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Solution and foaming properties of mixed aqueous solution of CTAB-Triton X-100

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The critical micelle concentrations (CMC) of mixed aqueous solution of cationic surfactant cetyltrimthylammonium bromide (CTAB) and nonionic surfactant polyoxyethylene *t*-octylphenol (Triton X-100/TX100) have been determined conductometrically at 35, 40, 45 and 50°C. The mixtures used are of various composition ratios of CTAB and TX100. The degree of ionization (α) of the mixed micelle has been computed from the slope of conductance versus concentration (C) plot above and below CMC. Foaming efficiency and viscosity of mixed surfactants have been measured at 45°C. Wetting property of the above systems has also been studied. The concentration of TX100 is kept constant and that of CTAB changed.

Pure surfactants are very rarely used in industry and are also very rarely found in biological systems. In most products and processes more than one surfactant is used to get the required result[1]. Ionic surfactants of like charges form stable mixed micelle at all ratios[2]. A number of solution properties of mixed surfactant system have been studied. Funasaki *et al.*[3] and Ingram[4] studied the mixed system by surface tension measurement. Nishikido[5] has used solubilization technique. Fokiwa *et al.*[6] and Bansal *et al.*[7] have used NMR; Lange *et al.*[8] and Heyer *et al.*[9] used conductance measurements. In mixed surfactant systems a sudden change in the physical properties as a function of concentration as in pure surfactant systems, is also observed. The concentration at which such changes occur is termed critical micelle concentration (CMC) of the mixed micelle[10]. Foaming is a property which is inherent to all surfactant solutions. The phenomenon of foaming is made use of in nature, industries and it also has domestic applications[11,12]. Surface active agents play a major role in a lot of applications e.g. to improve wetting of a surface, to stabilize emulsion and as detergent. Literature survey indicates that though there are many studies of mixed surfactant systems still more work is needed. Hence we thought of studying the behaviour of mixed surfactants in aqueous solutions. The critical micelle concentration (CMC), foaming efficiency, viscosity and wetting are some of the properties that we have studied and the results are presented here.

Materials and Methods

Cetyltrimethylammonium bromide (CTAB) from National Chemicals, Baroda was recrystallized thrice from acetone and dried at 100°C for 48 h before use. Polyoxyethylene *t*-octylphenol (Triton X-100/TX100) was from Koch Light Labs (England) and was used as received. Iodine (A.R. Sarabhai Chemicals) was resublimed before use. Water was doubly distilled and its specific conductance was ~ 3 × 10^{-6} S cm^{-1}. Teflon tape was obtained from Samson (India) and its surface was washed with chromic acid and water and dried before use.

The critical micelle concentration (CMC) of CTAB-TX 100 mixed system was determined conductometrically. A Mullard conductivity bridge (England) with a dip-type cell was used. The cell constant was 0.1417 cm^{-1}. Two procedures were followed for the conductance measurement. In the first method, the concentrated surfactant solution was diluted by adding known volume of solvent. In the second method, the concentration of surfactant solution was gradually increased by adding

Table 1—CMC of CTAB-TX 100 mixed systems at various temperatures in aqueous solution. The values in parentheses are α, the degree of ionization of micelle

CTAB/TX 100	CMC (mM) at				$-\Delta G^\circ_m$ (kJ/mole) at 318 K
	308	313	318	323 K	
10:0	1.04(0.322)	1.177(0.13)	1.2(0.166)	1.23(0.228)	32.8
9:1	0.91(0.27)	0.97(0.36)	1.04(0.399)	1.1(0.319)	29.7
7:3	0.81(0.567)	0.94(0.46)	0.99(0.54)	1.06(0.679)	28.1
5:5	0.64(0.78)	0.76(0.64)	0.84(0.7)	1.01(0.414)	26.9
3:7	0.46(0.88)	0.72(0.92)	0.8(0.83)	0.91(0.546)	25.8
1:9	0.45(0.776)	0.66(0.81)	0.8(0.77)	0.88(0.79)	30.7
0:10	0.234	0.225	0.216	0.199	32.9

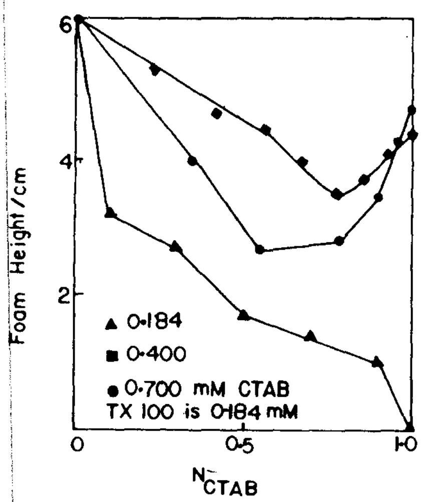

Fig. 1—Plot of foam height versus mole fraction of CTAB solution of various concentration in 4 ml mixtures (TX 100 is 0.184 m*M*). ▲ 0.184; ■ 0.4; ● 0.7 m*M* CTAB. Mole fraction of CTAB is mole of CTAB/(Mole of CTAB + mole of TX 100)

