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ORIGINAL ARTICLE

Micellar Growth in Cetylpyridinium Chloride/Alcohol System: Role of Long Chain Alcohol, Electrolyte and Surfactant Head Group

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Abstract The microstructural transition of aqueous 0.1 M cetylpyridinium chloride (CPC) in the combined presence of salt KBr and long chain alcohol (C_9OH-$C_{12}OH$) has been studied as a function of alcohol concentration, electrolyte concentration and temperature. The viscosity of the CPC/KBr micellar system showed a peaked behavior with alcohol concentration (C_0), due to alcohol induced structural transition, which was confirmed by dynamic light scattering (DLS) and rheological analysis. Besides C_0, the chain length of alcohol (n) was found to show a remarkable effect on the micellization behavior of CPC/KBr system. It was observed that the ability of alcohol to induce micelle growth diminishes with n, which was well supported by viscosity, rheology and DLS measurements. To examine the effect of the electrolyte on the micellar growth, the salt concentration was varied from 0.05 to 0.15 M and it was observed that with increase in [KBr], the peak position shifts towards lower C_0. The effect of temperature on the micellar system showed interesting phase behavior for CPC/KBr/Decanol. The system exhibited a closed solubility loop with an upper critical solution temperature (UCST) > the lower critical solution temperature (LCST), reminiscence of nicotine-water system. The role of surfactant head group on the structural evolution was revealed by comparing the present results with our previous report for similar micellar system, CTAB/KBr/long chain alcohol.

Keywords CPC · Long chain alcohol · UCST and LCST

Introduction

By virtue of their amphiphilic nature, surfactant molecules can self-assemble into a great variety of microstructures in solution. At low surfactant concentration, the microstructure is primarily spherical or short rods [1–3]. However, the shape and size of the micelles can be tuned by various factors like concentration and nature of surfactant, presence of suitable organic and inorganic additives, temperature, pH etc. [4–9]. This distinctive ability of micelles to alter their morphology, gained a special place in the field of smart materials. The micelle microstructure is correlated to the packing parameter, R_p, $R_p = v/la_o$ (v volume, l length of alkyl tail, a_o head group area) [10]. Both internal (organic and inorganic salts, alcohols, amines, hydrocarbons, etc.) and external stimuli (temperature, concentration, pH, etc.) alters R_p (by changing the ratio of volume and cross sectional area) and facilitates micellar growth [11]. Thus by the proper choice of additives, the micellar morphology can be tailored to obtain various microstructures like wormlike micelles, vesicles, liquid crystals etc. These aggregates offer great potential applications in numerous technological and industrial fields, for drag reduction, enhanced oil recovery, drug delivery, as a templating agent etc. [12–15]. Among the different additives studied, alcohol holds a special place, as it is one of the common co-

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surfactants added to surfactant mixtures to obtain microemulsions [16]. It has previously been reported that depending upon the chain length, alcohols can locate at various solubilization sites (micellar surface, palisade layer and/or core) and thus can modify the micellar morphology [17–20]. Furthermore, the properties of the surfactant–water–alcohol system can be enhanced by the presence of salts [20, 21]. This type of synergism (cooperative effect) is observed in surfactant systems in the congruent presence of salt and alcohol [22–24]. However, not many morphological transition studies are available with a simultaneous presence of salts and higher chain length alcohols with ionic surfactants [21, 22].

The phase behavior of surfactant mixtures is of great interest, both from the scientific and industrial perspective. Flory et al. [25, 26] has predicted the occurrence of phase separations in polymer solutions, either on cooling or on heating, called the upper critical solution temperature (UCST) and lower critical solution temperature (LCST) respectively. In surfactant chemistry, phase separation on heating (LCST) is quite commonly encountered in non-ionic surfactant systems, which is attributed to temperature assisted micellar growth [27, 28] whereas some zwitterionic surfactants displays UCST i.e., phase separation on cooling [29]. However there are only a few reports on the coexistence of UCST and LCST in the same system like PEO and nicotine-water system [30, 31]. The miscibility curve is closed in these systems with UCST lying above the LCST.

Cetylpyridinium chloride (CPC) is a well-known cationic surfactant with a bulky pyridinium head group and a critical micelle concentration (CMC) $\sim 1.2 \times 10^{-4}$ M in water. CPC generally self-assembles to form spherical micelles [32], but can be transformed into different morphologies in the presence of additives such as anionic hydrotropes, alcohols, amines, electrolyte, non-ionic surfactants [24, 33, 34] etc. Several authors have reported the effect of short and medium chain alcohols on the micellization behavior of CPC. Appel and co-workers [35, 36] reported rich polymorphism in a CPC-hexanol-brine system and demonstrated the predominant influence of hexanol on the phase behavior of the CPC-brine system. Chung et al. [37] studied the effect of short chain alcohol (methanol to propanol) on the micellization behavior of CPC and noticed an increase in the CMC for CPC/methanol and CPC/ethanol systems. However, a substantial decrease was noticed for CPC/propanol system. The authors interpreted it on the basis of solubilization of propanol (C_3OH) into the micelles and suggested that alcohol with chain length ≥ 3 have the tendency to get solubilized in the micelles and can alter properties like CMC, morphology etc. Later Kabir-ud-Din et al. carried out a systematic study to explore the effect of medium

chain alcohols (C_3-C_8OH) on the solution behavior of CPC and proposed that long chain alcohols are good candidates to induce micellar growth [38].

Apart from Kabir-ud-Din's work, no systematic studies have been carried out in CPC in the presence of long chain alcohol. Recently, we [39] initiated a study to monitor the effect of long chain alcohol (C_9-$C_{12}OH$) on the morphology of CTAB micelles and demonstrated fascinating microstructures such as wormlike micelles, vesicles etc. in the system. In this context, it is worth studying the effect of long chain alcohols (C_9-$C_{12}OH$) on a similar cationic surfactant system, CPC. Earlier research on the effect of salt on the micellization of CPC has shown that, smaller hydrated Br^- produces a favorable condition for micellar elongation than larger hydrated ions like Cl^- which motivated us to choose KBr as inorganic salt in our present work [40].

The objective of this paper is to investigate the combined effect of long chain alcohol and salt on the morphological transitions of CPC micelles. Here, we also made an attempt to examine the effect of electrolyte concentration and the nature of the surfactant head group on the morphological transitions of micelle.

