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Determination of critical micelle concentration of cetyltrimethylammonium bromide in presence and absence of KCl and NaCl in aqueous media at room temperature by viscosity measurement

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Abstract

Viscosity measurement of cetyltrimethylammonium bromide in presence and in absence of KCl and NaCl in aqueous media is done. The results showed a sharp increase in viscosity with increase in concentration of cetyltrimethylammonium bromide. Also, the viscosity increases with addition of salts. The viscosity of cetyltrimethylammonium bromide is found more in presence of KCl than NaCl in aqueous media. In presence of monovalent salts, the critical micelle concentration (cmc) value decreases which is explained on the basis of nature and ionic strength of the added ion. The graphs of viscosity versus concentration are used in determining the critical micelle concentration (cmc).

Keywords: Cetyltrimethylammonium bromide; Viscosity; Critical micelle concentration.

1. Introduction

Surfactant solutions exhibit complex behavior even at equilibrium. Above a critical micelle concentration, several tens of surfactant molecules aggregate to form micelles since the formation of micelles is entropically favorable as compared to a system of unassociated surfactant molecules in solution [1]. Micelles could exist in various shapes such as cylindrical, spherical or lamellar depending on the temperature and surfactant concentration in solution [1-6]. Micelle formation of a surfactant in solution is induced by the hydrophobic interaction between hydrocarbon parts of the surfactant molecules balanced by their hydration and electrostatic repulsive effects [7]. Cationic surfactants offer some additional advantages over other class of surfactants [8–11]. These substances besides their surface activity do show antibacterial properties and are used as cationic softeners, lubricants, retarding agents and antistatic agents and in some cases consumer use.

Aqueous solution of CTAB becomes extremely viscous on addition of small quantity of sodiumsalicylate (NaSal). The viscosity of 0.1M CTAB with 0.03M NaSal is about 10^{17} centi- poise. A similar increase in viscosity is observed with addition of KCl, KBr or NaCl with five times higher concentration [12]. The mechanism responsible for this large change in viscosity is expected to be different in two cases [13, 14]. Like all other surfactants CTAB also shows a rapid change in viscosity when the physical and chemical compositions of the solution are changed. This rise in viscosity has been mainly attributed to the change in the structure of the CTAB micelles depending upon the ambient condition to which it has been subjected. The structure change from spherical to rod like phases have been predicted [15]. In order to understand these phenomena considerable research studying have been done and reported. The cmc of CTAB depends directly upon the solvent and it has been determined by Berr [13] that CTAB forms large micelles in D_2O than in H_2O. The effective factors, such as the addition of electrolytes, buffer pH, temperature, addition of organic modifiers, ionic strength of the aqueous solution, and presence of additives can change the cmc value from that determined in pure water [16-18]. Addition of electrolyte in the surfactant solution decreases the cmc value [19]. Addition of an electrolyte causes a reduction in the thickness of ionic atmosphere surrounding the polar head groups which consequently decreases repulsion between them, because of the electroviscous effect which will be absent at high ionic strength. The lower the ionic strength thicker the particles diffuse layer and more evident the effect of reduced viscosity in absence of salt. Addition of surfactant to solutions lowers the viscosity dramatically [20-27]. Abuin and Scaiano [28] showed that this viscosity reduction is far stronger than the simple charge screening resulting from the addition of monovalent salt.

In this paper, we report a study of the aggregation process of CTAB at room temperature in absence and in presence of KCl and NaCl by viscometric method in aqueous media.

2. Experimental

The viscometric measurements were performed at room temperature using an Ostwald viscometer. Several independent solutions were prepared, and runs were performed to ensure the reproducibility of the results. To check whether the reduced viscosities depend on the shear rate in the concentration range investigated. This did not lead to different values of the reduced viscosity. Solvent medium from those of the surfactant solutions in presence and absence of salt was taken. The viscometer was always suspended vertically at room temperature. The viscometer was cleaned and dried every time before each measurement. The flow time for constant volume of solution through the capillary was measured with a calibrated stop watch.

The coefficient of viscosity of a given liquid can be calculated according to the following equation:

$$\eta_1 = \left(\frac{d_1}{d_2}\right)\left(\frac{t_1}{t_2}\right)\eta_2 \qquad (1)$$

η_1 = coefficient of viscosity of the solution
η_2 = coefficient of viscosity of the solvent
t_1 = time flow of the solution
t_2 = time flow of the solvent
d_1 = density of the solution
d_2 = density of the solvent

The density of any one solution must be known which is calculated by using the expression:

$$d_1 = \left(\frac{w_1}{w_2}\right) d_2 \qquad (2)$$

d_1 = density of liquid
d_2 = density of water
w_1= weight of liquid
w_2= weight of water

Cetyltrimethylammonium bromide (CTAB), KCl and NaCl were used as purchased from Loba Chemical, India. The water used in the experiments was doubly distilled. The solutions prepared at room temperature.

3. Results and Discussion

The specific viscosity increase with increase of concentration of CTAB and there is a pronounced break and then remains constant. The breaking point is known as critical micelle concentration, cmc (Fig. 1-3). Our results indicate that there is increase in viscosity with increase in concentration of salt added.

