Colloid Polym Sci (2008) 286:335–341
DOI 10.1007/s00396-007-1783-9

SHORT COMMUNICATION

A viscometric study of tuning micellar morphology by organic additives

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Received: 4 December 2006 / Revised: 17 August 2007 / Accepted: 14 October 2007 / Published online: 14 November 2007

Abstract The micellar morphology in aqueous 0.2 M sodium dodecyl sulfate (SDS) solutions has been studied in the simultaneous presence of organic salts (anilinium hydrochloride, AHC; *ortho*-toluidine hydrochloride, *o*THC; *para*-toluidine hydrochloride, *p*THC) and aliphatic alcohols (*n*-butanol, C_4OH; *n*-pentanol, C_5OH; *n*-hexanol, C_6OH; *n*-heptanol, C_7OH), aliphatic amines (*n*-butylamine, C_4NH_2; *n*-pentylamine, C_5NH_2; *n*-hexylamine, C_6NH_2; *n*-heptylamine, C_7NH_2), or hydrocarbons (*n*-hexane, C_6H; *n*-heptane, C_7H) by viscosity measurements under Newtonian flow conditions at 30 °C. Addition of alcohols and amines causes micellar growth which is found to be dependent upon chain length of the additive and nature of organic salt counterion. It is observed that amines are more effective in increasing the viscosity of the system if added in pure 0.2 M SDS solution, while SDS+*p*THC system was found versatile when alcohols were added to this system. The increased viscosity or the micellar growth is explained in terms of the site of solubilization of the respective additive and the interaction of the additive with micellar surface and salt counterion present in the head group region. Hydrocarbons are nearly ineffective in inducing micellar growth and can be used as 'micellar destroyer' for the grown micelles. The additives used are found effective in tuning the environment of the micelle which is reflected in viscosity behavior. This work may find use in micellar ultrafiltration as well as in mimicking the natural cell, which has several aspects common with the micelle.

Keywords Sodium dodecyl sulfate · Micellar morphology · Organic salts · Viscosity

Introduction

Life, the most complex form of organic compounds on earth, requires the construction of chemical bonds in aqueous environment. In nature, chemical conversions take place in a confined environment, which vary from nanometer-sized and relatively simple systems (such as enzymes) to micrometer-sized and extremely complex assemblies (such as cells). Although the construction of artificial cells is the ultimate fantasy, more simple systems such as micelles, vesicles, and other assemblies of amphiphilic molecules may already partly solve the problem [1]. The self-assembly of amphiphiles in water is driven by the hydrophobic effect [2, 3], which is probably best described by taking into consideration the solvation thermodynamics that play a role in the favorable overlap of the hydration shells of the hydrophobic parts of the molecules on self-assembly [4]. A variety of aggregate morphologies has been observed [5–7]. Morphology of self-assemblies formed by the amphiphilic molecules is a delicate balance of opposing forces, e.g., attractive tail–tail hydrophobic interactions, repulsive electrostatic interaction between head groups, hydration, etc. Various ways are devised to control the characteristics and morphology of these aggregates. These methods are synthesis of novel surfactants [8] (gemini surfactants [9]), use of surfactant mixtures [10], and surfactants in presence of suitable additives [11–16]. This last approach has been used to obtain various micellar morphologies when the additive is an appropriate salt. Presence of salt counterions, near the micellar surface, decreases the inter-head group repulsion,

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thus decreasing the average head group area per molecule (A_0) at the surface of the micelle. This A_0 decrease facilitates the formation of various morphologies consistent with the geometrical packing model of Israelachvili [17].

Organic counterions that contain a hydrophobic portion and have a charge opposite to that of the surfactant heads are responsible for unconventional properties of the surfactant solutions. Depending upon the surfactant+salt combination, solutions can have properties of living polymer [18], ionic surfactant solutions can show the clouding phenomenon [19], and even formation of hollow icosahedra if the two components are of comparable chain length [10]. It is now established that, with the addition of organic counterions, ionic micelles undergo unidimensional growth to form rod-like micelles [20]. We have shown that presence of quaternary counterions in anionic micellar solutions causes micellar growth and surface charge depletion [21]. Such counterions can interact with micelles hydrophobically (by penetrating some alkyl chains between monomers of the micelle [22]) and electrostatically (as counterions and micellar surface are oppositely charged). Recently, analogous micellar growth by the addition of aromatic salts, *para*-toluidine hydrochloride (*p*THC), *meta*-toluidine hydrochloride (*m*THC), *ortho*-toluidine hydrochloride (*o*THC), and anilinium hydrochloride (AHC), has been reported [13–16].

