



Vanillin based cationic surfactants mixed systems: Micellization and interfacial interaction behaviors in presence of nonionic conventional surfactant



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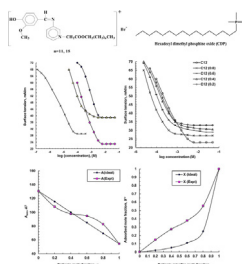
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HIGHLIGHTS

- Mixing of cationic and nonionic improves surface activity.
- Large contribution of cationics in micellar form was observed than the expected.
- Synergistic interaction appeared for the mixed micelles due to negative β^m .
- Low ΔG_{ex} values indicated the stability of the formed mixed micelles.

GRAPHICAL ABSTRACT



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ABSTRACT

The micellization and interfacial interaction behaviors of two cationic vanillin-based surfactants in presence of cetyl dimethyl phosphinate (CDP) were investigated at various molar ratios. Surface tension measurements were used to obtain the critical micelle concentration (CMC) values of the studied surfactants, these CMC values were obtained as functions of the composition. The mixed systems data were analyzed according to the regular solution model developed by Rubingh for mixed micelles. Two interaction parameters were obtained for each system, the interaction at the interface, and in the micellar phase. The properties of the mixed systems at interface and in bulk of the solutions were correlated to the individual surface properties of each surfactant. Results showed that the chemical structure and initial molar ratio of the cationic surfactants in the mixed systems affect their partitioning in the mixed micelles and adsorbed mixed monolayers. Negative interaction parameters of the systems in the bulk (mixed micelles) and at the interface (mixed adsorbed monolayer) indicate the synergism of the mixing process.

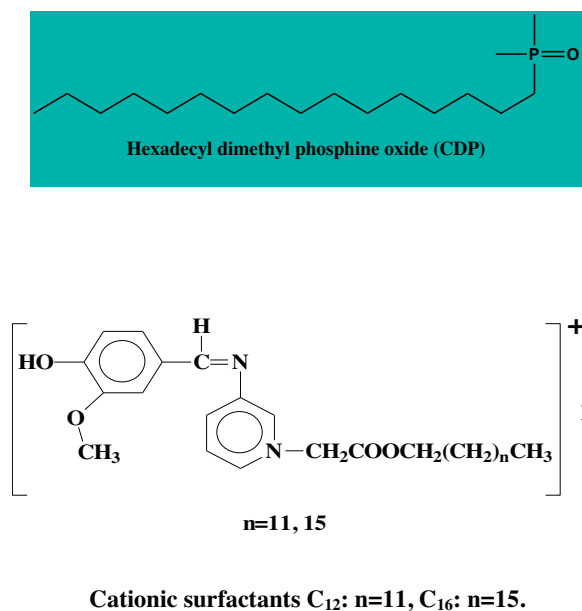
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1. Introduction

Industrial surfactant systems are typically mixtures of different chemical species such as ionic and nonionic surfactants,

electrolytes, dyes and fillers. Some of these species are added to obtain beneficial synergistic effects and others to control ionic strength, pH, viscosity and other physicochemical properties of the system [1,2]. Thus, in theory, desirable surface properties for specific applications can be obtained by adjusting the compositions of these systems. However, choosing an appropriate surfactant system requires an understanding of the adsorption phenomena in these systems as well as the interactions between molecules adsorbed at the interface. In other words, a theoretical model of

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Scheme 1. Chemical structures of the cationic and nonionic surfactants.

the adsorption process in mixed systems is required. Elaboration of such a model is no easy task due to the complexity of such systems. Previously, ionic–nonionic surfactant mixtures have been analyzed first by using an ideal solution model [3] and the micelle or the surface layer is treated explicitly as a separate phase with a composition distinct from that of the bulk [4]. Then, to better model these systems, nonideality of mixing has been taken into consideration by applying regular solution theory [5–8]. In previous work, ionic–nonionic surfactant mixtures were described by considering two effects not accounted for in regular solution theory, namely non-random mixing in the formation of mixed micelles and the effect of head group size [9]. Recently, several molecular thermodynamic theories have been developed for predicting the properties and interactions of binary surfactant systems [10–13]. Many studies have examined adsorption and micelle formation in binary mixtures of surfactants [14–18]. On the basis of these studies, it was noted that mixed adsorbed films of homologous surfactants behave like ideal mixtures [19] and that the assumption of ideal mixing of such surfactants in micelles can be helpful for predicting a number of their properties. However, the behaviors of mixtures of dissimilar surfactants (e.g., ionic and nonionic surfactants) in both surface films and micellar systems were non-ideal and could be described by a regular solution theory [20,21].

