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Tunable Thermo Reversible Viscoelastic Gels From Self Assembly of Surfactants

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Abstract: The phase behaviour of Cetyl Trimethyl Ammonium Bromide (CTAB) with n-octanol in presence of potassium bromide (KBr) is studied by viscosity, Differential Scanning Calorimetry (DSC), rheology and polarising microscopy. The addition of long chain aliphatic alcohols is found to promote the transformation of spherical micelles into supramolecular structures like wormy micelles and vesicle phases. A partial phase diagram based on DSC and polarizing microscopy at different temperature signals a characteristic transition temperature at which the gel-to-vesicle phase transition takes place with changes in concentration of octanol. The rheological behaviour of the viscoelastic system was described by the Maxwell model of a viscoelastic fluid, typical of systems of worm-like micelles.

Key words: Tunable gels, worm-like micelles, vesicles

INTRODUCTION

Highly viscoelastic micellar systems and vesicles have engrossed increasing attention due to their potential application in encapsulating active molecules and therefore apt for pharmaceuticals, cosmetic and oilfield industry (Moitzi *et al.*, 2005; Partal *et al.*, 2001; Schallchli and Auvray, 2002). The short chain alcohols form very simple phase diagrams with the surfactant CTAB, whereas medium chain alcohols, though less soluble in water, form different liquid crystal phases (Cortes *et al.*, 1999; Moya and Schulz, 1999). The rheological properties of concentrated aqueous solution of Cetyl Trimethyl Ammonium Bromide (CTAB) was studied by Coppola *et al.* (2004) found that thread-like micelles appeared in aqueous CTAB solution (above 11 wt.%) and forms an isotropic phase with in the concentration (0-25 wt.%) at 27°C. This rapid micelle growth is essentially due to the screening of the electrostatic interaction with increasing surfactant composition. As a consequence a hexagonal liquid crystalline phase is formed above 25% which consists of very long cylinders packed in a two dimensional hexagonal array (Coppola *et al.*, 2004). The binary system, Na-oleate and water, forms a visually transparent single phase solution with no birefringence. On gradual addition of increasing amount of co-surfactants into 200 mM Na-oleate, the system undergoes a phase transition. The solutions of Na-oleate with low concentration of co-surfactants form micellar solution with somewhat spherical or elongated micelles (Edwards *et al.*, 1995). The increasing co-surfactant concentration induces the phase transitions i.e., isotropic to vesicle phase (turbid). Gradzielski *et al.* (1999) have also been experienced the similar observation for the system of aqueous Na-oleate with octanol. For instance the addition of salts like sodium salicylate or potassium bromide results in a transformation into rod-like objects. The principal reason for this structural change is binding of the counter ion which

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suppresses the micellar charge and decrease the surface area per surfactant molecule by reducing the electrostatic repulsion between the head groups (Mata *et al.*, 2006; Nan *et al.*, 2005). This results in the growth of micelles from spherical to an elongated rod-like structure. In the present research, we simultaneously incorporated a salt, KBr and long chain alcohol, n-octanol as cosurfactant with aqueous CTAB micellar system and analysed the phase behaviour by varying the salt and co-surfactant concentration using viscosity, rheology, differential scanning calorimetry and polarising microscopy.

MATERIALS AND METHODS

Cetyl trimethyl ammonium bromide (BDH, England), potassium bromide (Ellis Dugal, India) and octanol (Merck, India) were used as supplied. The samples were prepared in Millipore ultra pure water and then kept in a hot bath at a temperature of 45°C with shaking for about 5 h for homogeneity. It is then kept over night without any disturbance at room temperature in order to avoid bubbles. The viscosity measurements were made at National Institute of Technology Calicut during June 2007, using a programmable Brookfield DV-II+ cone and plate viscometer (Brookfield Engineering Laboratories, Inc., USA) thermo stated in the temperature range 25-40±0.1°C.