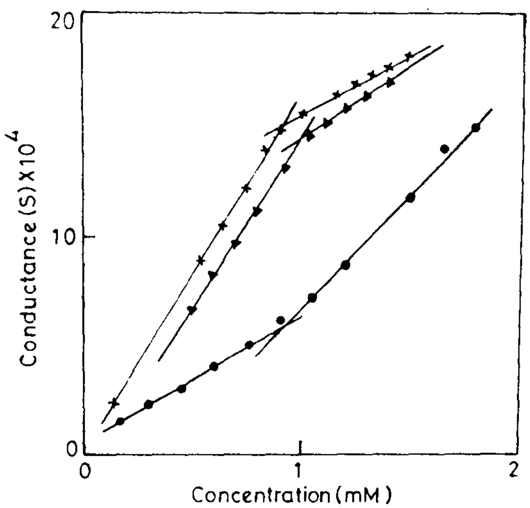

Fig. 2—Conductance versus concentration plots of mixed CTAB - Triton X 100 systems. × at 35°C (CTAB (9): TX100 (1)); ▲ at 50°C (CTAB (1): TX100 (1)); ● at 50°C (CTAB (3): TX100 (7))

concentrated solution with a microsyringe. By both methods same results were obtained. Conductance measurements were done at constant temperatures of 35, 40, 45 and 50°C (±0.05). The CMC of nonionic TX 100 was measured by iodine solubilization method [13] as discussed earlier using spectronic 20 colorimeter at the temperatures mentioned above.

Foaming efficiency

For foaming efficiency of surfactant mixtures, the initial foam height was measured. The foam was produced by blowing air into the surfactant solution in a graduated cylinder of internal diameter 1.55 cm. The blow time was ~ 12-14 s. All measurements were done at 45°C. Foam height was also measured for some systems with a Ross & Miles equipment[1]. The results obtained by both methods were same. The readings were repeated a few times to check on the reproducibility. The initial foam height values (Fig. 1) are with ± 2% error.

Contact angle measurement

Contact angle of the system was measured with the help of contact 'θ' meter[14]. The surfactant solution drop was placed on a very clean teflon surface. All readings were checked for reproducibility. The error in the contact angle was ± 2°. All measurements were done at room temperature. The drops were made with the help of a syringe. Viscosity of the surfactant solution was measured with the help of an Ubbelohde viscometer at constant temperature (45°C). Density of the surfactant solutions was determined with a pyknometer.

Results and Discussion

Figure 2 shows the representative plots of conductance versus concentration of CTAB - TX 100 mixed system. The point of intersection was taken as the CMC for that particular system. In the case of TX 100, the absorbance was plotted against concentration and the break point was taken as CMC. The TX 100 CMC tallies well with literature[15]. The

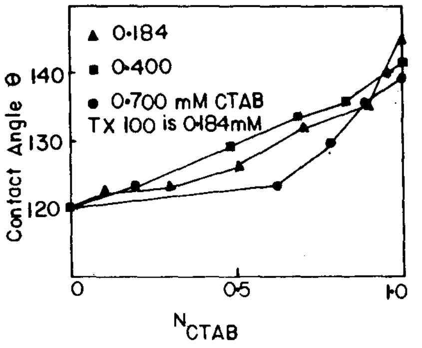

Fig. 3—Plot of contact angle versus mole fraction of CTAB in 1 ml mixtures (TX100 is 0.184 mM); symbols same as Fig.1 (mole fraction of CTAB was calculated as above)