We are engaged in a systematic study of micellar association due to the simultaneous presence of salts and an organic additive [11, 12, 22–25]. The exclusive attention given to these systems is the result of the fact that surfactants are always used in combination with one or more additives simultaneously for their scientific, experimental, industrial, and theoretical applications [15, 26–28]. These studies allowed to conclude that micellar growth takes place due to the combined effect of salt and organic additives. There is a certain range of [salt] and [organic additive] between which the phenomenon of micellar growth takes place. It has been proposed that interfacial partitioning of organic additives causes micellar growth, whereas interior solubilization produces swollen micelles [11, 12]. These two types of micelles impart different viscosity behavior to the micellar solution [26, 29]. As the viscosity is sensitive to morphology of objects in a homogeneous suspension, one can expect evolution of the micellar architecture to be reflected in the viscosity variations. It is of real importance to see the influence of various additives and their partitioning at a specific site of solubilization of micelles, as the same additive at different sites can influence the micellar association in a distinctly different manner. Once such phenomena are mechanized, one can mimic more complex biological systems.

The present study, therefore, deals with the viscosity behavior of 0.2 M sodium dodecyl sulfate (SDS) micellar solutions in the presence of different concentrations of AHC, *o*THC, or *p*THC either singly or in simultaneous presence of aliphatic alcohol (*n*-butanol, C_4OH; *n*-pentanol, C_5OH; *n*-hexanol, C_6OH; or *n*-heptanol, C_7OH), aliphatic amine (*n*-butylamine, C_4NH_2; *n*-pentylamine, C_5NH_2; *n*-hexylamine, C_6NH_2; or *n*-heptylamine, C_7NH_2), or aliphatic hydrocarbon (*n*-hexane, C_6H, or *n*-heptane, C_7H) at 30 °C. The ultimate goal of the research community is to mimic the complexity of cells and construct hybrids of fully synthetic cells. However, it will take many years before such a goal will be achieved. The work reported here may prove a forward step towards achieving this goal as both micelle and cell contain many aspects common, e.g., self-assembly and compartmentalization.

Materials and methods

Materials

SDS (for electrophoresis, purity approx. 99%) was purchased from Sigma (USA). AHC, *o*THC, and *p*THC were obtained from Fluka (Switzerland). All alkanols, C_4OH, C_5OH, C_6OH, and C_7OH were BDH high-purity chemicals and were used as received. All alkylamines, C_4NH_2, C_5NH_2, C_6NH_2, and C_7NH_2 were obtained from Fluka (Switzerland, purity >99%) and used as received. The aliphatic hydrocarbons (purity>99.5%), C_6H and C_7H, were from Merck (India). The water used to prepare the solutions was demineralized and double-distilled in an all-glass distillation apparatus. The specific conductivity of this water was in the range $(1–2)\times10^{-6}$ S cm^{-1}.

Method

Viscosities of the solutions were measured in an Ubbelohde viscometer that was thermostated at a fixed temperature (30 °C, accuracy ±0.1 °C). The method of measurement of viscosities under conditions of Newtonian flow was the same as described elsewhere [30]. The requisite amount of surfactant was dissolved in distilled water or in salt solution. These solutions were used as stock solutions to see the effect of additives. A nearly saturated solution was prepared for a typical additive, and further lower concentrations were made by dilution from above stock solutions.