The rheological characterization of the samples were carried out at Central Tuber Crops Research Institute, Thiruvananthapuram during August 2007, using a controlled stress rheometer (Anton Paar Physica MCR-51) with a cone and plate sensor (40 mm diameter, 3.988° angle). The sample thickness in the middle of the sensor was 0.050 mm. Experiment was performed at 30±1°C. The viscosity profile of the sample were noted by varying the shear rate from 0.3 to 500 sec⁻¹. Frequency sweep measurements were carried out by varying the angular frequency from 0.06 to 100 rad sec⁻¹. The experiments were carried out at 1% strain with in the linear viscoelastic range.

Textures of vesicle phase were observed by Leica DMR XP polarizing microscope at National Institute for Interdisciplinary Science and Technology, Thiruvananthapuram during December 2007. The samples were taken in a sealed flat capillary of inner width 150 µm. DSC traces were recorded in a high sensitivity calorimeter (TA Instruments, DSC Q-20), temperature range between -80 to 100°C with a heating rate of 2°C per minute.

RESULTS AND DISCUSSION

The viscosity behaviour of 0.1 M CTAB +xM KBr +n-octanol (x = 0.00 to 0.15 M) as a function of [octanol] at a temperature of 30°C is shown in Fig. 1a and the same solution with 0.10 M KBr at different temperatures (25-40°C) is shown in Fig. 1b. In the presence of salt, KBr imparts high viscosity to 0.1 CTAB solutions. It is intriguing to note that the incorporation of octanol results in a

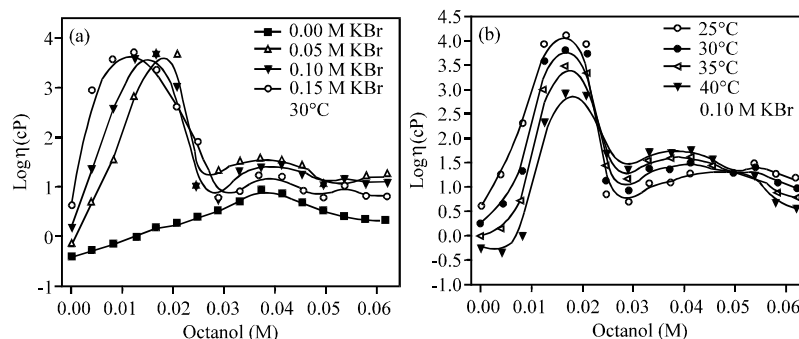


Fig. 1: (a) The viscosity behaviour of 0.1M CTAB +xM KBr+n-octanol as a function of [octanol] at 30°C, (b) Viscosities of solution with 0.10 M KBr at temperatures (25-40°C)

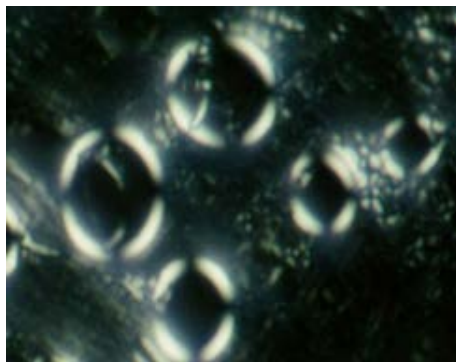


Fig. 2: Texture of vesicle phase taken by Leica DMR XP polarizing microscope

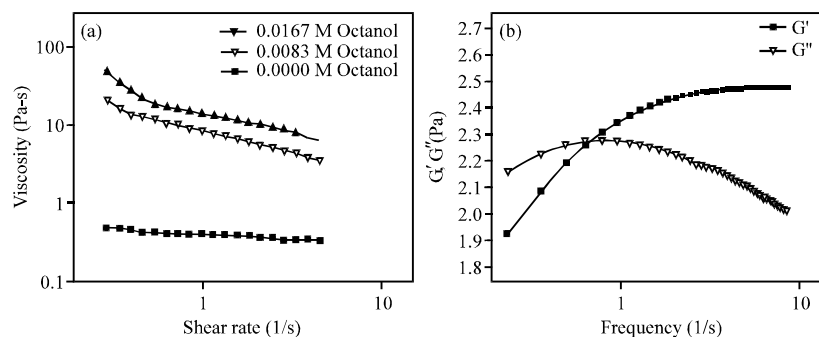


Fig. 3: (a) The steady-shear rheological response of CTAB + KBr + n-octanol micellar system at different concentrations of octanol (b) the dynamic rheological response of the same micellar system with 0.16 M octanol at 30°C

thousand fold increase in viscosity. The resulting samples are clear, viscoelastic solutions and showed an ability to trap bubbles for long periods of the time. These samples also exhibit flow birefringence and these are essential characteristics of worm-like micelles (Hoffmann, 1994).

