surfactant ratio was chosen to produce strongest viscoelasticity, i.e., 1:1 mole ratio. At low concentrations (<2 mM), CTAB, OTAB or CPB-naphthol solutions show shear thinning properties, typically observed in the case of a non-Newtonian fluid. But at higher concentrations (>2 mM; 25°C), present

experimental systems display interesting rheological phenomenon. Up to the applied shear rate of  $52 \text{ s}^{-1}$  (which is concentration dependent) for the CPB-2-naphthol system, solutions shear thin (Figure 4.3). An onset of viscosity rise is observed thereafter as a function of applied shear, and the viscosity share rate profile passes through a maximum, e.g., at  $102 \text{ s}^{-1}$  for the above system (Figure 4.3).

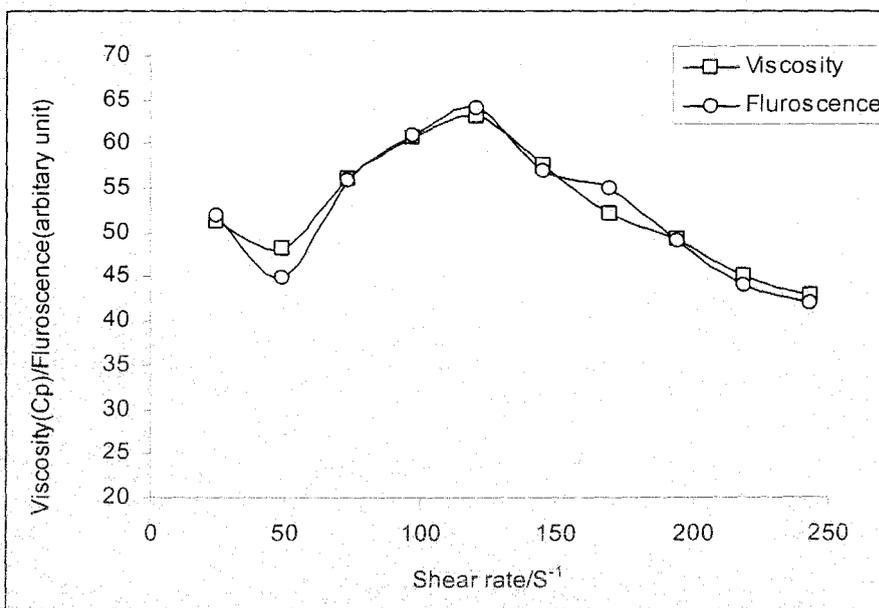
This behavior is consistent with building up of long wormlike micellar bundles[7]. The system recoils after the applied shear is withdrawn and takes a very long time (e.g., half-life period of viscosity decay of a CTAB-1-naphthol (7.0 mM) system equals 56 min; samples were sheared in a rotational viscometer at  $100\text{s}^{-1}$  for  $\geq 5$  min to ensure that the high viscosity regime was reached) to recoil completely and to return to an equilibrium unsheared state. Shear rates at which viscosity transition takes place and the shear rates at which maximum viscosity is displayed by various systems vary to some extent from system to system (Figure 4.2 -4.7). Systems which display shear induced nonlinear rheological changes (such as the present systems) bring about formidable problem in measuring unperturbed solution viscosity because the measuring techniques (e.g., torsional shear rheometry) often apply considerable stress on the system during measurement, and thus the zero-shear viscosity becomes obscure. Both the naphthols are well-known fluophores, and significantly, the quantum yield of emission of the naphthols is found to be very sensitive to the solution viscosity of the present systems.



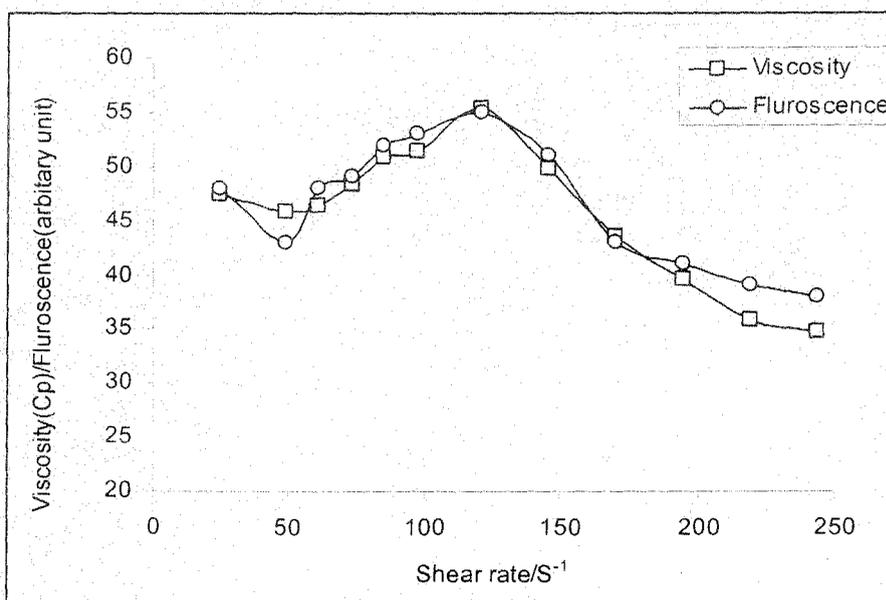
**Figure 4.2:** Variation of viscoelasticity and Fluorescence intensity of CPB-1-naphthol (10 mM) system with applied shear rate.



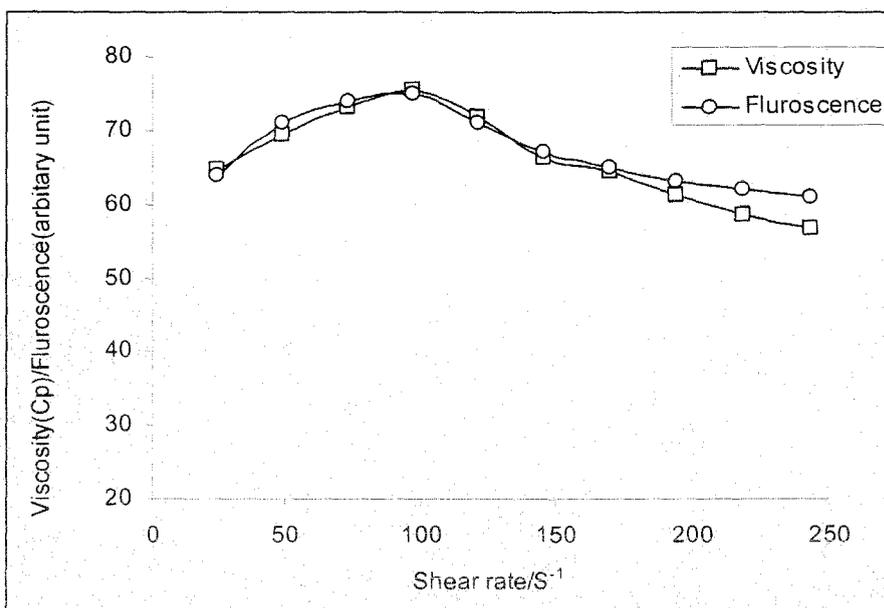
**Figure 4.3:** Variation of viscoelasticity and Fluorescence intensity of CPB-2-naphthol (10 mM) system with applied shear rate.