Materials and Methods

Materials

The surfactants CPC and CPB were procured from Merck and Sigma respectively. The additives used were KBr (Himedia), n-nonanol (Merck), n-decanol (Merck), n-undecanol (Merck) and n-dodecanol (Merck). All chemicals
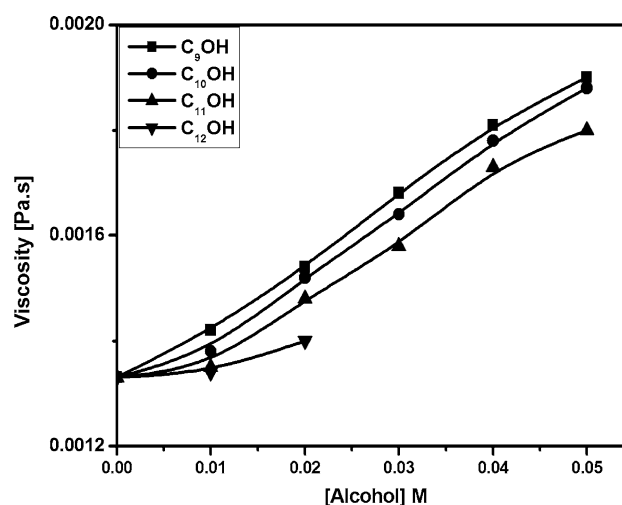

Fig. 1 The change of zero-shear viscosity of 0.1 M CPC micellar system with varying alcohols ranging from $n = 9$ to 12

were used as received. The micellar solutions were prepared using Millipore water.

Sample Preparation

The samples were prepared by dissolving the respective amount of alcohol in surfactant/salt stock solutions. The sample preparation is described in our previously reported work [39].

Viscosity

The absolute viscosity of samples under conditions of defined shear rate and shear stress were determined by a programmable Brookfield DV-II$^+$ cone and plate viscometer (Brookfield Engineering Laboratories, Inc-USA) thermostated over the temperature range 25–60 ± 1 °C. Prior to the measurement, samples are mounted for at least 30 min to attain thermal equilibrium [39].
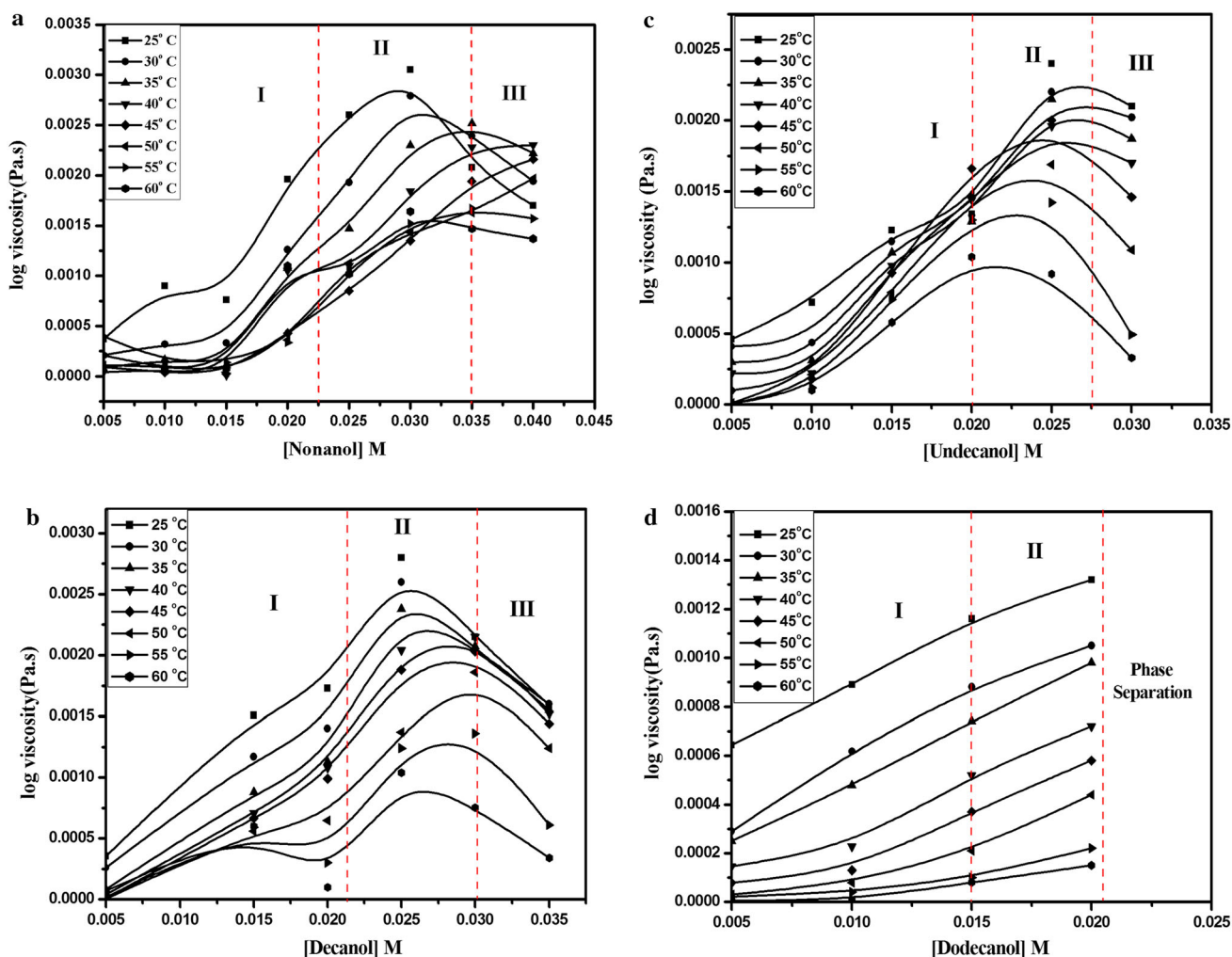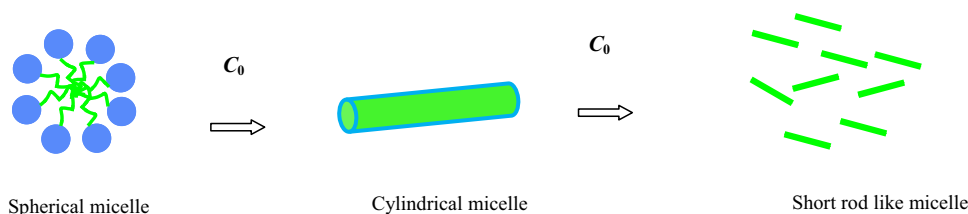

Fig. 2 Zero shear viscosity, log (Pa·s) of 0.1 M CPC/0.1 M KBr as a function of concentration of alcohol at temperatures ranging from 25 to 60 °C. **a** Nonanol, **b** decanol, **c** undecanol and **d** dodecanol

Scheme 1 Possible structural transition of CPC micelles with concentration of alcohol (C_0)

Rheology

The rheological experiments were performed on a controlled stress rheometer (Anton Paar Physica MCR-301) with a parallel plate sensor (50-mm diameter) and gap of about 1 mm. The samples were equilibrated for at least 15 min at the measuring temperature (25 ± 1 °C) prior to the measurement. The shear rate was varied from 1 to 100 s^{-1} [39].