Results and discussion

It has been reported that SDS micelles grow (spherical to rod shaped) in the presence of AHC, *o*THC, *m*THC, and *p*THC [13–16]. This is due to the adsorption of counterions on the surface of the micelles. NMR studies [13] confirm

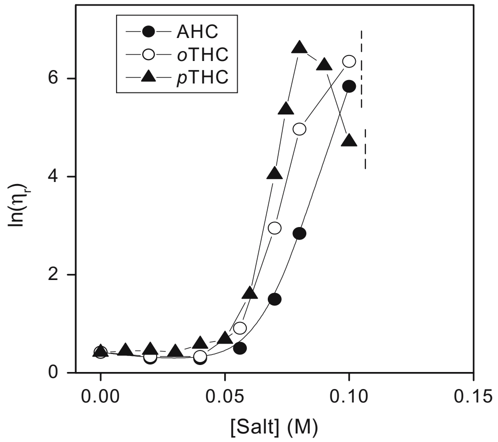


Fig. 1 Variation of relative viscosities of 0.2 M SDS micellar solutions at 30 °C with the cationic organic salt concentrations (up to the solubility limits indicated by *dotted lines*)

this adsorption and even allow to conclude that the aromatic ring is intercalated between the hydrocarbon chains in the micelle interior. This arrangement facilitates the damping of the electrostatic interactions and is favorable to hydrophobic interactions. Consequently, one can expect sharp increase in the solution viscosity, which indeed is observed (Fig. 1). The viscosity increase is comparatively more pronounced in case of adding *p*THC to that of AHC or *o*THC. This is possibly due to the difference in microenvironment felt by the additive near the head group region. The NMR studies have revealed that the *ortho* protons experience a hydrophilic environment, while the *para* protons experience hydrophobic one [13]. This may be the reason of the effectiveness of *p*THC in comparison to *o*THC or AHC. It is also noted that relative viscosity (η_r)− [salt] plot shows a peaked behavior (Fig. 1) in case of *p*THC. Based on the results of a host of techniques including DLS [13–16], we can safely conclude that the initial increase in η_r reflects a substantial growth of the rod-shaped micelles, which eventually convert into long, flexible entities [27]. The latter effect may be responsible for the drop in the viscosity at higher [*p*THC]. As the viscosity rise starts at ~0.06 M of each salt concentration (Fig. 1), we have chosen 0.2 M SDS+

Fig. 2 Variation of relative viscosities of 0.2 M SDS micellar solutions at 30 °C with added alcohols: **a** without salt, **b** with 0.06 M AHC, **c** with 0.06 M *o*THC, **d** with 0.06 M *p*THC (up to the solubility limits)