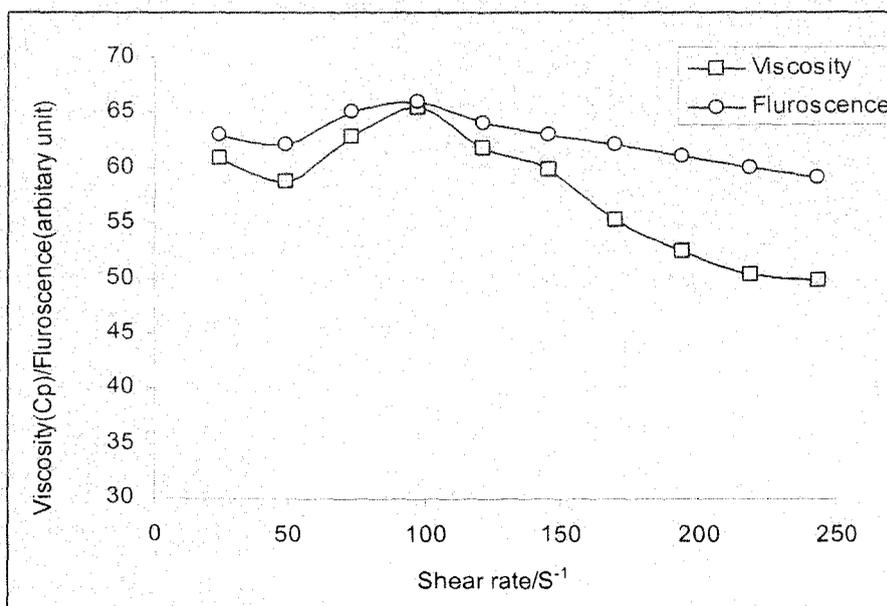
**Figure 4.4:** Variation of viscoelasticity of CTAB-1-naphthol (10 mM) system with applied shear rate.



**Figure 4.5:** Variation of viscoelasticity of CTAB-2-naphthol (10 mM) system with applied shear rate.



**Figure 4.6:** Variation of viscoelasticity of OTAB-1-naphthol (10 mM) system with applied shear rate.



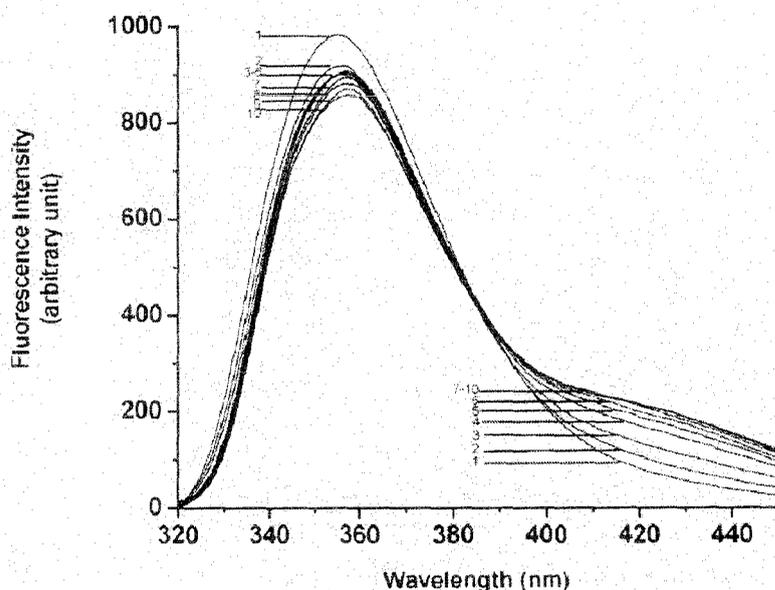
**Figure 4.7:** Variation of viscoelasticity of OTAB-2-naphthol (10 mM) system with applied shear rate.

This offers an interesting route for fluorescence monitoring of unperturbed viscosity as a function of applied shear (Figure 4.2-4.7). In a viscous medium, a fluorophore cannot transfer energy efficiently via nonradiative means because of delayed collisions with the surrounding molecules resulting in the increased emission quantum yield. Moreover, the dipole moment of the probe in the excited state is greater than that in ground state, and hence interaction of the excited probe molecule with its surrounding molecules is different from that before absorption. Reorientation and translation of nearest-neighbor molecules allow the probe molecule to relax gradually to its equilibrium excited singlet state ( $S_1$ ). In solutions of low viscoelasticity where these relaxations are very fast, fluorescence practically takes place from this equilibrium excited state  $S_1$ . In highly viscoelastic solutions, the relaxation of molecules surrounding the probe may be slow, and the probe molecules may emit before reaching their equilibrium excited state  $S_1$ , and a blue shift of the fluorescence spectrum may also be observed accompanying by an intensity enhancement. Similar situation is also encountered in a twisted intermolecular charge transfer state (TICT) formation where in a less viscous environment the probe molecules also display internal rotation and charge transfer, which results in the less emission quantum yield than that in a high viscous environment[18,19]. Furthermore, naphthols are weak acids in the ground state. In aqueous solution (pH 6.0-7.0), they exist almost completely in the acid forms. On excitation into the lowest singlet excited state, the  $pK_a$  values drop by several units (2-naphthol:  $pK_a^*$  2.78; 1-naphthol:  $pK_a^*$  0.40),[20-22] i.e., they undergo deprotonation in the excited state (DES)[23,24] As a result, the emission from the neutral forms of 1- and 2-naphthols at 360 and 357 nm, respectively, exhibits very low intensity than those of the anion forms near 450 or 420 nm, respectively. However, on binding to micelles, the DES process is restricted significantly causing a 20-90-fold increase in the intensity and life time of the neutral emission as well as in the rise time of the anion emission[25]. This is probably because of unavailability