With increase in octanol content micelles grow in solution followed by a rapid increase in viscosity resulting in the peak in Fig. 1a, b, here the entanglement of the micelles takes place and leading to the formation of worm-like structures. The further increase in octanol content after the peak results in a viscosity drop and the solution became turbid and optically birefringent. At high octanol concentration the worm-like micelles change in to vesicle phase (Edwards *et al.*, 1995) and the texture is shown in Fig. 2. From Fig. 1a, it is observed that with increase in [KBr] the first maxima was shifted to lower octanol content. Addition of salt reduces the inter micellar repulsion and induces the growth of micellar aggregates (Nan *et al.*, 2005). But the absolute viscosity with different (KBr) at the maxima region of these systems are almost the same. Therefore we have chosen the salt concentration 0.10 M for a detailed rheological investigation.

The rheological response of the samples at various concentrations is shown in Fig. 3a. At very low (octanol) the sample exhibit almost Newtonian behaviour, which is consistent with the presence of discrete spherical micelles. At higher concentrations, the samples switches to a shear-thinning response i.e., a drop in viscosity with shear rate and it is also noted that the zero shear viscosity is at a higher magnitude at (octanol) = 0.016 M. These rheological changes points to the structural transformation from sphere to worm-like micelles. A small spherical aggregate with Newtonian character is supposed to exist below 0.004 M octanol concentration and upto 0.008 M the viscoelastic

response indicates the sphere-to-cylinder transition. A dramatic increase in after 0.008 M octanol leads to a gel phase and subsequently to the shear-thinning behaviour (0.012-0.020 M octanol). The decreases of columbic repulsive force due to the presence of KBr and increase in hydrophobic interaction by octanol are favorable conditions for micellar growth. To characterize the viscoelasticity of CTAB/octanol worms, we tried to tune the dynamic rheology. Figure 3b shows the elastic modulus G' and the viscosity modulus G'' as a function of frequency of 0.16 M sample at 30°C. The sample showed a viscoelastic response typical of worm-like micelles, i.e., at high frequencies it behaves elastically ($G' > G''$), while at low frequencies it switches to a viscous behaviour ($G'' > G'$). The rheological behaviour of this system can be characterized by generalized Maxwell model. The dominant relaxation time, t_r of these viscoelastic samples can be estimated as $1/\omega$, where, ω is the frequency at which G' and G'' cross.

For a Maxwell fluid the variation of G' and G'' can be given as:

$$G' = \frac{G\omega^2 t^2}{1 + (\omega t)^2} \quad (1)$$

$$G'' = \frac{G\omega t}{1 + (\omega t)^2} \quad (2)$$

where, G is the shear modulus (Acharya and Kunieda, 2006). We noted that the Maxwell model fits the data reasonably well, especially at lower frequencies, while there is a slight discrepancy at very high frequencies. Maxwell fluid like behaviour is an indication of the presence of worm-like micelles in the solution and Eq. 1 predict a monotonous increase in G' and G'' . With increasing frequency, G' attains a plateau value G . This Maxwellian behaviour indicates a single exponential decay of the stress relaxation function. However, rheological behaviour of worm like micelles deviates from this at higher frequencies (Coppola *et al.*, 2004; Acharya *et al.*, 2004). The complex viscosity η^* is related to the elastic and viscosity moduli by the relation:

$$|\eta^*| = \frac{(G' + G'')^{\frac{1}{2}}}{\omega} \quad (3)$$

and is also related to the zero-shear viscosity η_0 , as:

$$|\eta^*| = \frac{\eta_0}{(1 + (\omega^2 t^2))^{\frac{1}{2}}} \quad (4)$$

The Eq. 4 allows us to estimate η_0 by extrapolating viscosity to zero-shear frequency; η_0 may also be calculated using the relation.