Conductance

Conductivity of the samples was measured using a digital conductivity meter (Phillips, India), thermostated at 25 °C.

Dynamic Light Scattering

Measurements were performed with a Malvern 4800 Autosizer employing a 7132 digital correlator at a scattering angle of 130 °. A vertically polarized light of

wavelength 514.5 nm from an argon laser was used as the incident beam. All solutions were filtered with a 0.2-mm membrane filter before the measurements to avoid interference from dust. The measured intensity correlation functions were analyzed by the method of cumulants 33 where unimodal distribution of relaxation time is considered. The size distribution is obtained using the CONTIN algorithm wherever needed [39].

Phase Behavior with Temperature

The phase behavior of the samples was monitored visually by heating the sample in a temperature-controlled water bath (heating rate was 0.1 °C/min).

Cryo-TEM

Vitrified cryo-TEM specimens were prepared in a controlled environment vitrification system (CEVS), at 25 °C and 100 % relative humidity to avoid loss of volatiles,
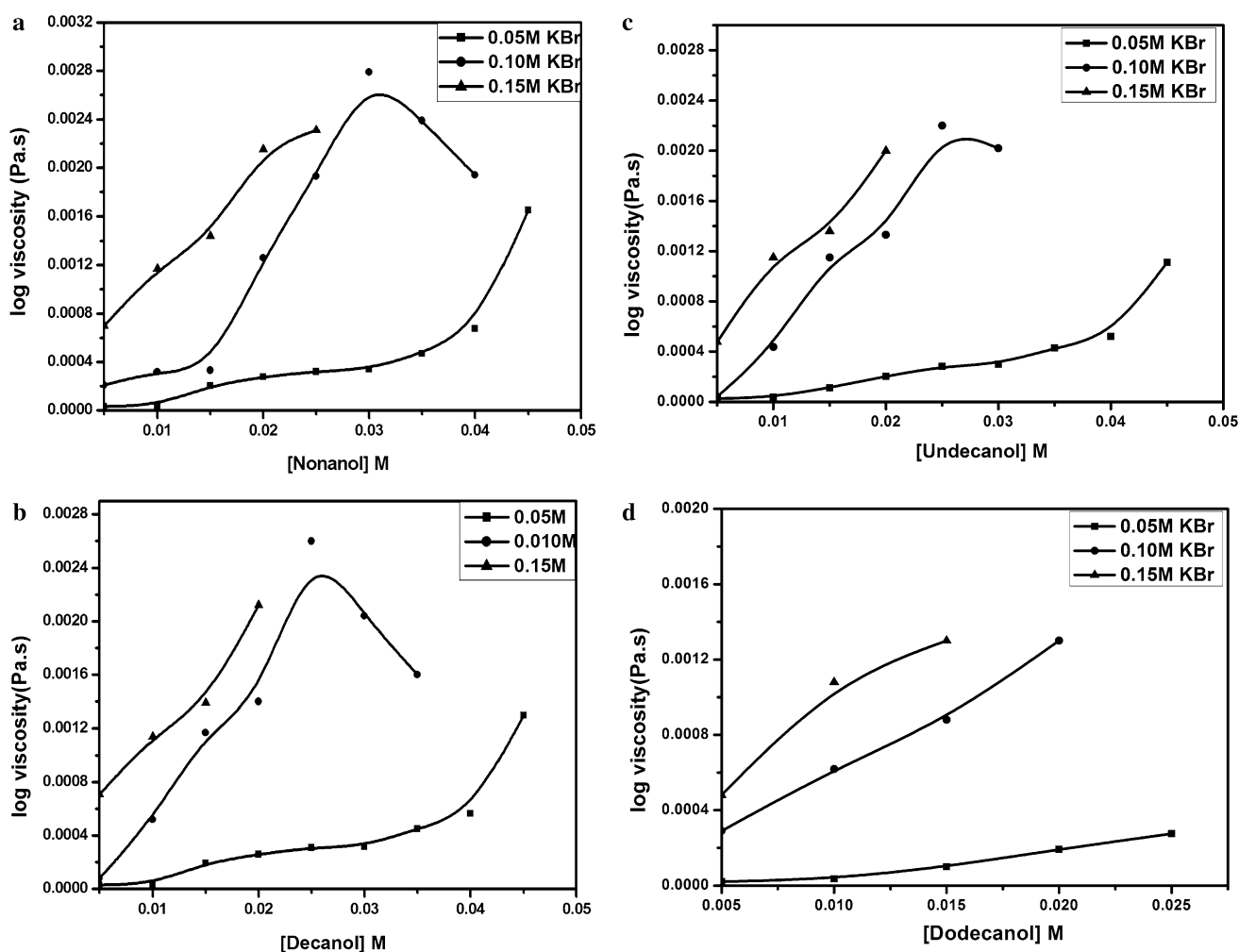

Fig. 3 The zero shear viscosity of 0.1 M CPC/xM KBr/alcohol solutions as a function of C_0 at 30 °C. x = 0.05–0.15 M

followed by quenching in liquid ethane at its freezing point. The specimens, kept below −178 °C, were examined by an FEI T12 G2 transmission electron microscope, operated at 120 kV, using a Gatan 626 cryo-holder system. Images were recorded digitally on a Gatan US1000 high-resolution cooled-CCD camera using the Digital Micrograph 3.4 software package in the low dose imaging mode [39].

Results and Discussion

Synergistic Effect of KBr and Long Chain Alcohol on the Viscosity Behavior of CPC Micellar system

The aqueous 0.1 M CPC solution showed water-like viscosity, and on addition of alcohol a slight increase in the viscosity was noticed (Fig. 1). However, the combined presence of salt and alcohol in the system produced favorable conditions which do not exist in the presence of either the salt or the alcohol alone (Fig. 2). Such type of synergism has previously been reported by Kabir-ud-Din *et al*. in the CPC/KCl system [22]. Viscosity profile of CPC/KBr micellar system as a function of C_0, showed a peaked behavior with three distinct regions (region I–III). Variation in viscosity thus indicates long chain alcohol induced micellar structural transition (Scheme 1).