of an adequate number of water molecules in the vicinity of the naphthol molecules embedded inside the micelle to hydrate the proton released during photolytic deprotonation[25]. Therefore, at low surfactant concentrations (<2 mM; DES is significant), emissions from the deprotonated anion forms of the naphthols were monitored at higher wavelengths, whereas in the presence of high concentrations of surfactant, emission from neutral form of 2-naphthol were monitored at lower wavelengths (where DES is insignificant) in the present experiments (1-naphthol shows very low quantum yield for neutral emission). Figure 4.2-4.3 also compares the shear induced viscosity data with that of fluorescence intensity of the present CPB-2-naphthol system. While the overall feature of the shear-induced viscosity profile is identical with that of the emission, they are not exactly superimposed on one another possibly because of the perturbation imposed on the system during viscosity measurement. However, we failed to observe any direct effect of applied shear on the DES process. This is apparent from the nonvariant ratio of emission intensities of protonated to deprotonated naphthols as a function of applied shear. This also indicates that the shear does not influence the availability of water molecules to hydrate the liberated protons, i.e., the microstructure around the naphthol molecules in the wormlike micelles remains unchanged in SIS. However, as shown in Figure 4.2, it seems like that in the high applied shear rate ( $>180 \text{ s}^{-1}$ ) the viscosity and fluorescence have opposite variation with the applied shear rate. Partial modification/disruption of wormlike micelles under high shear may change the compactness causing redistribution of naphthols in the micellar gel expelling some of the inner site naphthols to the outer site (better accessible to water molecules), resulting in the slight increase in the fluorescence intensity due to modified DES process[26]. In an experiment where hydrotropic promoter for micellar shape transition is not a fluophore, a probe must be added from the outside for the above measurement. This, in turn, may alter the hydrophobic trait of the system and affect the rheology. Therefore, one should be careful in using external fluorescence probes for monitoring viscosity.

### 4.3.3 Fluorescence Spectroscopy

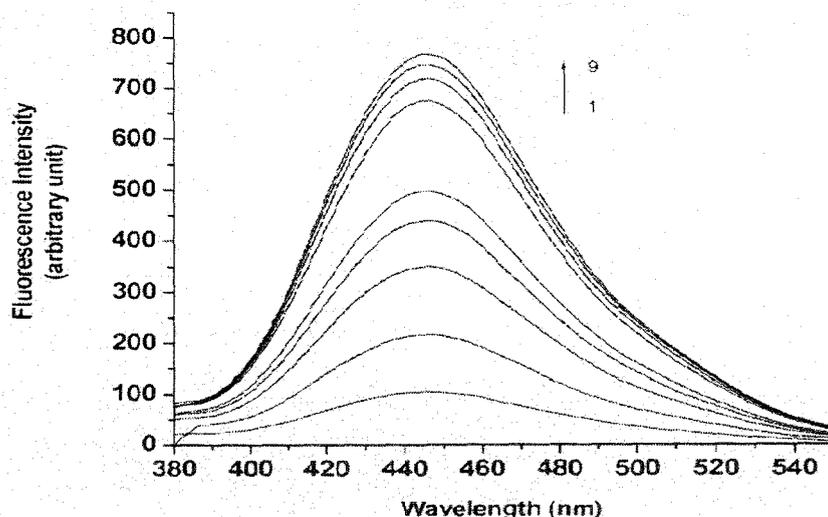
It has been reported that fluorescence quenching can be induced by the hydrogen-bonding interactions for fluophores in the hydrogen-bonding surroundings and is explained by the hydrogen bonding dynamics in the fluorescence state [27-32]. Therefore, it may be presumed that intermolecular H bonding in micelle-embedded naphthols can be studied effectively by observing fluorescence quenching (static and dynamic).



**Figure 4.8:** Fluorescence spectra of 2-naphthol ( $0.25 \times 10^{-5}$  mol/L) in aqueous CTAB solutions in presence of 0.1 M HCl. [CTAB]: (1) 0.0 mM, (2) 3 mM, (3) 2.5 mM, (4) 2 mM, (5) 1.5 mM, (6) 1 mM, (7) 0.75 mM, (8) 0.5 mM, (9) 0.25 mM, and (10) 0.12 mM

However, excited-state proton transfer (ESPT) or DES process of hydroxy aromatic compounds such as naphthols seems to make the situation somewhat difficult. The ESPT rates of these compounds in aqueous solutions are limited by the time water takes to wrap itself around the charge because a water cluster of 4 (1 molecules is the proton acceptor in each case[33]. The first two steps in the ESPT process are, therefore, (i) the H-bonded complex formation of electronically excited state of naphthols with water molecules and (ii) hydrogen-bonded complex formation with

water clusters required for protolytic dissociation[23]. ESPT process of 1- and 2-naphthols in organized media including different micelles have been investigated in considerable detail, but the results are not always unambiguous[23,24,34,35]. It has been shown that the ultrafast proton-transfer processes in ESPT became significantly retarded for 1-naphthol in micelles due to lack of water availability (as has already been mentioned), and the decay of the emissions are often multiexponential due to different solubilization sites in anionic and nonionic micelles, although a monoexponential decay process has also been observed for similar systems[34,35]. On the other hand, for CTAB micelles, the retardation effect is somewhat compensated by the catalytic effect of the micellar potential[35]. Although a previous study did not find convincing evidence that all of the naphthols in micelle are definitely in the form of H-bonded complex with several water molecules, which is required for photodissociation, possible existence of intermolecular H bond in electronically excited states of naphthols under identical condition of wormlike micelle formation have been re-examined in the present study[23]. Figures 4.8 and 4.9 show the emission spectra of 2- and 1-naphthols, respectively, in 0.1 M HCl in presence of CTAB. Addition of high excess of hydroxonium ion is to shift the acid-base equilibrium toward neutral naphthol (protonated) to facilitate intermolecular H-bond

