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Micellization and interfacial behavior of binary and ternary mixtures in aqueous medium

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ABSTRACT

The surface and micellization behavior of binary and ternary mixtures of cetylpyridinium chloride (CPC), sodium dodecyl sulfate (SDS) and polyethylene glycol hexadecyl ether (BRIJ-56) in different mole fractions have been studied in detail by surface tension measurement. The critical micelle concentration (CMC), activity coefficients, mutual interaction parameters, interfacial adsorption, minimum area per molecule, and energetic parameters for binary and ternary systems have been determined. Here we used the Clint, Rubingh and Rubingh–Holland models to analyze the results.

1. Introduction

Surfactants or SURFace ACTive AgeNTs are the multifaceted products of the chemical industry, including automobiles, pharmaceuticals, detergents, and petroleum. The surfactants also have great value in modern-technological areas such as electronics (printing, magnetic recording), and biomedical research (biotechnology, virology). Therefore, its unusual properties, phase behavior, and physical chemistry, are essential for most industrial chemists [1–3].

In most of the practical applications, mixtures of surfactants are used since they work better than pure micelle (e.g., detergency, cosmetics, flotation, dispersion/flocculation, emulsifying, drug delivery, corrosion inhibition, enhanced oil recovery, and nanolithography) [4,5]. Therefore, the mixed micelle systems make an extensive contribution to the field of both academic and commercial applications of surfactants as well as the surfactant-containing systems [6]. Some cases, clouding phenomena occur during mixed micellization. The clouding phenomenon is a well-known and observed in non-ionic surfactants [7]. Under special conditions ionic surfactants undergo phase separation [8]. Researchers found that some amphiphilic drugs, like ionic surfactants undergo pH, concentration, and temperature dependent phase separation [9–11]. In some cases, they are involuntarily mixed or in other cases, they are voluntarily mixed to improve the properties of the final product. In most of the cases the surfactants are purposely mixed to obtain synergism, the condition in which the properties of the mixture are better than those attainable by the individual components. The solubilized substances, also called a penetrating additive [12], may be located in the hydrocarbon core [13], or the hydrophilic mantle [14]. The mixed micellization is a special case of solubilization. The *CMC* of mixed micelles falls within the highest and lowest individual *CMC* values of components as shown for binary and tertiary mixtures [15]. In aqueous solutions of two or more surfactant mixtures synergistic (attractive) interactions result in *CMC*'s, which can be substantially lower than those in the solution containing the constituent single surfactants. On the other hand, antagonistic interactions result in mixture *CMC*'s that can be considerably higher than the *CMC*'s of the constituent single surfactants [16,17].

The mixtures of surfactants (binary), cationic/cationic, cationic/nonionic, cationic/anionic, anionic/anionic, nonionic/nonionic, anionic/nonionic, anionic/biosurfactant, have been studied by using the different models such as Clint, Rubingh, Motomura, Rosen and Blankstein [18–22]. The regular solution approximation (RSA), extended regular solution approximation (ERSA) and thermodynamic theory have been utilized in ternary surfactant systems to calculate the critical micelle concentration and other micellar parameters on the basis of solution composition.

Previously, we have explored many binary mixed systems [23–34], their physical properties (physicochemical and thermodynamics) have been analyzed in detail. Compare to binary surfactant systems, ternaries are studied less, and physicochemical properties have been only limited work on them [35–39]. The present study demonstrates a detail surface and micellization properties of CPC, SDS and BRIJ-56 (Polyoxyethylene

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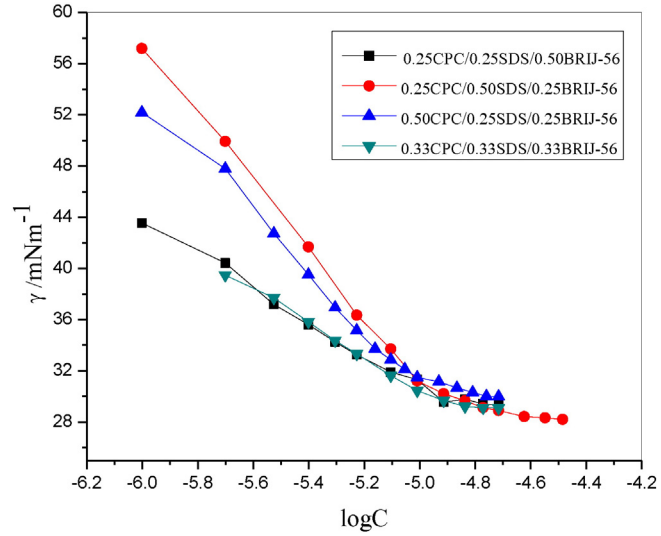

