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MIXED MICELLES OF *N*-ALKYLPYRIDINIUM BROMIDE AND TRITON X-100 IN AQUEOUS MEDIA

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ABSTRACT

The mixed micellization process of binary mixtures formed by *n*-alkylpyridinium bromide including tetradecylpyridinium bromide ($C_{14}PB$), dodecylpyridnium bromide ($C_{12}PB$), decylpyridinium bromide ($C_{12}PB$) and *tert*-octylphenylpolyoxyethylene ether (Triton X-100) was examined, by surface tension method. The mixed CMC (C*) values were determined and in all cases a negative deviation from the ideal behavior was observed. However, the interaction parameter (β) as given by regular solution theory (RST) was found to be dependent on the micellar composition.

Key words : Micelles, Triton-x-100, N- Alkylpyridinium bromide

INTRODUCTION

In most practical applications, mixtures of surfactants, rather than individual surfactants, are used purposely, or unavoidably in the case of some commercial surfactants. The behavior of a mixture is often quite different from that of a single surfactant, and in some cases, synergistic effects are observed[1,2]. One method of decreasing the environmental impact of surfactants is to use mixtures of known surfactants whose inter-facial properties exhibit synergism. Consequently, lower quantities of surfactants are required to gain the same effect or performance for the mixture with synergism than without synergism.

There is a rich background of information available on surfactant mixing, as a result of classical measurements such as surface tension[3], the extensive thermodynamic descriptions, such as regular solution theory, (RST)[4], and the more recent but related theoretical approaches[5,6] . In recent years, new experimental developments, such as the application of the neutron scattering techniques of reflectivity[7], small angle scattering[8], NMR[9], second harmonic generation, sum frequency[10,11] and atomic force microscopy

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(AFM)[12], have created a newer interest.

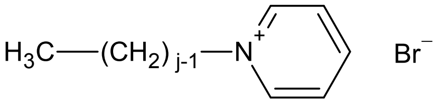
The phase behaviour of cationic and anionic surfactant mixtures has been studied extensively in recent years[13-15]. Although most of the mixed systems investigated are concerned with mixtures of anionic and nonionic surfactants, those formed by cationic-nonionic mixtures are also interesting from both; fundamental and practical points of view. For example, pure cationic surfactants are poor detergents since they neutralize the negative charges on fibers or solutes but it has been shown that this property can be improved by using a cationic-nonionic mixture[16-18].

The present paper reports that marked synergistic phenomena in surface activity as well as in micellization were found for three combinations of a typical cationic surfactant *n*-alkylpyridinium bromide with *tert*-octylphenylpolyoxyethylene ether (Triton X-100) by means of surface tension measurements.

EXPERIMENTAL

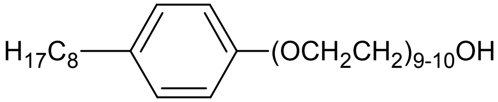
Materials and methods

The cationic surfactant tetradecylpyridinium bromide ($C_{14}PB$), dodecylpyridinium bromide ($C_{12}PB$) and decylpyridinium bromide ($C_{10}PB$) were synthesized in our laboratory and were recrystallized five times from acetone before use. The chemical structure of *n*-alkylpyridinium bromides is -



***n*-Alkylpyridinium bromide (*j* = 14, 12 and 10)**

The nonionic surfactant Triton-X-100 is a *tert*-octylphenlypolyoxyethylene ether and it was obtained from Sigma Chemical Company, U.S.A. Its structure is as follows:



Triton X-100

Triple-distilled water (conductivity = 10^{-6} S cm^{-1}, surface tension = 71.8 mN m^{-1} at

30^0C) from an all-pyrex glass apparatus was used for the preparation of solutions.

Surface tension measurements were carried out by a modified drop volume method using an 'Agla' micrometer syringe (Burroughs Welcome Co., London). The tip (radius 0.191 cm), determined using a cathetometer of the syringe, was immersed in a dry test tube. The drops were developed in about three minutes time; more time was given after 80% of the drop size was formed. The drop acquires equilibrium within this time as no ageing effect was seen. The volume of a single drop was averaged from five to six measurements. Surface tension for different concentrations of surfactant was calculated using the following equation:

$$\gamma = \frac{V\,(d_1 - d_2)}{r} \times g\,f \qquad \ldots(1)$$

Where, V is the measured volume of a single drop, r is the radius of the tip, g is the acceleration due to gravity, d_1 and d_2 are the densities of aqueous phases, respectively. f is the volume correction factor for the radius of dropping tip given by Harkins and Brown[19] which depends upon V/r^3 values. For studies at air-water interface, d_2 the density of vapour phase was neglected. The surface tensions for pure air-water interface at 30^0C were close to the literature values. The surface tension data were reproducible to ± 0.3%.

