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Viscometric studies on aqueous gemini micelles in the presence of additives

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Abstract

Surfactant molecules produce different types of morphologies in water above their critical micelle concentrations. This article presents the viscosity results obtained on gemini surfactants alkanediyl-α,ω-bis(cetyldimethylammonium bromide) ($C_{16}H_{33}$ Me_2N^+ $–(CH_2)_s–$ $N^+Me_2C_{16}H_{33}$, $2Br^-$; 16-*s*-16, $2Br^-$, where $s = 4, 5, 6$) in pure aqueous solutions and also in the presence of different additives (KBr, *n*-hexanol, *n*-pentanol, *n*-butanol and *n*-hexylamine). The data are compared with a conventional surfactant cetyltrimethylammonium bromide (*n*-$C_{16}H_{33}N^+Me_3$, Br^-; CTAB). In pure aqueous solutions, the viscosity was found to increase rapidly with geminis in comparison to CTAB on increasing surfactant concentration. It was also observed that among geminis, the viscosity increase was sharper lower the spacer chain length. This is due to the fact that with a lower spacer chain length, the headgroup area is smaller that leads to more orderly packing in the micelle (i.e., micellar growth) resulting in sharp viscosity changes. Addition of KBr to 30 mM surfactant solutions again shows that viscosities are much higher with geminis (of lower spacer length) in comparison to CTAB. Addition of *n*-alcohols and *n*-hexylamine also causes increase in viscosity of 30 mM 16-4-16 solutions. However, the increase was more with *n*-hexanol which can be understood in the light of hydrophobic ranking of the two types of additives. A combined presence of KBr and either of the alcohols or *n*-hexylamine shows a synergistic effect on the viscosity increase of 16-4-16 solution. This increased effectiveness of the organic additives in presence of added KBr has been discussed in terms of electrostatic and hydrophobic forces operating in the solution. The data allow to conclude that in micellar growth the presence of a salt and organic additive produces favorable conditions which are absent when the additive is present singly.

Keywords: Geminis; Viscosity; Organic additives; Salt; Micelles

1. Introduction

Surfactant molecules produce various morphologies of aggregate(s) when they are dissolved in aqueous media above a certain concentration [1]. At the molecular level, a balance of interfacial forces controls the curvature of the surfactant film which, in turn, determines the shape of the surfactant aggregates. The molecular architectures of surfactants profoundly influence the properties of these surfactants. Towards this end, a new class of surfactants (known as ‘gemini’ surfactants) has been introduced to the scientific world in the recent past [2,3]. Gemini surfactants comprise of two amphiphilic moieties connected at the level of headgroups by a suitable spacer [4,5]. In the last decade, interest in geminis has swelled because of their far better properties like lower critical micellar concentration (cmc), higher viscoelasticity and enhanced propensity for lowering the air/oil–water interfacial tension in comparison to their conventional counterparts [2,3,6,7]. Geminis have already shown promise in various potential areas of surfactant applications [3].

The rising demand for newer materials with improved and novel properties has changed the emphasis to studies of surfactant–additive systems. As of today, in most of their applications, surfactants with additives (combinations such as surfactant–surfactant, surfactant–electrolyte, surfactant–polymer, and surfactant–cosurfactant), rather than pure, are preferred. As such systems often exhibit exceptional properties through synergism [8–13], studying the properties of surfactant–additive systems would, therefore, be of great relevance to cope with the ever increasing demand of surfactant

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systems for diverse fields of life. In this direction, we have been involved in studying the effect of a variety of additives (salts, denaturants, cosurfactants, hydrocarbons, aromatic acids, etc.) on the solution (consolute behavior) and association properties (micellization, sphere-to-rod transition (s → r), micellar growth/destabilization) of monomeric surfactant systems using viscometry, cloud point measurement, small-angle neutron scattering (SANS), dynamic light scattering (DLS) [14–23], etc. The findings of the study involved two new problems: (i) "is there any synergism when additives are present simultaneously", and (ii) "can an additive be used as an effective 'weapon' to produce synergism in a surfactant system?" It has been demonstrated that the viscosity increased with the increase of (additive) and that the magnitude of viscosity was substantial when organic additives were added in the presence of an inorganic salt. Surfactant solutions containing spherical micelles are of isotropic nature and of low viscosity [24] whereas presence of rod-shaped micelles imparts higher viscosity to the solution [25,26]. The findings based on viscosity results were well supported by SANS [14,16,17] and DLS measurements [22,23].