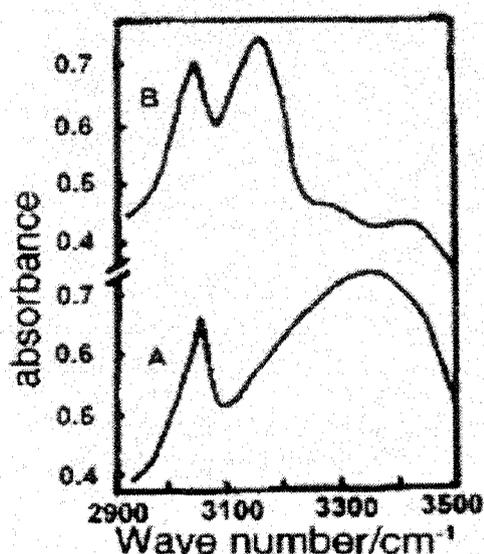


**Figure 4.9.** Fluorescence spectra of 1-naphthol ( $0.25 \times 10^{-5}$  mol/L) in aqueous CTAB solutions in presence of 0.1 M HCl. [CTAB]: (1) 0.0 mM, (2) 0.25 mM, (3) 0.5 mM, (4) 0.75 mM, (5) 1.0 mM, (6) 1.5 mM, (7) 2.0 mM, (8), 2.5 mM, and (9) 3.0 mM.

formation. While 1-naphthol exhibits only anion emission ( $pK_a^* 0.40$ ), which is enhanced substantially in presence of CTAB, emission from 2-naphthol in water was essentially from the neutral naphthol molecules under the above condition ( $pK_a^* 2.78$ ). The effect of CTAB concentration on neutral as well as the anion emission of 2-naphthol is interesting (Figure 4.8). While addition of CTAB in the submicellar concentration range increases the intensity at 420 nm region depicting catalytic effect of CTAB charge on the excited-state deprotonation, further addition of CTAB above the cmc ( $>1$  mM) decreases the emission intensity indicating a retardation of the deprotonation rate for the lack of water availability in the micelles. Intensity of neutral emission, however, is increased slightly on the addition of CTAB in the submicellar concentration range, while in the post micellar concentration range no appreciable change of emission intensity is observed. Moreover, no detectable shift of neutral emission wavelength or the fluorescence quenching on CTAB addition is observed. Therefore, neither any extensive disruption of H bonds that might exist between the electronically excited state of naphthols and the water clusters nor the formation of new intermolecular H bond among the embedded naphthols in the photoexcited state is obvious from the above result.

### 4.3.4 FTIR Spectra:

The FTIR spectra of 2-naphthol in the presence and absence of CTAB micelles are shown in Figure 4.10 (A and B). The spectra of vacuum dried samples (25 °C) provided interesting results (in KBr pellets). (Studying the spectral feature of OH group of naphthols in aqueous solution was not possible (in CaF<sub>2</sub> cell) due to overlapping of IR peaks with that of water.) The broad band around 3354 cm<sup>-1</sup>, which is assigned to the OH stretching of 2-naphthol (typically observed in phenols) is shifted to 3163 cm<sup>-1</sup> due to partitioning in the micelles.



**Figure 4.10.** FTIR spectra of 2-naphthol (A) in the absence of CTAB and (B) in the presence of CTAB.

Comparatively sharper peak at higher wavelength confirms the presence of well-defined and stronger H bond in naphthols, which are embedded inside CTAB micelles. The peak at 3050 cm<sup>-1</sup>, which remains almost unchanged upon gelation, may be assigned to aromatic CH stretch. Above shifting of OH stretching frequency is very much reproducible and consistently displayed by a wide variety of wormlike micellar systems promoted by naphthols. It seems apparent that H bonding plays an

important role in micellar shape transition[36]. The result also shows that vacuum drying at room temperature did not destroy the microstructure completely although may have modified it to some extent.

#### 4.4 Reference

1. H. Rehage and H. Hoffmann, *J. Phys. Chem.*, **92**, 4712 (1988) .
2. H. Rehage and H. Hoffmann, *Mol. Phys.* **74**, 933 (1991) .
3. M. Cates and S. J. Candau, *J. Phys.: Condens. Matter* **2**, 6869 (1990).
4. Y. Hu, C. V. Rajaram, S. Q. Wang and A. M. Jamieson, *Langmuir* **10**, 80 (1994)
5. S. L. Keller, P. Boltenhagen,; D. J. Pine and J. A. Zasadzinski, *Phys. Rev. Lett.*, **80**, 2725 (1998)
6. B. Boltenhagen, Y. Hu, E. F. Matthys and D. J. Pine, *Phys. Rev. Lett.*, **79**, 2359 (1997)
7. C. Liu and D. J. Pine, *Phys. Rev. Lett.* **77**, 2121 (1996)
8. C. Manohar, In *Micelles, Microemulsions, and Monolayers; Science and Technology*; D. O. Shah, Ed.; Marcel Dekker, Inc.: New York, 145(1998)
9. P. M. Lindemuth and G. L. Bertrand, *J. Phys. Chem.*, **97**, 7769 (1993)
10. N. Hedin, R. Sitnikov, I. Furo, U. Henriksson and O. Regev, *J. Phys. Chem. B*, **103**, 9631 (1999)
11. H. Yin, S. Lei, S. Zhu, J. Huang and J. Ye, *Chem.-Eur. J.*, **12**, 2825 (2006)
12. N. Israclachivli, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc., Faraday Trans.*, **72**, 1525(1976)
13. R. K Rao, C. Manohar, B. S. Valaulikar and R. M. Iyer, *J. Phys. Chem.* **91**, 3286 (1987)
14. J. Drummond, F. Grieser and T.W. Healy, *J. Chem. Soc. Faraday Trans. I*, **85**, 521 (1989)
15. C.J. Drummond, F. Grieser and T.W. Healy, *J. Chem. Soc. Faraday Trans. I*, **85**, 537 (1989)
16. C.J. Drummond, F. Grieser and T.W. Healy, *Faraday Discuss. Chem. Soc.*, **81**, 95 (1986)