Modification of packing parameter, R_p with C_0 seems to be the most plausible explanation for alcohol induced transition. Being water insoluble, the long chain alcohol would preferentially solubilize in the palisade layer of micelles, thereby increasing V and decreasing a, eventually leading to an increase in R_p. This increase in R_p could trigger the transformation from spherical to non-spherical micelles (rod-like micelles). The viscosity decrease with C_0 is quiet complicated to understand. The
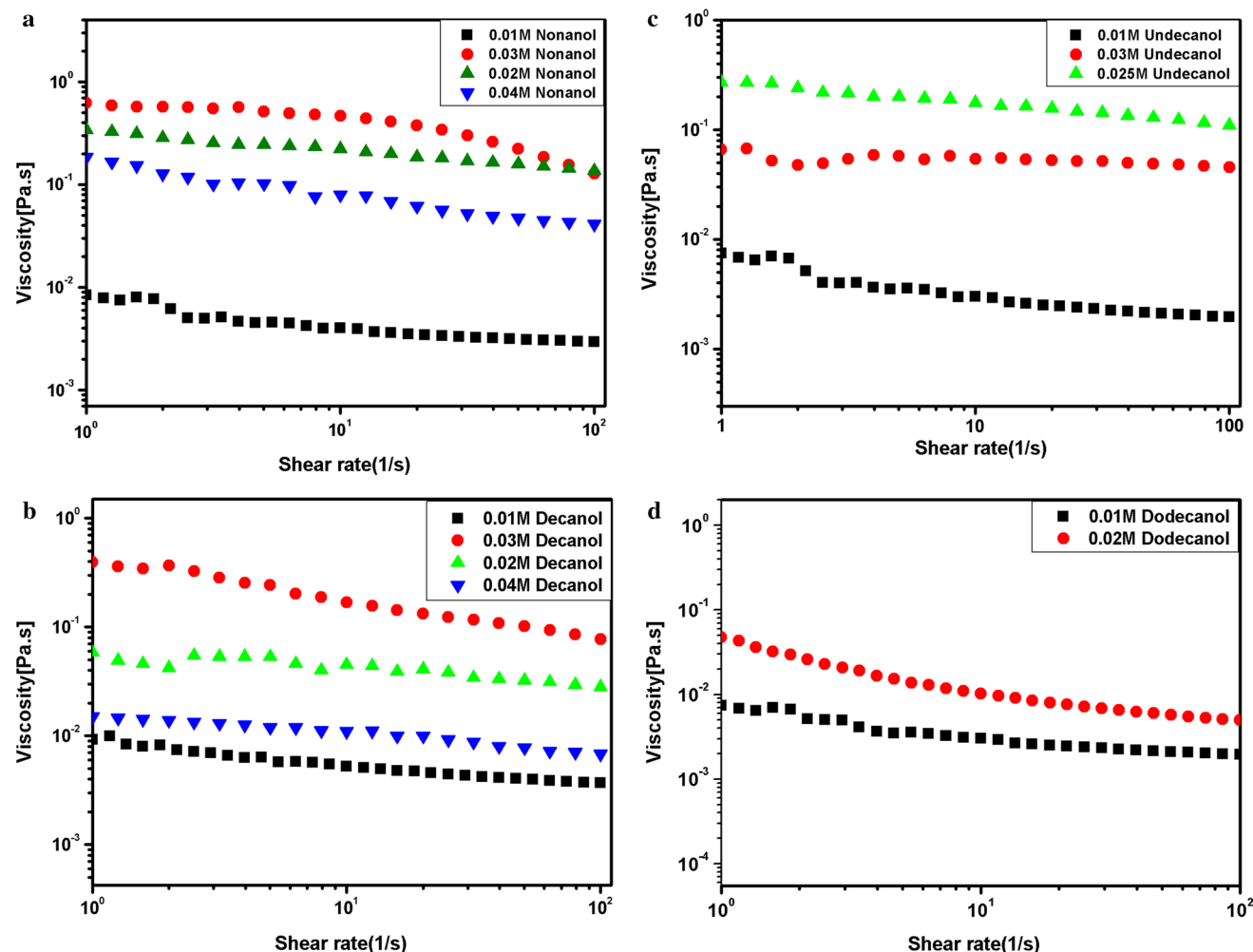

Fig. 4 The steady shear rheological response of 0.1 M CPC/0.1 MKBr as a function of C_0. a Nonanol, b decanol, c undecanol and d dodecanol

presence of vesicles or swollen micelles was noted for the viscosity decrease at high C_0 [7, 21, 41]. A similar explanation can be extended to explain the decline in viscosity at high C_0 in our system. At high C_0, the palisade layer becomes saturated and the alcohol molecules tend to solubilize in the micellar core. The swollen micelles can easily flow, thus resulting in a decline in viscosity.

The evidence of synergism is obtained by monitoring the viscosity at different KBr concentrations (Fig. 3). It can be seen that with an increase in [KBr], the maximum shifts to lower concentrations of alcohol, suggesting that the synergistic effect is dominant only in certain concentrations of salt and additive. This is explained by the salting out nature of KBr. At high salt concentration, the salting out nature increases and reduces the water solubility of the alcohol. As a result, the interfacial concentration of alcohol in the micelles increases. Thus with an increase in [KBr], the alcohol starts going to the interior of micelles causing a reduction in the viscosity.