A vast majority of experimental data are available on solution/aggregational behavior of conventional surfactants in presence of different class of additives. However, this is not the case with the gemini surfactants. All the generalization of conventional surfactants are not followed by geminis, e.g., cmc's can be higher for longer chain geminis than for shorter chain counterparts (just the reverse of normal conventional case) [27]. Studies of solubilization of organic compounds in gemini micellar solutions are still scarce [28,29]. Addition of KBr to a solution of gemini surfactant brought about the formation of a lamellar phase followed by phase separation [30]. Apart from above scanty reports, no systematic attempt has been made to study the effect of additives on gemini micellar solutions. All these facts prompted us to study the effect of salt (KBr) and/or organic additives (*n*-butanol, *n*-pentanol, *n*-hexanol, *n*-hexylamine) to extend our understanding of the synergistic effect in gemini micellar solutions using viscosity measurements. Measurements were also performed with a conventional surfactant (cetyltrimethylammonium bromide, CTAB) for comparison purposes.

2. Experimental

2.1. Materials

Cetyltrimethylammonium bromide (CTAB, 99%), *N*,*N*-dimethylhexadecylamine (≥95%), 1,4-dibromobutane (≥98%), 1,5-dibromopentane (≥98%), 1,6-dibromohexane (≥97%) were purchased from Fluka. Potassium bromide (KBr, 99%) was from E. Merck (India), while all the alcohols (*n*-butanol, C_4OH; *n*-pentanol, C_5OH; *n*-hexanol, C_6OH) were BDH (Poole, England) 'high purity' chemicals and were used as supplied. The *n*-hexylamine (C_6NH_2) of 'purum grade' was obtained from Fluka (Buchs, Switzerland). Water was distilled twice over alkaline $KMnO_4$ in an all-glass still.

The gemini surfactants were obtained by refluxing the corresponding α,ω-dibromoalkane ($Br(CH_2)_sBr$, $s = 4, 5, 6$) with *N*,*N*-dimethylhexadecylamine in dry ethanol for 48 h. The solvent was removed under vacuum from the reaction mixture and the solids thus obtained were recrystallized from hexane/ethylacetate mixture for at least thrice to obtain pure compounds. The overall yields of the surfactants ranged from 70 to 90%. All the three geminis gave ^{1}H NMR spectra and elemental analyses data consistent with their assigned structures [31].

2.2. Methods

The critical micelle concentrations (cmc's) were determined at 30 °C by conductometry using ELICO (type CM 82T) bridge equipped with platinized electrodes (cell constant = 1.02 cm^{-1}). Plots of specific conductance versus surfactant concentration gave sharp breaks corresponding to cmc(s); 2.83×10^{-5}, 3.63×10^{-5}, 4.37×10^{-5} M for 16-4-16, 16-5-16, 16-6-16, respectively, which very well match with the literature values [31].

The viscosity measurements were carried out by using a Ubbelohde viscometer thermostated at 30 ± 0.1 °C. At higher additives/salt concentrations, viscosities were dependent on rate of flow. Viscosities of such solutions under Newtonian flow conditions were obtained as described elsewhere [16]. Density corrections were not made since these were found negligible [32].

3. Results and discussion

Fig. 1 shows the variation of relative viscosity ($\eta_r = \eta/\eta_0$, η and η_0 represent the viscosities of surfactant solution and solvent water, respectively) with surfactant concentration. We can see that η_r increases with all the surfactants but the increase is significant with geminis in comparison to CTAB. Higher viscosities with smaller spacer chain reflects the ability of gemini surfactants of short spacers to give rise to rod-shaped micelles at fairly low concentrations. Similar type of behavior was observed

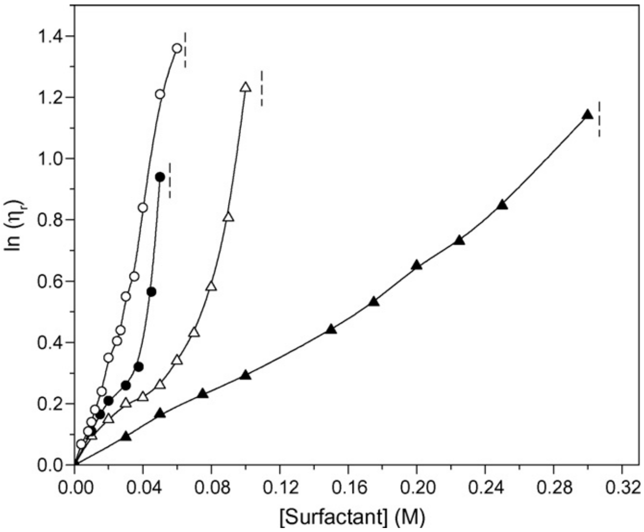

Fig. 1. Variation of ln(η_r) with the [surfactant] at 30 °C (up to the solubility limit indicated by dotted lines): 16-4-16 (○); 16-5-16 (●); 16-6-16 (△); CTAB (▲). Lines are drawn as a guide to the eye.