17. G. Lamm and G.R. Pack, *J. Phys. Chem. B.*, **101**, 959 (1997).
18. C. E. Kung and J. K. Reed, *Biochemistry* **25**, 6114 (1986).
19. W. Retting and R. Lapouyade, In *Topics in Fluorescence Spectroscopy*; J. R. Lakowicz, Eds.; Plenum Press: New York, **4** 109(1994).
20. S. P. Webb, S. W. Yeh, L. A. Philips, M. A. Tolbert and J. H. Clark, *J. Am. Chem. Soc.*, **106**, 7286 (1984).
21. C. M. Harris and B. K. Selinger, *J. Phys. Chem.* **84** 1366 (1980).
22. C. M. Harris and B. K. Selinger, *J. Phys. Chem.* **84**, 891(1980).
23. K. M. Solntsev, Y. V. Ilichev, A. B. Demyashkevich and M. G. Kuzmin, *J. Photochem. Photobiol. A* **78**, 39 (1994).
24. Y. V. Ilichev, A. B. Demyashkevich and M. G. Kuzmin, *J. Phys. Chem.*, **95**, 3438 (1991).
25. D. Sukul, S. K. Pal, D. Mandal, S. Sen and K. Bhattacharya, *J. Phys. Chem. B*, **104**, 6128 (2000).
26. N. Pappayee and A. K. Mishra, *Photochem. Photobiol.*, **73**, 573 (2001).
27. S. Das, K. George Thomas, R. Ramanathan and M. V. George, *J. Phys. Chem.* **97**, 13625 (1993).
28. G. Zhao and K. Han, *J. Phys. Chem. A*, **111**, 2469 (2007).
29. G. Zhao and K. Han, *J. Phys. Chem. A*, **111**, 9218 (2007).
30. G. Zhao, J. Liu, L. Zhao and K. Han, *J. Phys. Chem. B*, **111**, 8940 (2007).
31. V. Samant, A. K. Singh, G. Ramakrishna, H. N. Ghosh, T. K. Ghanty and D. K. Palit, *J. Phys. Chem. A* **109**, 8693 (2005).
32. G. Zhao, *J. Chem. Phys.*, **127**, 024306 (2007).

33. J. Lee, G. W. Robinson, S. P. Webb, L. A. Philips and J. H. Clark, *J. Am. Chem. Soc.* **108**, 6538 (1986).
34. D. Mandal, S. K. Pal and K. Bhattacharyya, *J. Phys. Chem. A*, **102**, 9710 (1998).
35. S. Abou-al Einin, A. K. Zaitsev, N. K. Zaitsev and M. G. Kuzmin, *J. Photochem. Photobiol. A* **41**, 365 (1988).
36. Y. Y. Waguespack, S. Banerjee, P. Ramannair, G. C. Irvin, V. T. John and G. L. McPherson, *Langmuir* **16**, 3036 (2000).

## **Section-B**

In the treatment of the properties of very dilute polymer solutions it is convenient to represent the molecule as a statistical distribution of chain elements, or segments, about the centre of gravity. The average distribution of segments for a chain polymer molecule is approximately Gaussian [1], its breadth depends on the molecular chain length and on the thermodynamic interaction between polymer segments and solvent. According to hydrodynamics, the specific viscosity of a Newtonian liquid containing a small amount of dissolved material should depend in first approximation only upon the volume concentration and the shapes of the suspended particles. By suitable application of such hydrodynamical considerations to solutions of long chain molecules, it is possible in a rough fashion to derive the Staudinger-Kraemer equation, denoting proportionality between specific or intrinsic viscosity and molecular weight[2]. It is an experimental fact, however, that the proportionality constant,  $K_m$  is dependent not only upon the type of polymer concerned, but also upon the temperature and the nature of the solvent. A relationship between intermolecular and intramolecular agglomeration tendency is established. Solutions of polystyrene, rubber and cellulose acetate in the solvent-non solvent systems were investigated by Alfrey and co-workers[2]. They observed that the specific viscosity of a dilute solution of polystyrene or rubber is strongly dependent upon the nature of solvent, the specific viscosity is high in a good solvent and low in a poor solvent or a solvent-non solvent mixture. This has been interpreted as being due to changes in mean molecular shape. The specific viscosities of cellulose acetate solutions are not so sensitive to the nature of solvent. Besides this, the extrapolated specific viscosity at the limit of solubility is in the same range for several different solvent-non solvent systems. The effect of temperature upon intrinsic viscosity should depend strongly upon the nature of solvent. Alfrey and co-workers also noted that the effect of a temperature increase is to lower the specific viscosity of rubber or polystyrene solutions in a good solvent, but to increase the specific viscosity in a mixture of solvent and non-solvent. Unperturbed dimensions of flexible linear macromolecules can be obtained from

intrinsic viscosity-molecular weight data in any solvent, good or poor, if (as is almost always true) the hydrodynamic draining effect is negligible and if an estimate can be made of the viscosity expansion factor  $\alpha_n$  defined by[3]

$$[\eta] = K_\theta M^{1/2} \alpha_n^3 \quad (1)$$

In principle this can be done graphically from the relation alone if a reliable expression is available for the dependence of  $\alpha_n$  on  $M$ . In particular, it has been shown from theoretical considerations that the intrinsic viscosity should depend on the molecular weight  $M$ , temperature  $T$  and solvent type in accordance with the relationships,[4-6]

$$\alpha^5 - \alpha^5 = 2\psi C_M (1 - \theta/T) M^{1/2} \quad (2)$$

where  $K_\theta = k_1 T / \psi_1$

$$K_\theta = \phi_0 (r_o^2 / M)^{3/2} \quad (3)$$

$$\begin{aligned} C_M &= 27(d^{5/2} / \pi^{3/2} N) (v^{-2}/v_1) (M/r_o^2)^{3/2} \\ &= 1.4238 \times 10^{-24} (v^2/v_1) (\theta_o/K_\theta) \end{aligned} \quad (4)$$

Where  $\psi_1$  is entropy parameter,  $k_1$  is the enthalpy parameter,  $\theta$  is the temperature and  $K_\theta$  is the unperturbed dimension of the polymer,  $\phi_0$  is the Flory's universal constant. Here,  $v$  is the partial specific volume of the polymer and  $v_1$  is the molar volume of the solvent.

Intrinsic viscosities of polyisobutylene fractions ( $M = 1.8 \times 10^5$  to  $1.88 \times 10^6$ ) and polystyrene fractions ( $M = 70 \times 10^4$  to  $1.27 \times 10^7$ ) have been determined in various pure solvents and in several solvent mixtures at several temperatures by Fox and Flory[7-8]. They observed that the parameter  $K_\theta$  in the equation (54), is same in different solvents but decreases somewhat with temperature ( $1.08 \times 10^{-3}$  at  $24^\circ$  to  $0.91 \times 10^{-3}$  at  $105^\circ$  for polyisobutylene and  $8.0 \times 10^{-4}$  at  $34^\circ$  to  $7.3 \times 10^{-4}$  at  $70^\circ$  for polystyrene). The root-mean square end-to-end  $(r_o^2)^{1/2}$ , unperturbed by

intramolecular interactions (other than hindrance to free rotation) for a polyisobutylene molecule and polystyrene molecule with  $M=10^6$  has been calculated to be  $795\text{\AA}$  and  $730\text{\AA}$  at  $25^\circ\text{C}$  respectively. The solution properties of poly (methyl acrylate) in various solvents by light scattering, osmometry, and viscosity techniques have been investigated by many co workers[9-21]. Many empirical and semi empirical methods for the estimation of  $K_\theta$  from viscometric measurements in good solvents have recently been proposed[22-35].