In the present study, we investigated the mixed micelle and adsorption properties of binary surfactant systems containing the cationic surfactants (C₁₂ and C₁₆) and the nonionic surfactant cetyl dimethyl phosphinate (CDP). The surface excess (Γ_{\max}) and minimum area per molecule (A_{\min}) were also evaluated from surface tension plots. The mixed systems parameters were obtained at the mixed interface, and in the mixed micelles.

2. Experimental

2.1. Materials

Surfactants used in this study were: cationic Schiff base ammonium surfactants (C₁₂, C₁₆) prepared in the previous work [22], and hexadecyl dimethyl phosphinate (nonionic surfactant) (Sigma–Aldrich, 99.9%), (Scheme 1). The water used was bidistilled water using Pyrex apparatus. Buffer solution was a standard phosphate solution obtained from Merck.

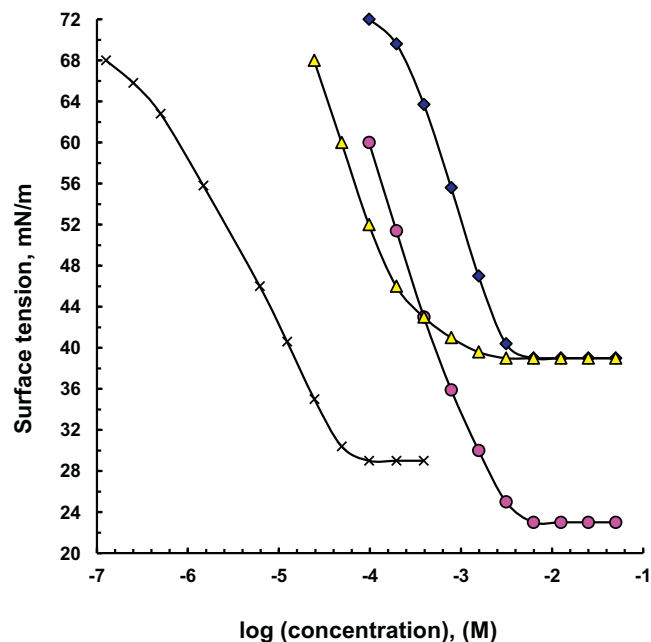


Fig. 1. Surface tension vs. $-\log$ (concentration) of: \blacklozenge CTAB, \bullet C12, \blacktriangle C16, \times CDP surfactants at 25 °C.

2.2. Surface tension measurements

The surface tension (γ) was measured by the ring method using a K6 tensiometer (Krüss GmbH, Germany) at temperature of 25 °C [23]. The temperature (± 0.5 °C) was maintained by circulating thermostated water through a jacketed vessel containing the solution. The ring was cleaned by heating in alcoholic flame. The measurements were taken until constant surface tension values indicated that equilibrium had been reached. In all cases the measurements were conducted for the single cationic surfactant and the different mixed systems in the presence of phosphate buffer to maintain the pH of the medium at 7. The accuracy of γ measurements was within ± 0.5 mN/m.

3. Results and discussion

3.1. Behaviors at the solution–air interface

Fig. 1 represents the relationship between the concentration of the studied surfactant and its surface tension at 25 °C. The surfactant molecules have the tendency to adsorb at the air–water interface in which the head groups are attached to the surface by the attraction force. While, the hydrophobic chains are oriented in parallel position to decrease the interaction with the aqueous phase which consequently decreases the surface tension values. As a result, increasing the concentration of the surfactants in the solution decreases the surface tension gradually, as well as the adsorbed amounts of the surfactant molecules at the interface.

Fig. 2a and b represents the relation between the surface tension and $\log C$ of the mixed surfactant systems (cationic–nonionic) at various initial mole fractions of cationic surfactants (C₁₂ and C₁₆) at 25 °C. The amount of adsorbed surfactant molecules can be calculated using Gibb's equation (Eq. (1)) [24]:

$$\Gamma_{\max} = \frac{(d\gamma/d \ln C)}{nRT} \quad (1)$$

The term $d\gamma/d \ln C$ is related to the migration of surfactant molecules from the bulk of the solution to the air–water interface and define the influence of the concentration variation on the

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