Results from rheological experiments performed on CPC micelles with varying concentrations of alcohol show shear thinning behavior when the alcohol concentration is >0.01 M (Fig. 4), indicating the presence of non-spherical micelles. At high C_0 ($\geq$0.03 M), the viscosity decreases drastically and the samples show nearly Newtonian behavior, indicating a microstructural transition with C_0. The presence of short rod like micelles is expected in this region.
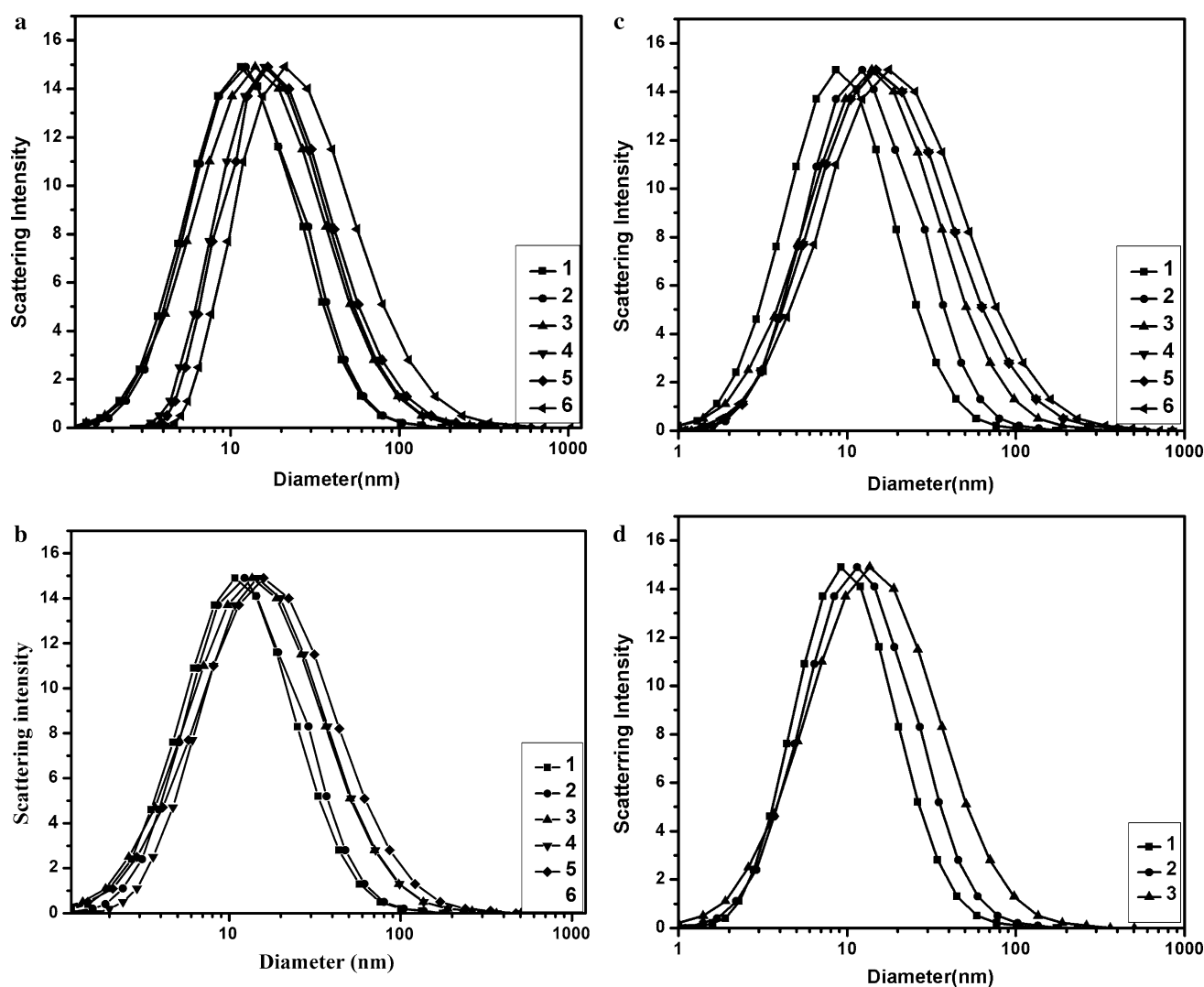

Fig. 5 The average hydrodynamic diameter of 0.1M CPC/0.1M KBr micellar solutions as a function of C_0. **a** Nonanol, **b** decanol, **c** undecanol and **d** Dodecanol. Concentration ranging from 1 to 6 as 0.005–0.03 M
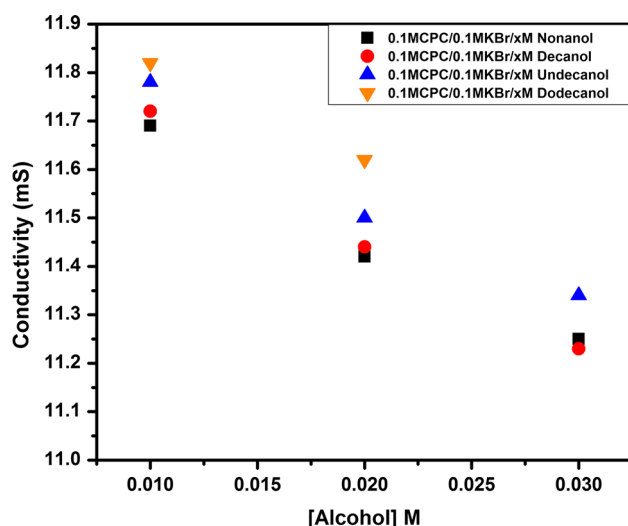
Fig. 6 Conductivity of CPC/KBr micelles as a function of alcohol concentration at 25 °C. (*black squares*) nonanol; (*red dots*) decanol; (*blue triangles*) undecanol; (*upside down orange triangles*) dodecanol

To get a better understanding of the structural transition in micelles, dynamic light scattering studies were performed. The hydrodynamic diameter (D_h) is obtained by the Stokes–Einstein equation.

$$D_0 = kT/3\pi\eta D_h$$

where D_o is the diffusion coefficient, k is the Boltzmann constant, T is the temperature in Kelvin scale and η is the dynamic viscosity of the medium. Dynamic light scattering (DLS) results is in conformity with viscosity studies. The distribution of the apparent diameter of the CPC/KBr micelles with C_0 is summarized in Fig. 5a–d. The manifold increase of average hydrodynamic diameter, Z_{av} with C_0, confirms the presence of large micelles.

Figure 6 shows the effect of C_0 on the conductivity of 0.1 M CPC/0.1 M KBr solutions. It is evident from the graph that the conductivity of systems decreases with C_0. The conductance of micellar solutions may increase or decrease in the presence of added additives. Desai *et al*. [42] reported a significant decrease in conductivity of CTAB/C_8OH system with [C_8OH] and attributed this to the presence of large micelles. Hence, the decrease in conductance observed in our system indicates sphere-to-rod transition.

The role of alcohol chain length on the behavior of CPC/KBr micelles was investigated by viscosity, rheology and DLS techniques. Based on the studies we found that the C_9OH incorporated sample showed a pronounced viscosity (Fig. 2a), a pronounced shear thinning rheological response (Fig. 7a) and a greater hydrodynamic diameter (Fig. 7b) than other alcohol.