The viscosity behaviour of poly (methyl methacrylate) in four solvents was studied within the temperature range of  $25^\circ$  to  $60^\circ\text{C}$  and the thermodynamic parameters were evaluated and discussed using Fox-Flory[6], Burchard Stockmayer-Fixman[36,37], Kurata-Stockmayer[38,39] and Berry[40] equations by Lenka and Co-workers[41]. On the other hand, for evaluation of  $K_\theta$  from  $[\eta]$  at  $T > \theta$  (in good solvent), a number of equations relating  $[\eta]$  and  $M$  through  $K_\theta$  (after eliminating linear expansion factor ( $\alpha$ ), hydrodynamic expansion factor ( $\alpha_n$ ), lattice co-ordination number ( $z$ ) etc.) have been suggested. These equations are shown below (where symbols have their usual meanings). Fox and Flory equation[6]

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + K_\theta^{5/3}C_T (M/[\eta]) \quad (5)$$

Kurata-Stockmayer (K-S) equation[38,39]

$$[\eta]^{2/3}/M^{1/3} = K_\theta^{2/3} + 0.363 \phi B[g(a_n)M^{2/3} / [\eta]^{1/3}] \quad (6)$$

Burchard-Stockmayer and Fixman (B.S.F) equation[36,39]

$$[\eta] / M^{1/2} = K_\theta + 0.51\phi BM^{1/2} \quad (7)$$

Berry equation[40]

$$([\eta] / M^{1/2})^{1/2} = K_\theta^{1/2} + 0.42 K_\theta^{3/2} B(r_0^2/M)^{3/2} (M / [\eta]) \quad (8)$$

According to these equations, the value of  $K_\theta$  may be obtained from the intercepts on the ordinates of the lots of the quantity on the left hand side versus a

function of  $M$  and  $[\eta]$  on the right hand side . The unperturbed dimensions for polymethylacrylate, polyethylacrylate, polybutylacrylate, polyacrylonitrile, and polyvinyl pyrrolidine have been calculated by Lenka and co-workers[42] using an expression relating to the cross- over point concentration,  $C_x$ , of the polymer in a number of solvents with the unperturbed dimension of polymer molecule ( $r_o^{1/2}$ ).

$$([\eta] / M^{1/2})^{5/3} = K_\theta^{5/3} + 0.627 \phi_o^{5/3} (\langle R^2 \rangle / M) B M^{1/2} \quad (9)$$

And Bohdanecky derived the following equation[51]

$$[\eta] / M^{1/2} = 0.80 K_\theta + 0.65 K_\theta K^{0.7} M^{0.35} \quad (10)$$

The unperturbed dimensions of polystyrene and poly (2-vinylpyridine) have been measured in solvent-precipitant mixtures of various compositions using the Stockmayer-Fixman representation by Dondos and Benoit[44]. They obtained a linear relationship between  $K_\theta$  and  $\Delta G^E$  (the excess free enthalpy of mixing of the solvents) if, instead of using the bulk composition of the mixture one introduces its 'local' composition. This composition is calculated from the values of the preferential adsorption coefficient measured by light scattering.

In a resin-solvent system, the change in temperature initiates conformational transition in polymer chains[3] and the process of aggregation on precipitation is caused ;by such transitions[45] Raju and Yaseen reported that the continuous decrease in limiting viscosity number of Nylon-6 in m-cresol at temperatures ranging from 20° to 75°C was due to the contraction of the dimensions of the polymer coil[46]. Quoting the view of other workers they explained that a partial helix-coil type polymer chain transition occurs in polyamide-6 in solution and results in higher value of limiting viscosity number of nylon-6 in m-cresol at lower temperatures which in turn favours the dissolution [47]. They also observed that limiting viscosity number of Nylon-6 in phenol increase with temperature and the system attained a state of optimum dissolution at 55°C and further increase in temperature and had adverse effect. Chatfield reports that solvent power of an alcohol-ether mixture for

nitrocellulose increases with lowering of temperature and at  $-50^{\circ}\text{C}$ , methyl alcohol alone becomes a solvent for cellulose ethers[48]. Recently, Savas and Zuhai have determined the unperturbed dimensions of anionically polymerized poly (*p*-ter-butylstyrene) at various temperatures and found the  $\theta$  -temperature of the polymer of the order of  $31^{\circ}\text{C}$  and  $32.7^{\circ}\text{C}$  in 1-nitropropane and 2-octanol respectively[49]. Several other workers reported the conformational transition of polymers in solution with change in temperature.[31,50]. Coil dimensions of poly (methylacrylate) in the cosolvent medium of  $\text{CCl}_4$  and MeOH have been investigated by Maitra and Nandi[52]. They observed that the intrinsic viscosity exhibited a maximum for all fractions of polymer at a composition,  $\phi_{\text{CH}_3\text{OH}}$  (volume fraction of methanol) = 0.33 and also Huggins constant showed a minimum at the same composition. The unperturbed dimension ( $K_{\theta}$ ) exhibited a maximum and molecular extension parameter  $\alpha_n$ , showed a minimum at  $\phi_{\text{CH}_3\text{OH}} = 0.33$ . The experimental data for the solution properties of poly (N,N- dimethylacrylamide) and poly (N-isopropylacrylamide) show that the hydrodynamic and configurational characteristics of these two N-substituted polyacrylamide, in methanol and water are different, showing a peculiar behaviour in water, which cannot be easily interpreted in terms of random coil molecules[53,54]. Also, the unperturbed dimensions estimated from data in good solvents are found to depend more on the lateral substituent structure than on its dimensions. Chintore and co-workers found that behaviour of poly (N-methylacrylamide) molecules in aqueous solution was quite abnormal, as indicated by the values of the second virial coefficients, lower than those measured in methanol[53,54]. Therefore, the hypothesis was made that the solvation of N-substituted poly acrylamides by water would occur with large dipole interaction and/or hydrogen bonding with the structural units of the polymers in such a way as to give a large chain expansion with low chain flexibility, so that the polymer molecules could no more be treated as random coils in aqueous solutions. It has been pointed out that polyacrylamide, in which the lack of N-substituents increases the chances of intramolecular interactions, has the highest unperturbed