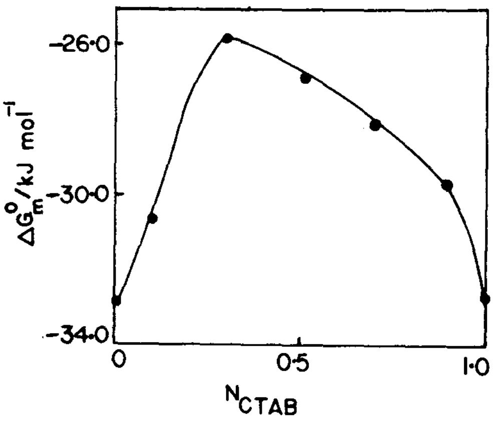

Fig. 4—Plot of ΔG°_{m} (kJ mol^{-1}) versus mole fraction of CTAB at 318 K

CMC of the mixed systems and pure surfactants at various temperatures are listed in Table 1. These data show that CMC increases with increase in temperature. This is quite common in the case of ionic surfactants as micellization is due to hydrophobic interaction[1]. As temperature increases the mobility of molecules increases and hence higher concentration is required for the cluster formation. But in the case of nonionic surfactants CMC decreases with increase in temperature, due to coiling of hydrocarbon chain as well as due to the absence of the repulsive force. In mixed system CMC increases with increase in temperature, indicating that the system behaves more like ionic surfactant.

The degree of ionization of mixed micelles (α) was computed from the slope of conductance versus concentration plot above and below the CMC[16]. The ratio of the two slopes is equal to the degree of ionization, α. These are listed in Table 1. The degree of ionization of micelle does not show any regularity either with temperature or with composition. The composition effect is due to the micellar geometry. The temperature has no regular effect which indicates that the mixed micelle is ionic and its composition changes with temperature depending upon the bulk composition.

Figure 1 shows the plot of initial foam height against the CTAB mole fraction (N_{CTAB}) in various mixtures. The concentration of CTAB solution was varied (0.7 mM, 0.4 mM and 0.184 mM) though TX100 concentration was kept at 0.184 mM. All concentrations are well below the CMC of individual surfactants. From the plot it can be concluded that for the system where various volumes of 0.184 mM TX100 was mixed with 0.184 mM CTAB, the foam height of the mixtures was higher than that of CTAB solution. However, as the amount of CTAB increases, the foam height increases (mole fraction CTAB 1.0). With reasonably higher CTAB concentration the foaming of the mixed systems are lower than either of the pure surfactant whereas at low CTAB concentration foaming increases with more TX 100. However, no linear relation was observed. These systems show that at higher CTAB concentration there is reduction in foaming efficiency. One can conclude that foaming efficiency is the function of both the amount and mole fraction of the surfactants.

The viscosity of mixed system CTAB-TX 100 at 45°C was determined. It was observed that the viscosities of the surfactant solutions were almost same (for these compositions) as that of pure water. This indicates no significant structural changes in micellar systems within the present concentration range studied.

Figure 3 shows the plot of contact angle versus mole fraction of CTAB. The contact angle of CTAB solution was higher than that of TX 100. In mixed system contact angle increased with increase in amount of CTAB. However, the contact angle study shows that the wettability of the teflon surface does not change much whether surfactants used are pure or mixed. As the amount of CTAB increased, the contact angle of solution decreased as reported earlier[17]. As is true for foam height, the contact angle also is somewhat dependant on the amount and mole fraction of the surfactant.

The Gibbs free energy of micellization can be calculated by using relation[16]

$$\Delta G_m^{\circ} = (2-\alpha)\, RT \ln a_{\pm cmc} \quad \ldots (1)$$

where $a_{\pm \mathrm{cmc}}$ is the mean activity of the surfactant and α is the degree of micelle ionization as mentioned earlier (Table 1). The standard state is assumed to be the hypothetical system where $a_{\pm \mathrm{cmc}}$ is unity. The value of $a_{\pm cmc}$ was calculated using the Debye-Huckel limiting law for the ionic component of the surfactant i.e. $\log \gamma_{\pm cmc} = -A\sqrt{I}$ where I is the ionic strength. The product of $\gamma_{\pm cmc}$ with cmc (i.e. concentration) gives the $a_{\pm cmc}$. For nonionic TX 100, the $\triangle G^{\circ}_{m} = RT \ln \mathrm{CMC}$ (ref.13). In Table 1, the $\triangle G^{\circ}_{m}$ at 318 K is presented for all mixed systems. In Fig.4 a plot of $\triangle G^{\circ}_{m}$ against N_{CTAB} is given. It is quite obvious that the mixed micelle formation is relatively more unstable than pure micelles (maximum in the curve). However, the micelle formations are favoured in absolute terms.

It can be concluded from the above observations that the mixed micelle of CTAB-TX 100 mixed system in aqueous solution behaves as ionic. At higher concentrations of CTAB, the above system shows lower foaming than either of individual surfactants. At very low concentration the (i.e. well below the CMC) systems do not show any structural changes. The foaming and wetting properties are dependant on both mole fraction and amount of surfactant. The formation of micelles are preferred though mixed micelles are relatively less preferred.

Acknowledgement

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