We propose this as a change in the solubilization site of alcohol with the chain length of alcohol (n) (Scheme 2).
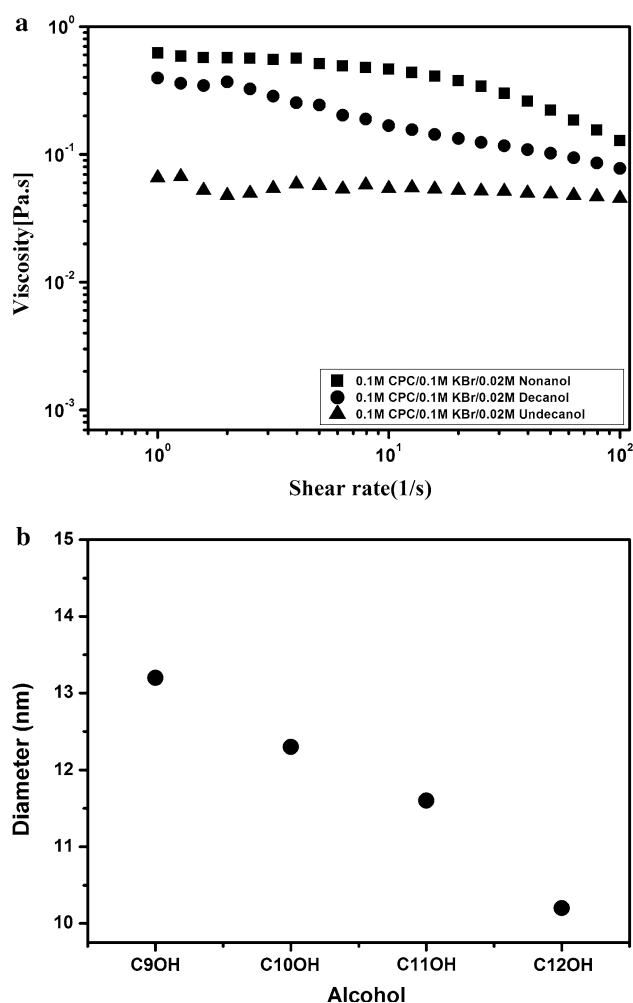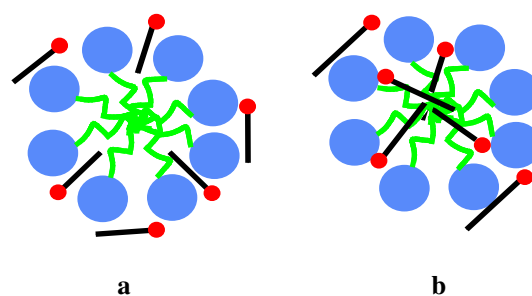

Fig. 7 a Zero shear viscosity of CPC/KBr/0.02 M C_9OH-C_{11}OH at 25 °C and **b** hydrodynamic diameter of CPC/KBr/0.01 M C_9OH-C_{12}OH

Scheme 2 Proposed solubilization site for C_9OH and C_{10}OH in CPC/KBr micelles [39]

With increase in n, the alcohol become more hydrophobic and intercalate more deeply into the micelle core. Hence more hydrophobic dodecanol (C_{12}OH) would preferentially get solubilized deeper to the core and is less effective in inducing micellar growth.
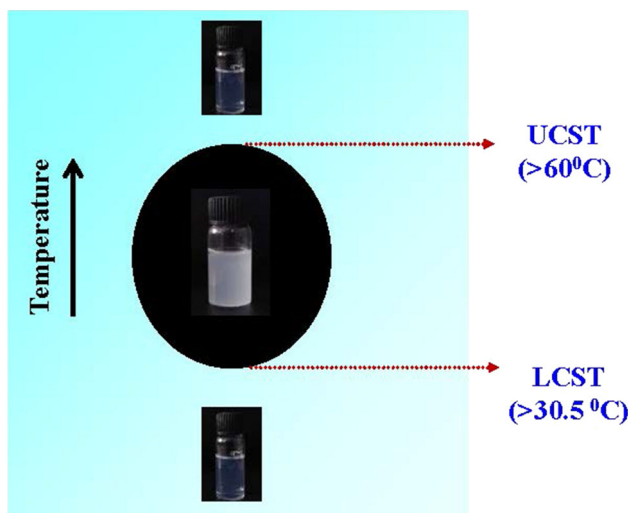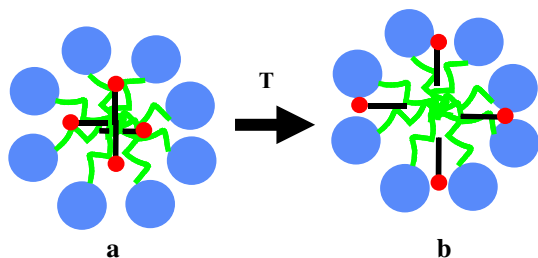
Fig. 8 Phase behavior of CPC/KBr/0.04 M decanol with temperature

Scheme 3 Proposed schematic motif for the change in solubilization site of decanol in CPC/KBr system with temperature **a** core solubilization and **b** palisade layer solubilization
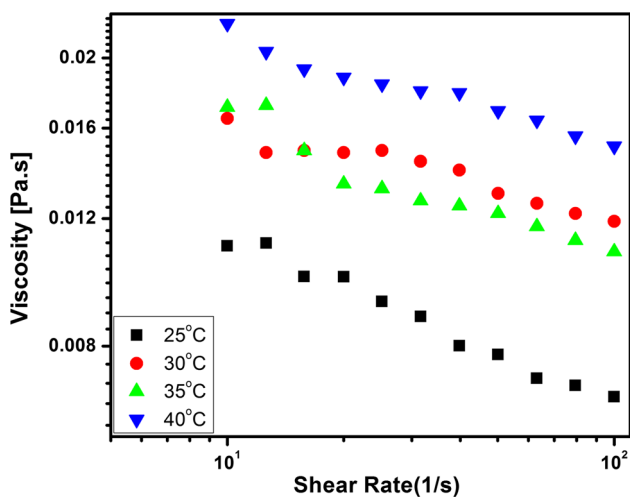