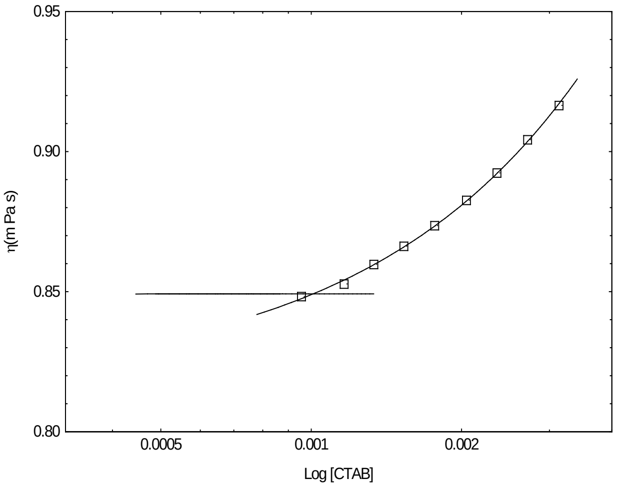

Fig. 1

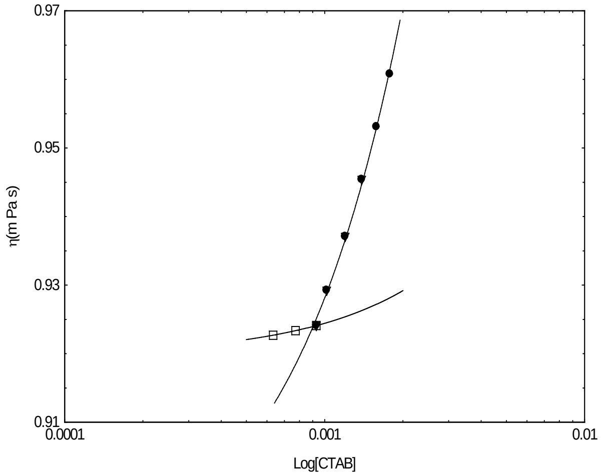

Fig. 2

Figure 1: Viscosity of CTAB in pure water as a function of the surfactant concentration.
Figure 2: Viscosity of CTAB in presence of NaCl as a function of the surfactant concentration.

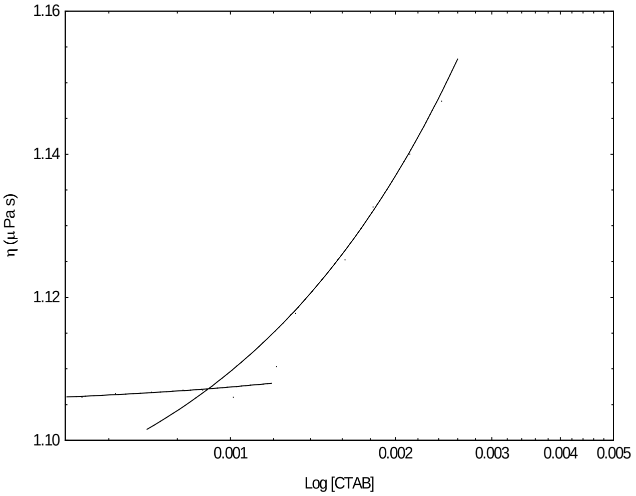

Figure 3: Viscosity of CTAB in presence of KCl as a function of the surfactant concentration.

The viscosity of CTAB in presence of KCl is more than in presence of NaCl(Table1), this is because while NaCl is absorbed on the surface of the micelle, KCl remains in the bulk of the solution [29]. Addition of salt is known to decrease cmc of the solution [1]. Increasing the salt concentration reduces the electrostatic Debye screening length around the surfactant, which encourages the formation of longer micelles at equilibrium. This, in turn contributes to the changes in cmc. Fujio (1998) [30] found that spherical micelles associated to form into rod-like micelles when salt concentration exceeded a threshold concentration. Salts decrease the cmc of surfactant in the order: NaCl<KCl [31]. Here Na^+ is least effective in decreasing the cmc due to small size and large hydrated radius and would act as a water-

structure promoter decreasing the availability of water to the micelles. Therefore, upon addition of NaCl and KCl; KCl is more effective in reducing the cmc. Hence in our case KCl decrease the cmc more than NaCl(Table 2).

Table 1: Viscosity of cetyltrimethylammonium bromide in pure water and in presence of NaCl and KCl at room temperature

Solvent	Concentration (mol/l^{-1})	Viscosity [η (mPa.s)]	Solvent	Concentration (mol/l^{-1})	Viscosity [η (mPa.s)]
Pure water	0.003150	0.9164	KCl	0.002400	1.1474
	0.002713	0.9042		0.002100	1.1400
	0.002355	0.8924		0.001800	1.1326
	0.002045	0.8826		0.001594	1.1258
	0.001762	0.8756		0.001314	1.1167
	0.001533	0.8683		0.001174	1.1114
	0.001335	0.8597		0.000829	1.1068
	0.001164	0.8527		0.000773	1.1069
	0.001031	0.8478		0.000725	1.1064
	0.000865	0.8492		0.000649	1.1072
	0.000749	0.8492		0.000553	1.1066
	0.000650	0.8492		0.000465	1.1056
	0.000563	0.8492			
	0.000488	0.8492			
NaCl	0.002014	0.9743			
	0.001787	0.9629			
	0.001592	0.9543			
	0.001392	0.9449			
	0.001205	0.9357			
	0.001029	0.9273			
	0.000877	0.9204			
	0.000775	0.9200			
	0.000649	0.9194			

Table 2: Critical micelle concentratiom (cmc) obtained from viscosity methods of cetyltrimethylammonium bromide in pure water and presence of NaCl and KCl at room temperature

T (K)	Water *cmc* (mM)	0.01 mol.L^{-1} NaCl *cmc* (mM)	0.01 mol.L^{-1} KCl *cmc* (mM)
301.15 K. (Room temperature)	0.99	0.90	0.78

4. Conclusion

The following conclusions have been drawn from above results and discussion. The results showed an increase in viscosity of cetyltrimethylammonium bromide with addition of salts. The viscosity of cetyltrimethylammonium bromide is found more in presence of KCl than NaCl in aqueous media whereas in the presence of KCl, the cmc of cetyltrimethylammonium bromide decreases more in comparison with presence of NaCl.

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