RESULTS AND DISCUSSION

The critical micelle concentrations (CMC) of n - alkylpyridinium bromide (C_{j-1}PB) and Triton X-100 surfactant at 30^0C are given in Table 1.

Table 1: Critical micelle concentration of n-alkylpyridinium bromide and Triton X-100

Surfactant	CMC (mM)
C_{14}PB	3.5
C_{12}PB	11.1
C_{10}PB	40.2
Triton X-100	0.5

Since ionic surfactants repel each other and that is why the CMC of an ionic surfactant is higher than the CMC of a nonionic surfactant.

The nature and strength of interactions between two surfactants may be decided by calculating the values of interaction parameter β. According to Clint[20], if two surfactants are mixed, the ideal *CMC* of the mixed system can be predicted by following equation

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{(1 - \alpha_1)}{C_2} \qquad \ldots(2)$$

Where α_1 stands for the mole fraction of surfactant 1 in the mixture; and C_1, C_2 and C^* represent the *CMC* of surfactants 1, 2, and that of the mixed system, respectively. It is usually noticed that experimental values for mixed surfactant systems seem to deviate from those calculated by using equation (2). The nonideality in mixed micelle formation was taken into account by Rubingh[4] by means of his regular solution theory (RST), which takes into consideration the activity coefficients f_1 and f_2 of surfactants 1 and 2 involved in micellization. This way, the *CMC* of mixtures can be calculated as:

$$\frac{1}{C^*} = \frac{\alpha_1}{f_1 C_1} + \frac{(1 - \alpha_1)}{f_2 C_2} \qquad \ldots(3)$$

For ideal behavior $f_1 = f_2 = 1$, and equation (3) becomes equation (2). On the basis of Rubingh's theory[4], X_1, the mole fraction of surfactant 1 in a mixed micelle, can be calculated from the following equation:

$$\frac{X_1^2 \ln\left[\dfrac{C^*\alpha_1}{C_1 X_1}\right]}{(1 - X_1)^2 \ln\left[\dfrac{C^*(1 - \alpha_1)}{(1 - X_1)C_2}\right]} = 1 \qquad \ldots(4)$$

Substitution of the value of X_1 into equation (4) gives the value of interaction parameter β for each mole fraction.

$$\beta = \frac{\ln\left[\dfrac{C^*\alpha_1}{C_1 X_1}\right]}{(1 - X_1)^2} \qquad \ldots(5)$$

The value of β is a measure of the extent of interaction between the surfactants leading to their deviation from ideal behavior. The negative values suggest synergism whereas positive values indicate antagonism.

In cationic-nonionic surfactant mixtures, C* values observed experimentally are below than those obtained using ideal theory. The negative β value for these systems indicates that unlike interaction (cationic-nonionic) prevails over the like interactions in pure micelles. For the *n*-alkylpyridinium bromide + Triton X-100 systems, negative values of β indicate synergistic interactions. Scamehorn[21] reported that in nonionic surfactants consisting of ethylene oxide (EO) groups, oxonium ions are formed in the hydrophilic portion of the surfactants. Existence of synergism in our systems indicates that oxonium ions are too few to effect any substantial intramicellar head group repulsion.

A remarkable aspect observed in all the systems is that variable (β values at different compositions of the system were obtained. Specifically, we have found that β values becomes less negative as the mole fraction of the co-surfactant increases. This is explained by the repulsive interactions of the head groups of the *n*-alkylpyridinium bromide surfactants in the stability of the mixed systems. In fact, the interaction of a nonionic surfactant monomer between two ionic monomers shields the repulsive interactions between them, improving the electrostatic stabilization of the mixed micelle. Desai and Dixit[22] have found similar variations of β with the composition in mixtures composed of cationic and polyoxyethylenic non-ionic surfactants. They have explained this effect on the basis of repulsive interactions between the head cationic groups and oxonium ions formed in the hydrophilic moiety of the nonionic surfactant. The β_{AVe} values are - 3.5 for C_{10}PB -Triton X-100, - 2.28 for C_{12}PB.-Triton X-100 and - 2.2 for C_{14}PB - Triton X-100, respectively. The negative value of the interaction parameter (β in the Triton X-100-*n*-alkylpyridinium bromide system was attributed to the ability of POE chains of Triton X-100 to envelope the n-alkylpyridinium group. The negative interaction parameters and its absolute values (- 3.5, - 2.28 and - 2.2) also suggest a special interaction, which is far superior to the hydrophobic interaction between hydrocarbon chains.

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