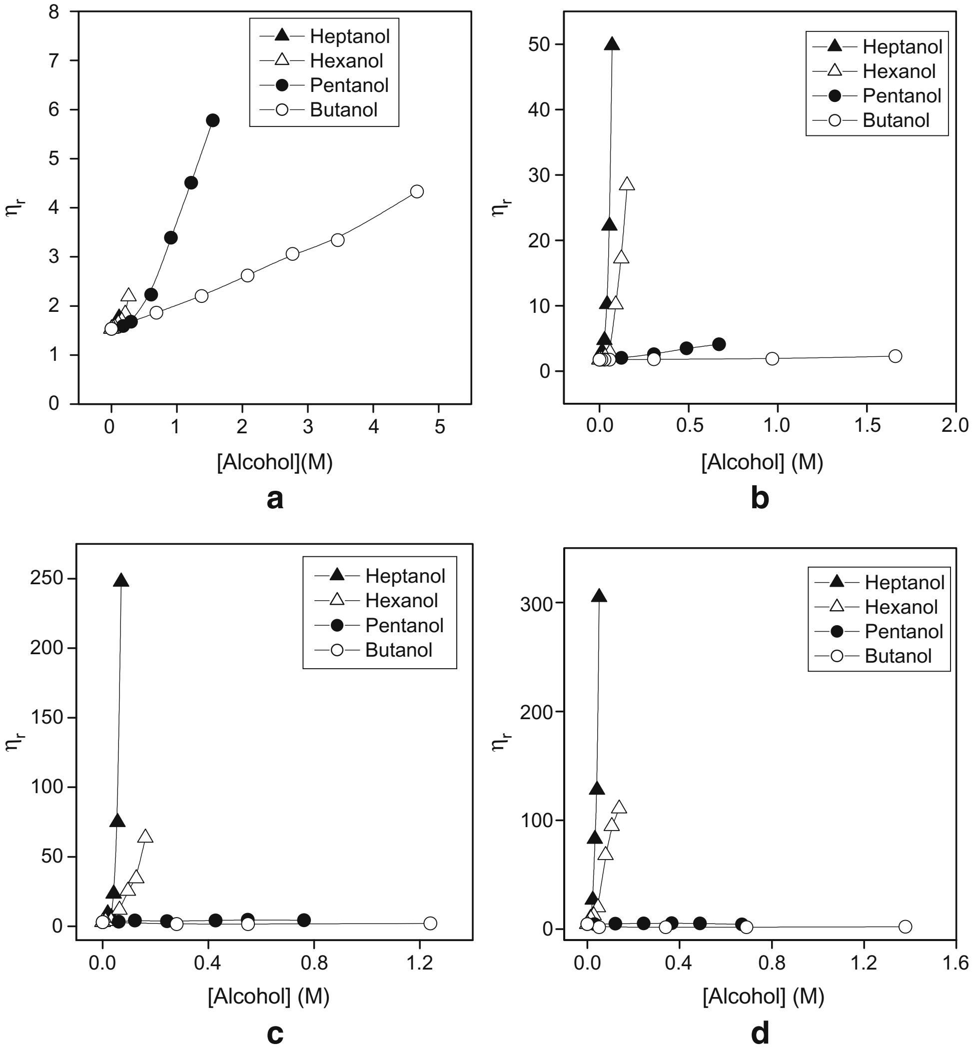
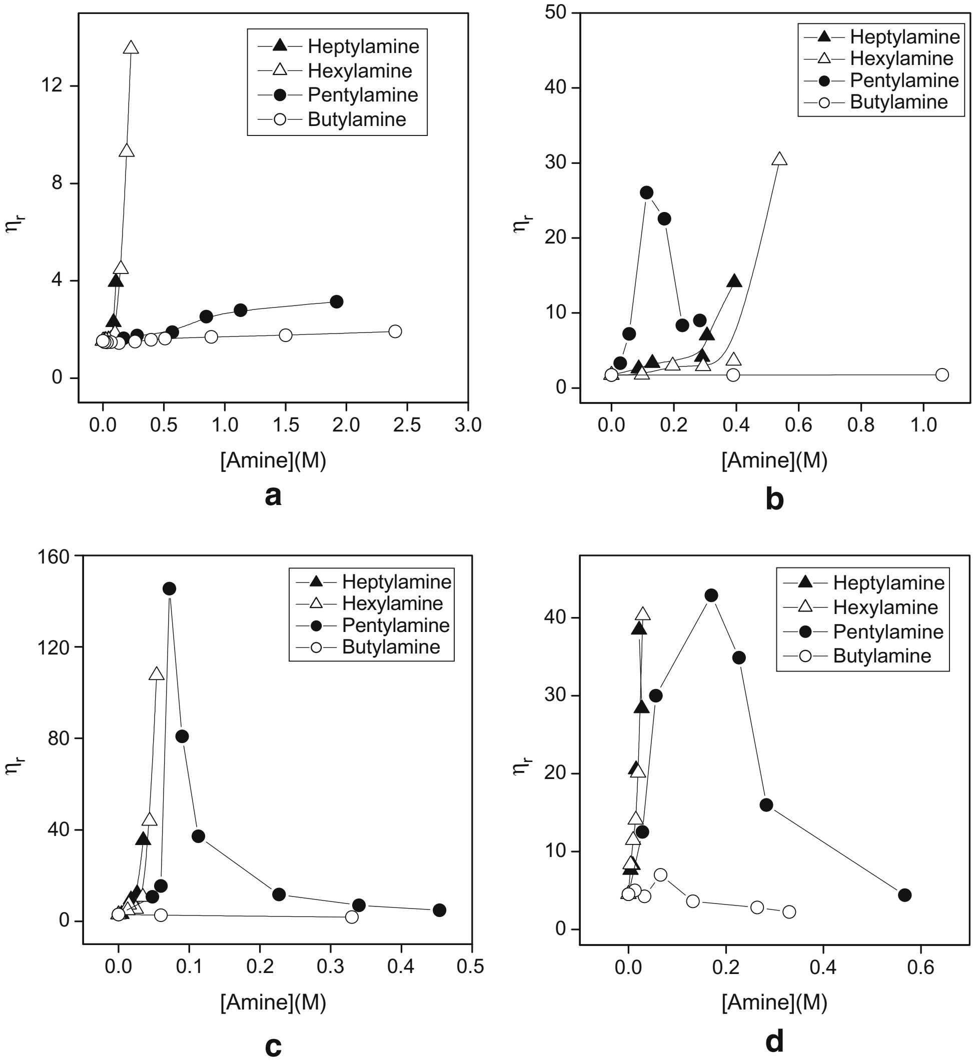