Fig. 9 Shear viscosity for CPC/KBr/0.04 M decanol with temperature
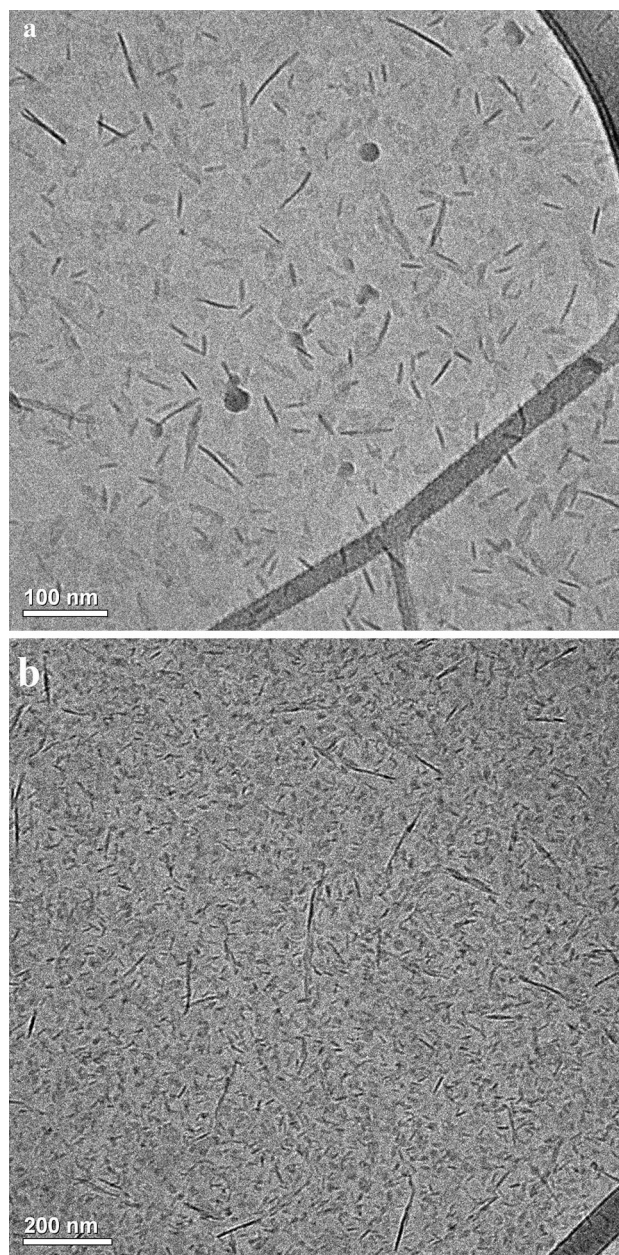
Fig. 10 Cryo-TEM images of the CPC/KBr/0.04M decanol with temperature. **a** <30 °C and **b** >30 °C

Table 1 LCST and UCST for CPC/KBr/decanol at different concentrations of CPC/KBr

[CPC]	[KBr]	[Decanol]	LCST (°C)	UCST(°C)
0.1	0.1	0.04	30.5	61
0.075	0.075	0.035	25.2	69
0.025	0.025	0.025	24.4	73
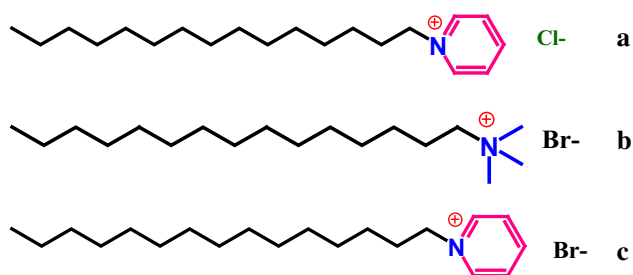
Scheme 4 Structure of surfactant **a** CPC, **b** CTAB and **c** CPB

Phase Behavior of CPC/KBr/Long Chain Alcohol with Temperature

While studying the influence of long chain alcohols on CPC/KBr systems, we came across a closed miscibility loop for the CPC/KBr/C_{10}OH system with temperature. The phase behavior of the system as a function of temperature is shown in Fig. 8. At low temperatures, the sample is slightly turbid (bluish) and in single phase. The turbidity may occur due to large vesicles which do not phase separate on standing [7]. The solutions show conventional clouding (above 30 °C) which may be due to fusion of large vesicles to bigger aggregates (dehydration process). At further high temperature (>60 °C), counterion dissociation is expected to dominate the process with increased charge on the aggregates and conversion to clear solution again (above UCST). A similar type of liquid–liquid demixing on warming was reported for binary mixtures of certain ionic surfactants and water [43, 44]. Since the upper critical solution temperature (UCST) was higher than LCST, the phase diagram exhibited a closed solubility loop similar to the other reported system [31].