dimensions[55]. The aqueous solutions of polyacrylamides are suspected to contain fibrous aggregates of very high molecular weight. These aggregates were observed by electronic microscopy[56] and the disaggregation kinetics studied by viscometry[57,58]. This phenomenon is generally attributed to intermolecular hydrogen bonds and is evidenced by an important decrease of viscosity with time. Boyadjian and co-workers have noticed differences of measured molecular weight by light scattering, according to the nature of solvent and have concluded the presence of aggregates broken up by the effect of salts in pure water but not in formamide[59]. However, even for non-hydrolysed polyacrylamide, there is a lack of reliable data in the literature concerning the chain conformation in salt water solutions and its relation to intrinsic viscosity, particularly in the range of molecular weights of interest[60,61]. However, Francois and Sarazin and co-workers were successful in studying molecular weight dependence of radius of gyration, viscosity sedimentation and diffusion on a set of fractions in the same range of molecular weight[35]. It has been shown recently that, the unperturbed dimensions of polyacrylamide could be determined by light scattering measurements in methanol-water system[61]. These authors concluded that the high value of the exponent (0.64) of the molecular weight dependence of the radius of gyration was not related to a great expansion of the macro molecular coil, and the determination of the unperturbed dimensions by extrapolation of viscosity measurements in good solvents at  $M \rightarrow 0$  should be possible and works of Okada and Yamaguchi provide such determinations[62,63]. Fundamental parameters of poly (2-acrylamido-2-methyl propane sulphonamide) which is soluble in water and formamide are obtained by light scattering, and viscometry in these good solvents by Gooda and Huglin[64] and has been analysed by extrapolation procedures to yield the unperturbed dimensions  $(r_o^2 / M_w)^{1/2}$ , steric factor ( $\sigma$ ) and characteristic ratio ( $C_\infty$ ). There was a good accord between the values of  $(\langle r^2 \rangle_o / M_w)^{1/2}$ ,  $\sigma$  and  $C_\infty$  thereby obtained directly and those derived indirectly, the mean values being  $8.73 \times 10^{-9} \text{ cmg}^{1/2} \text{ mol}^{1/2}$ , 4.07 and 32 respectively. Bohdanecky and Petrus and co-workers investigated the solution of 9

polyacrylamide fractions (molecular weight 3300-800,000) in water at 25°C and in a mixed  $\theta$  solvent (3.2 volume, H<sub>2</sub>O-MeOH) at 20°C by light scattering, sedimentation and viscometry[65]. Measurements in water gave the configuration character ratio  $C_{\infty} = 8.5$

The fundamental parameters of the polyacrylamide obtained previously by viscometry in good solvent i.e. water and in a  $\theta$  solvents have been analysed by viscosity molecular weight relationship procedures suggested by several workers (Scholtan[60], Newman[66] and Misra[67]). High value of excluded volume exponent, as was observed in some cases, once thought to be the result of great expansion of polyacrylamide in aqueous solution as mentioned above[35,61]. This arose doubts on the applicability of the method of extrapolation of the viscosity data in determining unperturbed dimension of the polymer in water. Further study, however, confirmed that the high value of the exponent of molecular weight dependence of the radius of gyration was not due to a great expansion of the macromolecular coil in water and it is now believed that determination of the unperturbed dimension by extrapolating viscosity data in good solvents is possible[61]. Although some studies on the solution viscosity properties of acrylamide in water are available in the literature, similar studies in other solvents or cosolvent systems are surprisingly little[61-65] in a binary liquid mixture. It is the interaction between the liquids that governs the solubility of a polymer in the mixture. Expansion of coil are also occurred due to two main reasons (i) variation of molecular extension factor ( $\alpha_n$ ) and (ii) change of the unperturbed dimension of the polymer due to interactions of two component liquids[68,69]. In the present chapter, the results of our investigation on unperturbed dimension, interaction parameter and related aspects of unhydrolyzed polyacrylamide in water –DMSO mixtures have been described. The intrinsic viscosities  $[\eta]$  of the polymer have been measured for different molecular weight fractions of the polymer and also in different compositions (water/DMSO) of the cosolvent mixture. From the  $[\eta] - M$  relation, the unperturbed dimension ( $K_{\theta}$ ) and molecular extension factor ( $\alpha_n$ ) have been measured. The

Huggins constant value in each case was also determined in order to study the influence of cosolvent system on the aggregation of polymer[52]. While DMSO is a poor solvent for PAM, water-DMSO mixture acts as a cosolvent in all proportions. In the previous chapters, we have reported the technique by which the molecular weight of the polyacrylamide in aqueous solution may be controlled by trapping the initiator component in the interlayer space of montmorillonite. This method has been adopted selectively to prepare polymers of varying molecular weights for the solution property studies as presented in this chapter.

## Reference

1. P. Devye and I. M. Krieger (unpublished) have shown that the average distribution of each segment about the centre of gravity is exactly Gaussian for random chain unperturbed by intramolecular interactions
2. T. Lafrey, A Bartovics and H. Mark, *J. Am. Chem. Soc.*, **64**, 1557 (1942)
3. P.J.Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, N.Y. , Chap. XIV, (1953).
4. P.J. Flory, *J.Chem.Phys.*, **17**303 (1949).
5. T.G.Fox, Jr., and P.J.Flory, *J. Phys. Colloid Chem* **53** 197 (1947).
6. P.J.Flory and T.G.Fox, Jr., *J. Am. Chem. Soc***73** , 1904 (1951)
7. T.G.Fox, Jr.<sup>2</sup> and P.J.Flory, *J.Am.Chem.Soc.*, **73**, 1909 (1951)
8. P.J.Flory, Jr.<sup>2</sup>, and P.J.Flory, *J.Am.Chem.Soc.*, **73**, **1915** (1951)
9. J.M.G. Cowie, *Polymer*, **7**, 487 (1966)
10. T. Brandrup and E.H.Immergut (eds), Polymer Handbook, Wiley interscience, New York, p. 47 (1966).
11. G.V. Schulz and R.Kriste, *Z.Phys, Chem(F. furt)*, **30**, 171 (1961)
12. S.N.Chinal and C.W.Bondurant, Jr. *J.Polymer. Sci.*, **22**, 555 (1956)
13. H. Lutje and G. Meyerhoff, , *Makromol. Chem.*, **68**, 180 (1963)
14. T.G.Fox, *Polymer*, **3**, 111 (1962).
15. M. Bohdanecky, *Collect. Czech. Chem. Commun.*, **30**, 1576 (1965)
16. H. Inagaki and S. Kawai, *Makromol. Chem.*, **79**, 42 (1964)
17. M. Bohdanecky, *Collec. Czech. Chem. Commun.*, **34**, 407(1969)
18. V.V.Varadaiah and V.S.R. Rao, *J. Sci, Ind. Res.*, **20B**, 280 (1961)
19. S.N.Chinal, J.D.Matlack, A.L. Resnick, and R.S.Samuels, *J. Polym.; Sci.*,**17**, 391 (1955).
20. W.R.Moore and R.J.Fort., *J. Polym.; Sci.*,**A1**, 929 (1963)..
21. S. Gundiah, R.B.Mohite and S.L.Kapur, *Makromol. Chem.*, **123**, 151(1969)
22. S.Arichi, *Bull. Chem. Soc. Jpn.*, **39**, 439 (1966).
23. U.Bianchi and A.Peterlin, *J.Polym.Sci.*, A-2, **6**, 1759 (1968)
24. D.W.Van Krevelen and P.J.Hoftzyer, *J. Appl. Polym. Sci.*, **11**, 1409 (1967).