Fig. 3 Variation of relative viscosities of 0.2 M SDS micellar solutions at 30 °C with added amines: **a** without salt, **b** with 0.06 M AHC, **c** with 0.06 M *o*THC, **d** with 0.06 M *p*THC (up to the solubility limits)



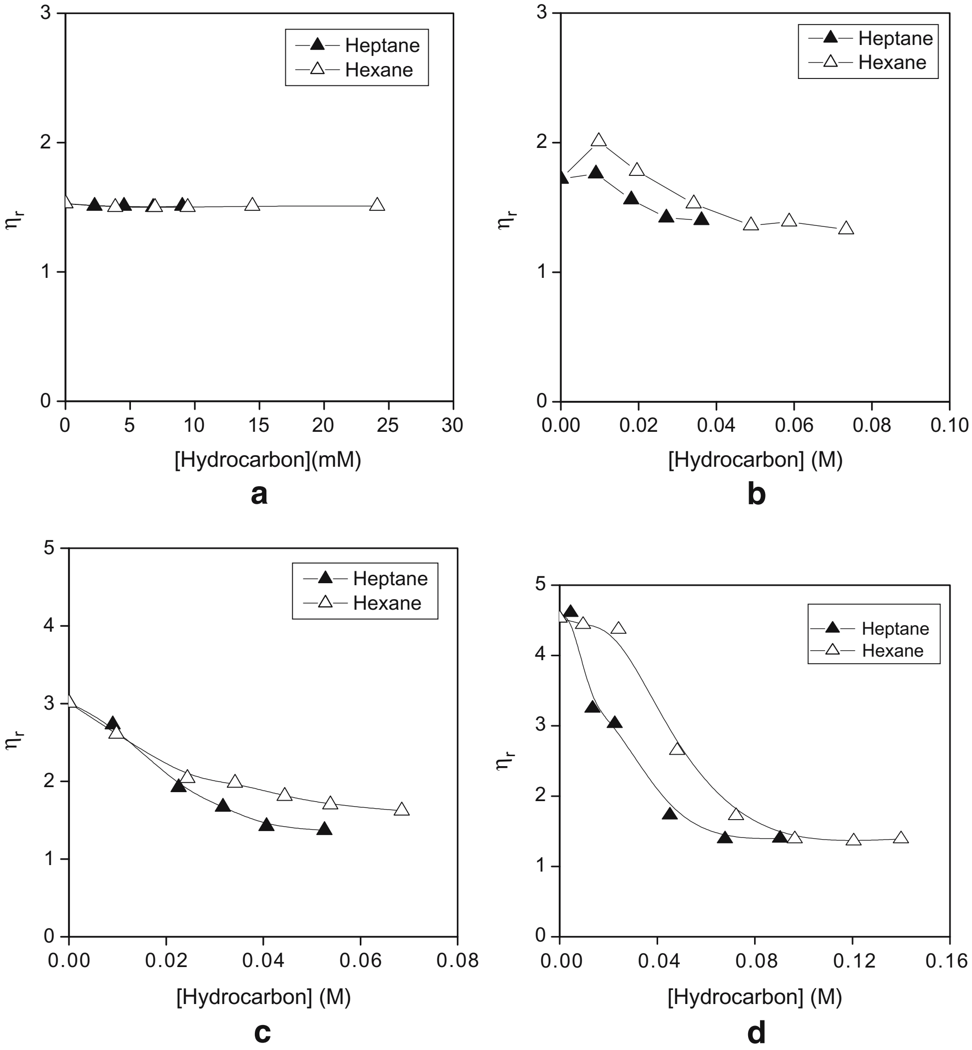
0.06 M organic salt systems for investigating the effects of other organic additives in detail.

Before making an attempt to discuss the role of various organic additives (aliphatic alcohols, amines, or hydrocarbons), it is relevant to have an idea about various available solubilization sites in micelles for organic additives and their subsequent effect on micellar morphology. This discussion would certainly help in mimicking an artificial cell by taking simple examples of association structures of the amphiphilic molecules.