$$\eta_0 = G.t \quad (5)$$

Figure 4 shows the distinct DSC tracing of vesicular sample containing 0.02 M octanol. The first two peaks at lower temperature signals the freezing point of octanol and water, respectively. Peak at higher temperature attribute to phase transformation from vesicle to highly viscous isotropic phase. Above the transition temperature, the 0.020-0.062 M samples showed moderate zero shear viscosity indicative of the formation of higher order aggregates. More studies on these supramolecular structures

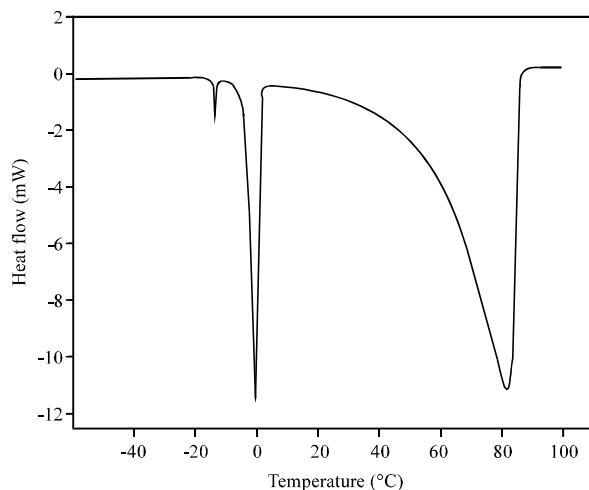


Fig. 4: DSC curve of vesicle with octanol concentration 0.04 M, with heating rate 2°C/min

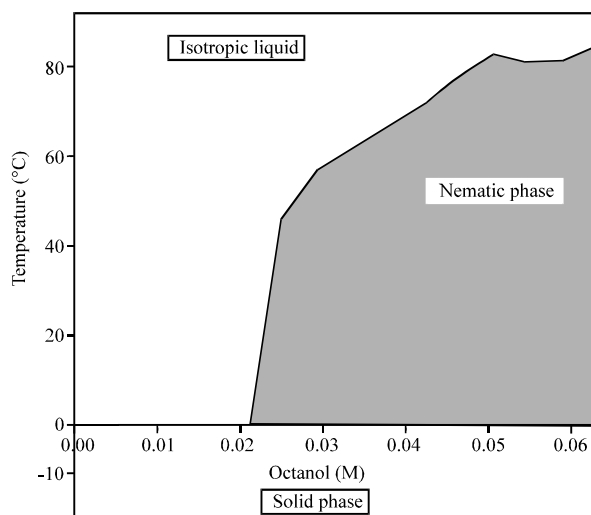


Fig. 5: Partial phase diagram of 0.1M CTAB + 0.1 M KBr + n-octanol micellar system

like cryo-TEM is under progress. The polarizing microscopic studies at different temperature, illustrates a characteristic transition temperature signaling the vesicle-to-gel phase transition. A partial phase diagram constructed on the bases of DSC and polarizing microscopic studies is shown in Fig. 5.

CONCLUSION

The rheology and phase behaviour of CTAB/KBr/n-octanol-water systems were studied at different temperatures. Micellar solutions are formed at low cosurfactant (octanol) concentration. With successive addition of cosurfactant sphere-to-wormlike transition occurs and the system switches to a viscoelastic solution above certain concentration of octanol as indicated by the sharp increase in viscosity, subsequent addition leading to vesicle phase. The rheological behaviour of the viscoelastic

system was described by the Maxwell model of a viscoelastic fluid, typical of systems consist of wormlike micelles. Their formation can be explained as the continuous lowering of the mean spontaneous curvature on micellar interfaces, when co-surfactants are mixed with single chain surfactants. The reason for this change in curvature is due to the small area which a co-surfactant occupies at a micellar interface. As a consequence of this change in curvature, the system undergoes several phase transitions with increasing the concentration of co-surfactants (Kim *et al.*, 1997; Bergmeier *et al.*, 1998; Gradzielski *et al.*, 1999, 1997). They try to come as close as possible to the spontaneous mean curvature without spending much bending energy by adjusting the two principal curvatures on the micellar aggregates.

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