25. D.W.Van Krevelen and P.J.Hoftyzer, *J. Appl. Polym. Sci.*, **10**, 1331 (1968).
26. K.Kanide, *Kobunshi Kagaku*, **25**, 781 (1968); *Chem. Abst.*, **70**, 88348Y (1969).
27. V. S. R., Rao, *J.Polym.Sci.*, **62**, S157 (1962).
28. H.L.Bhatnagar, A.B. Biswas and M.K.Gharpurey, *J. Chem. Phys.*, **23**, 88 (1958)
29. H. Yamakawa, *J.Chem. Phys.*, **34**, 1360 (1961).
30. T. Sakai., *J.Polym.Sci.*, A-2, **6**, 1535 (1968)
31. P.Vasudevan and Santappa, *Makromol. Chem.*, **137**, 261 (1970)
32. S.Gundiah, R.B.Mohite, and S.L.Kapur, *Markromol. Chem.*, **123**, 151 (1969)
33. P. Vasudevan and M. Sentappa, Unpublished Result.
34. P.C.Deb and S.R.Chatterjee, *Makromol. Chem.*, **120**, 49(1968).
35. P.C.Deb and S.R.Chatterjee, *J. Indian Chem. Soc.*, **46**, 468 (1969)
36. W.Burchard, *Makromol Chem.*, **50**, 20 (1960)
37. W. H. Stockmayer and M. Fixman, *J.Polym. Sci.*, **C1**, 137 (1963)
38. M.Kurata, W.H.Stockmayer , *Fortschr, Hochpolym. Forsch*, **3**, 196(1963).
39. H. Kurata, W.H.Stockmayer, and A. Roig, *J. Chem. Phys.*, **33**, 151 (1960)
40. G.C.Berry, *J.Chem. Phys.* **46**, 1338 (1967)
41. S.Lenka, P.Nayak and M.Dash, *J. Macromol. Sci. Chem.*, **A 20 (4)** 467 (1983)
42. S.Lenka, P.Nayak and M.Dash, *J. Macromol. Sci. Chem.*, **A 19 (3)** 321 (1983)
43. G. Tanaka, *Macromolecules*, **15**, 1028 (1982)
44. A. Dondas and H. Benoit, *Macromolecules*, **6 (2)**, 242 (1973)
45. I.W. Vanden Berg, G. Vande Ridder, and C.A. Smoldevs, *Eur, Poly. J.*, **17**, 935 (1981)
46. G. Tanaka, K.V.S.N. Raju and M. Yaseen, *J. Appl. Polym. Sci.*, **43**,1533 (1991)
47. H. Haneczek, E. Turska, *Polymer*, **24**, 1590 (1983)

48. H.W. Chatfield, "Varnish Constituents", Leonard Hill Ltd., London, 412, 419 (1953)
49. K.Savas and K. Zuhai, *Polymer Communications*, **31 (1)**, 35 (1990)
50. I. Nishio, S.T. Sun, G. Swislow and T. Tanaka, *Nature*, **281**, 208 (1979)
51. M. Bohdanecky, *J. Polym. Sci. (B)*, **3**, 201 (1965)
52. B. Maitra and A.K. Nandi, *Polymer*, **34 (6)**, 1260, 1993
53. O. Chintore, M. Guaita and L. Trossarelli, *Makromol. Chem.*, **180**, 2019 (1979)
54. O. Chintore, M. Guaita and L. Trossarelli, *Makromol. Chem.*, **180**, 969 (1979)
55. M. Kurata, Y. Tsunashima, M. Iwama and K. Kamada, in : "Polymer Handbook", edited by J. Brandrup and E. H. Immergut, 2<sup>nd</sup> edition, Wiley-Interscience, NewYork, IV- 36, (1975)
56. J. W. Herr and W. G. Routson, paper number SPE 5098, 49<sup>th</sup> Ann. Fall. Meeting (1974)
57. W.P. Shyluk and F.S. Stow, Jr, *J. Appl. Polym. Sci.*, **13**, 1023 (1969)
58. N. Narkis and M. Rebhun, *Polymer*, **6**, 507 (1966)
59. R. Boyadjian, G. Seytre, P. Berticat and G. Vallet, *Eur. Polym. J.*, **12**, 401 (1975)
60. W. Scholtan, *Makromol. Chem.*, **14**, 169(1954)
61. T. Schwartz, J. Sabbadin and J. Francois, *Polymer*, **22**, 609 (1954)
62. C. Okada, K. Kamada, T. Yoshihara, J. Hasoda and A. Fumuro, 'Reports on Progress on Polymer Phymer Physics in Japan', XX5, (1977)
63. N. Yamaguchi, N. Onda and Y. Hirai, 'Reports on Progress on Polymer Phymer Physics in Japan', XX1, 63 (1978)
64. S. R. Gooda and M. B. Huglin, *Polymer*, **34 (9)**, 1913 (1993)
65. M. Bohdanecky, V. Petrus and B. Sadlacek, *Makromol. Chem.*, **184 (10)**, 2061 (1983)
66. S. Newman, W. R. Krigbaum, C. Laugier and P.J. Flory, *J. Polym. Sci.*, **14**, 451 (1954)
67. G. S. Misra and S. H. Bhattacharya, *Eur. Polym. J.*, **15**, 125 (1979)