We presume this phase behavior results from a change in the solubilization site of decanol with temperature. This behavior was noticed in systems with high concentration of decanol (near to its phase separation concentration). As most of the decanol would have been solubilized in the micellar core at high C_0, a slight perturbation in the form of temperature might be sufficient for decanol to transfer from
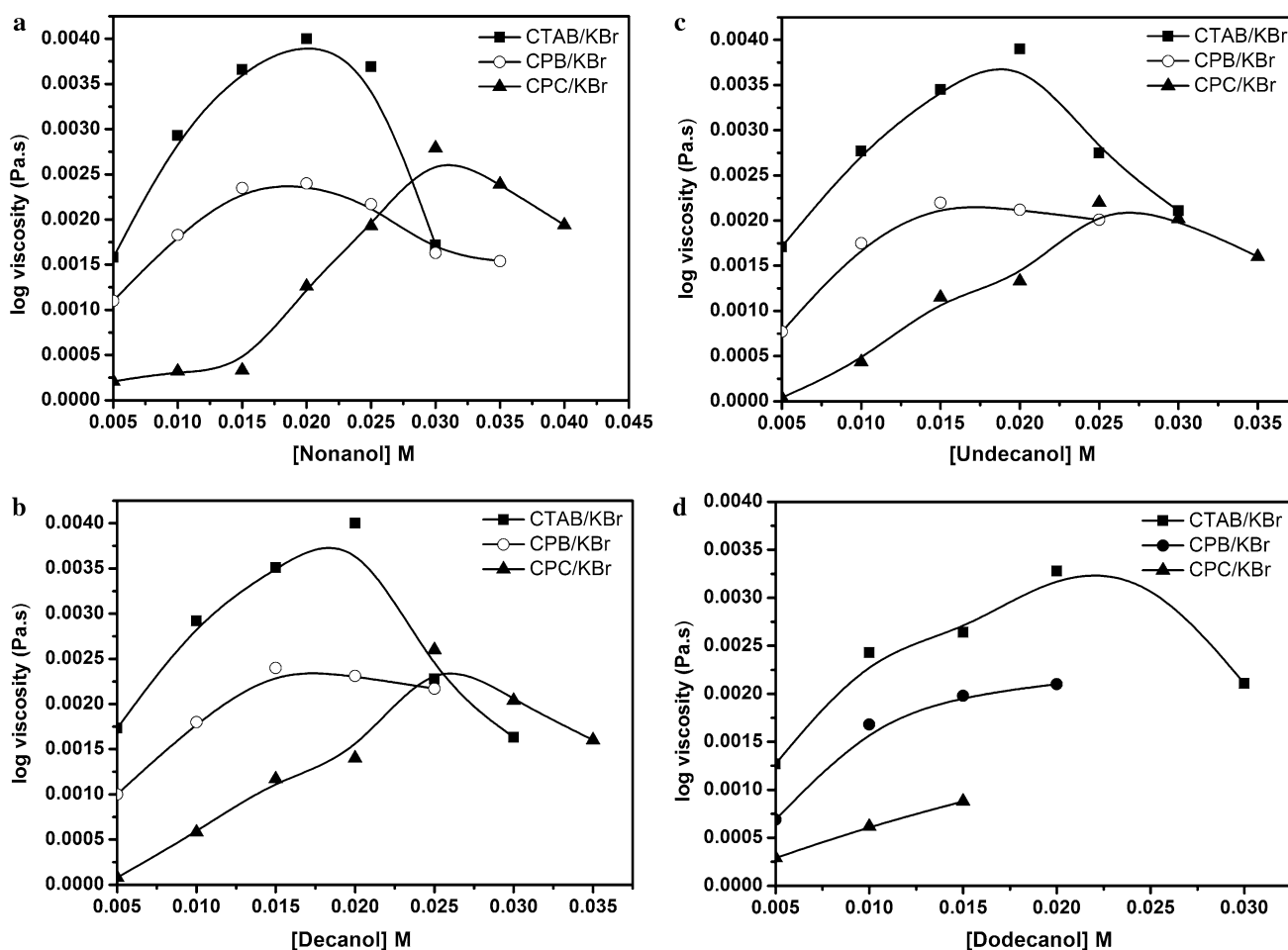

Fig. 11 The viscosity plot for 0.1 M surfactant + 0.1 M KBr system having a common hydrophobic tail but different headgroups at 30 °C: O, CPB; (*black triangles*), CPC; (*black squares*), CTAB respectively

the core-palisade layer to the bulk water phase, leading to phase separation. At very high temperature (>60 °C), the extra thermal energy compensates the miscibility problem and the system might have changed again to single phase (Scheme 3).

In order to shed more light on the phase behavior, the rheology of the samples at different temperatures was measured and is shown in Fig. 9. A substantial increase in viscosity of the system with temperature was observed, which further strengthen our assumption of change in the solubilization site of alcohol with temperature.

The Cryo-TEM images of the samples with temperature showed the coexistence of spherical and short rod-like micelles at low temperature, Fig. 10a, b. However, upon increasing the temperature, only short rod micelles were seen, thus confirming temperature-induced transition.

The effect of concentration of [CPC] and [KBr] on the phase behavior of CPC/KBr/decanol was studied by varying the concentration of CPC/KBr from 0.025 to 0.2 M. The value of LCST and UCST obtained for CPC/KBr/ Decanol micellar system at different fixed concentration of CPC/KBr are summarized in Table 1. Thus it can be concluded that a closed solubility profile was observed in samples containing an equal number of moles of surfactant and salt. However, no such behavior was noticed when the CPC/KBr concentration exceeds 0.1 M.

Effect of Head Group of the Surfactant on the Micellar Growth

Three different cationic surfactants (CPC, CTAB and CPB) with the same hydrophobic tail length (Scheme 4) but with different hydrophilic head groups were selected to examine the effect of the surfactant head group on the viscosity behavior of the surfactant-alcohol system in the presence of KBr (Fig. 11).

It was noted from Fig. 11 that the viscosity of the surfactant-alcohol system increases in the order CTAB > CPB > CPC. This could be due to the presence of different head groups and counterions in the system. CTAB with a strong binding Br^- ion and a small trimethyl ammonium head group may have a greater tendency to grow in the presence of alcohol than CPC with weakly binding Cl^- and a bulky pyridinium head group. Furthermore, the comparison of CPC/salt/alcohol and CPB/ salt/alcohol systems, will shed some light on the effect of the counterion on micellar behavior of the surfactant/alcohol. The electrostatic interaction is stronger in CPC as it is more highly charged than CPB. As a result, the CPC will form smaller micelles than CPC [22]. The DLS analysis further supports this viscosity trend (Table 2).

Table 2 Hydrodynamic diameter of 0.1 M surfactant/0.1 M KBr/ 0.01 M alcohol micellar system

Surfactant	Alcohol	Hydrodynamic diameter (nm)
CTAB	Nonanol	25.8
	Decanol	24.2
	Undecanol	23.6
	Dodecanol	17.5
CPB	Nonanol	18
	Decanol	17.1
	Undecanol	16.2
	Dodecanol	15
CPC	Nonanol	13.2
	Decanol	12.3
	Undecanol	11.6
	Dodecanol	10.2

Conclusion

The micellar growth in CPC/alcohol system with respect to the role of long chain alcohol, electrolyte and surfactant head group was summarized as follows:

1. Long chain alcohols (C_9OH-$C_{12}OH$) were found to be good candidates to induce structural changes in the CPC/KBr micellar system. The CPC/KBr/(C_9OH-$C_{12}OH$) micellar system showed the transformation of a low viscous solution (spherical micelles) to a viscous fluid (rod-like micelles) with C_0, which was confirmed by rheology, conductivity and DLS techniques. Among the four different alcohols studied, C_9OH incorporated samples showed pronounced viscosity and micellar growth which was inferred to be the influence of the chain length of the alcohol that resulted in micellar growth.

2. The micellar properties of surfactant/alcohol systems could be tuned by varying the salt concentration and head group of the surfactant.

3. An unusual phase behavior with temperature was noted for a CPC/KBr/decanol micellar system with a closed solubility loop, which is rarely reported in an ionic surfactant system.

4. Comparing the present results with our previous results [39], it is evident that micellar properties (viscosity, rheology) of surfactants (CPC and CPB) in the combined presence of salt and alcohol are mostly similar. However CPC/KBr/alcohol systems show a unique closed solubility loop, which is rarely reported in ionic surfactant systems.

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