Organic compounds can exist in a variety of regions available in micellar solutions: main locations are the surrounding bulk phase, the head group region, and the micellar interior [12, 31–33]. According to Mukerjee [34], an additive that is surface active to a hydrocarbon/water interface will be mainly solubilized in the head group region and will promote micellar growth. Greater partitioning of the organic additives to the core was shown to retard micellar growth by virtue of releasing the requirement of the monomer tails to reach the center of the micelles [35]. This maintains the morphology with higher surface area, that is, swollen micelles. The picture emerging on micellar solubilization is thus the concept of "two-site localization": Added organic molecules are either dissolved in the hydrocarbon core or adsorbed at the interface. The 'adsorbed' and 'dissolved' states of the guest (e.g., organic additives) molecules have different effects on the surfactant parameter R_p ($=V_c/l_cA_0$, V_c being the volume of the hydrocarbon tail region per surfactant and l_c the optimal chain length) [17] with accompanied changes in the micellar morphology.

Figure 2 shows the viscosity variation of 0.2 M SDS micellar solutions (with or without 0.06 M organic salts) on addition of various aliphatic alcohols (C_4OH, C_5OH, C_6OH, C_7OH) at 30 °C. It is clear (see Fig. 2a–d) that addition of C_4OH (or, to some extents, C_5OH) shows marginal change in η_r. The pattern did not change even in presence of the organic salts. Short chain alcohols, being

Fig. 4 Variation of relative viscosities of 0.2 M SDS micellar solutions at 30 °C with added hydrocarbons: **a** without salt, **b** with 0.06 M AHC, **c** with 0.06 M *o*THC, **d** with 0.06 M *p*THC (up to the solubility limits)



amphiphilic, have significant solubilities in water but small in micelles. Due to this reason, they are not able to affect micellar structure appreciably, and hence, no substantial change occurs in the viscosity indicating that micellar morphology (more or less) remains unchanged. The higher chain length additives (e.g., C_6OH or C_7OH) have a strong chance to get embedded between monomers comprising the micelles. This embedding helps to overcome inter-head group repulsion by holding the above longer chain alcohols in between head groups of similar charge and is, therefore, responsible for the decrease in head group area (A_0) of the surfactant molecule. Consequently, the R_p increases. Thus, SDS+0.06 M organic salt systems with higher chain length alcohols should have a tendency to form larger micelles (change in micellar morphology), and this indeed is reflected from the viscosity rise of micellar solutions. Small-angle neutron scattering [36] studies have proved that the volume of the SDS micelle increases with the increase of chain length of the alcohol, which is due to the increase in the aggregation number as well as due to increase in alcohol molecules in the micelle. Such a volume change in the SDS micelle is expected here also and explains the viscosity rise in the systems shown in Fig. 2. It is worth noting that, for an equal concentration of salt and additive, the viscosity rise is higher with *p*THC compared to other salts. This difference in viscosity and hence in the growth behavior, as pointed out earlier, could be understood in view of the difference in microenvironments of the substituent groups in the salt [13–16].

Figure 3 shows the variation of η_r with the addition of aliphatic amines (C_4NH_2, C_5NH_2, C_6NH_2, C_7NH_2) to the 0.2 M SDS with or without organic salts (AHC, *o*THC or *p*THC). When the amines were added to 0.2 M SDS solutions containing no salt (Fig. 3a), the viscosities were higher in comparison to alcohol additions (Fig. 2a). It has earlier been reported that C_4–C_{10} *n*-alkylamines are solubilized in SDS micelles by electrostatic and hydrophobic effects with amine group left on the surface of the micelles [37]. Their partial dissociation into $-NH_3^+$ and OH^- (although feebly) affects electrostatic interactions with anionic head groups of the SDS micelles that facilitates higher micellar growth. This is substantiated by the present viscosity data also (see Figs. 2a and 3a).

The overall chain length effect of amines is similar to that of alcohols. Interestingly, amine addition in presence of organic salts (AHC, *o*THC, *p*THC) causes less increase in the viscosity for the same concentration of the corresponding alcohol. The key lies in the fact that organic counterions and protonated amines compete for the same solubilization sites, as both contain positive charge. Due to this reason, when both are present simultaneously in the system, a repulsive interaction could take place between protonated amines and organic cations, and counter the effect of each other and hence a less increase in viscosity is observed.

Another important observation is of peaked behavior in η_r vs [*n*-pentylamine] profiles in each system (Fig. 3b–d). The viscosity increments at low [C_5NH_2] can be interpreted in terms of the formation of large micelles (micellar growth) due to its solubilization/incorporation into the micelles. Due to this solubilization, the pentyl chain of C_5NH_2 would interact hydrophobically with the C_{12} chain of SDS. Further addition of the C_5NH_2 beyond the optimum concentration affects the water structure predominantly (the effect is also assisted by the repulsion between $C_5NH_3^+$ and organic cations), resulting in breaking up of grown micelles to relatively smaller units; hence, a gradual decrease in viscosity is observed.

It is further noted that the viscosities are higher with C_5NH_2 than the other amine (C_6NH_2 or C_7NH_2) combinations with AHC. C_5NH_2 will be more protonated than the above higher chain length amines. Due to this reason, the $C_5NH_3^+$ effective fraction would be greater for the same concentration of the other amines. The interaction of $C_5NH_3^+$ and negatively charged SDS head groups causes a greater electrostatic attractive force (charge neutralization) with a simultaneous growth of the micelles resulting in a more viscosity increase with AHC+C_5NH_2 combination than the AHC+C_6NH_2 or AHC+C_7NH_2 (Fig. 3b). If we consider *o*THC+amine (Fig. 3c) and *p*THC + amine (Fig. 3d) combinations, it is clear that viscosities are higher in the case of the former, whereas in the case of alcohol additives, *p*THC was the most effective salt. Probably, orientation of the above two salt counterions decides of the relative efficacy of alcohols and amines. In this study, amine interaction with salt cations resists its partitioning in the head group region, but in case of *o*THC, its partitioning in the head group region would experience less opposition and hence amine+*o*THC combination is more effective in viscosity rise than the amine+*p*THC.

Figure 4 represents the variation of η_r of 0.2 M SDS + 0.06 M organic salts with the added hydrocarbons (C_6H or C_7H). Like alcohols and amines (without salts), the hydrocarbons also produce practically no change in the viscosity of the solutions. This is due to the fact that 0.2 M SDS micellar solution contains roughly spherical micelles that, on solubilization of hydrocarbons (in micellar core), do not change their shape and hence no change in viscosity is observed. However, when the hydrocarbons are added in presence of the organic counterions, already grown micelles get converted to swollen (spherical) micelles. Due to the increased sphericity, the micelles flow easily with an eventual drop in the solution viscosity [12]. However, initially, a maximum is observed with η_r vs [hydrocarbon] that is more prominent with C_6H. Presence of counterions driven from AHC near the interfacial region may provide a hydrophobicity (not much significant rise) to this region. As C_6H is less hydrophobic than C_7H, there is less chance of C_6H to get solubilized in the micellar interfacial region (especially in lower concentration regime) and may cause a small increase in viscosity as obtained in the initial part of the curve between η_r vs [hydrocarbon] (Fig. 4b). At this stage, we are tempted to mention that AHC is behaving somehow in a special manner (see Figs. 3b and 4b) for which no specific reason(s) could presently be assigned. Further studies employing other techniques are needed for resolving the matter.

Conclusion

In this paper, micellar morphology of SDS is studied by organic additives through viscometric method. Organic additives can be used strategically to tune the size and the shape of the micelles. SDS micelles grow in the presence of AHC, *o*THC, and *p*THC. When aliphatic alcohols, amines, or hydrocarbons are added to the mixture, the viscosity of the solution changes, which implies that the micellar morphologies have changed. In this paper, we have shown how organic additives can be used strategically to tune the size and the shape of the micelles. The results of the study can assist in designing systems that can mobilize pollutants in different parts of the micelle and find use in micellar enhanced ultrafiltration. Although extremely simple in concept, the tuning of micellar morphologies can assist in the simplest mimic of a cell. The application of specific amphiphilic systems to construct unique morphologies or drug-delivery systems has by contrast expanded rapidly, resulting to date in numerous commercial applications, with many more to come.

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