Fig. 1. Determination of the *CMC* of ternary combinations of CPC, SDS and BRIJ-56 at different mole ratios at 298 K.

(10) cetyl ether) in binary and ternary mixtures in an aqueous medium. The different theoretical models have been used to understand the interaction among the components in mixed micelles.

2. Experimental

2.1. Materials

Cetylpyridinium chloride (CPC), Sodiumdodecyl sulfate (SDS) and BRIJ-56 were purchased from Merck, BDH and Sigma with purity >90%. The solution was prepared in double distilled deionized water having specific conductivity 1 to 2 μS cm^{-1}.

2.2. Surface tension measurements

Surface tension measurements were made with an Attension tensiometer (Sigma 701) by platinum ring detachment method at 298 K. The temperature was maintained within ±0.1 K by constantly circulating thermostated water through a jacketed vessel containing the solution. The Du Nouy principle is obeyed by the Attension Tensiometer. According to the Du Nouy principle the force to lift the ring from the surface of a liquid is related to the surface tension of that liquid by the relation:

$$F = 2\pi (r_1 + r_2)\gamma \quad (1)$$

where r_1 and r_2 are the radius of inner ring and outer ring of the liquid film respectively. The concentration of a solution was varied by the aliquot addition of stock surfactant solution of known concentration to a known volume of solvent in the vessel. For each set of experiments, the ring was cleaned by heating it in an ethanol flame. The measured surface tension values were plotted as a function of the logarithm of surfactant concentration (Fig. 1). The accuracy of the measurements was within ±0.1 m Nm^{-1}.

3. Results and discussion

3.1. Adsorption at the surface and thermodynamic parameters

When surfactants adsorbed at the air/solution interface, the cohesive force among water molecules decreases, and thus the surface tension of water decreases on the progressive addition of the surfactant solution. This process continues up to complete saturation of the interface by the surfactants. Beyond this limit, surfactants get aggregated in bulk solution to form micelles without hampering the interface. The point of discontinuity in a γ vs. log *C* indicates *CMC*.

The amount of surfactant adsorbed per unit area of surface (Gibbs surface excess) has been calculated from least square slopes of π vs. log *C* by using Gibbs adsorption Eq. (2),

$$\Gamma_{max} = -\frac{1}{2.303nRT}\left[\frac{\partial\gamma}{\partial \log C}\right]_T \quad (2)$$

where dπ = surface pressure ($\gamma_w - \gamma_s$), γ_w and γ_s are the surface tension of solvent and solution respectively.

Γ_{max} = the surface excess concentration.

when γ is in dyn/cm and $R = 8.314 \times 10^7$ ergs mol^{-1} K^{-1}, then Γ_{max} is in mol/cm^2; when γ is in mN/m and 8.314 J mol^{-1} K^{-1}, then Γ_{max} is in mol/1000 m^2. The *n* is the number of solute species whose concentration at interface changes with change in the value of *C*. In the present context, for binary mixtures (CPC/SDS, CPC/BRIJ-56, SDS/BRIJ-56), the value of *n* were 4, 3 and 3, respectively; for ternary mixtures (CPC/SDS/BRIJ-56) n was 5. The Γ_{max} value is called the adsorption effectiveness and describes the adsorption tendency of surfactant molecules at the interface. The adsorption effectiveness is an important factor determining vital properties concerning foaming [40], wetting emulsification [41], solubilization [42], drug delivery [43] and biological activities [44]. It is observed that the higher Γ_{max} values the higher the surface activity. So, CPC is more surface active than that of SDS and BRIJ-56. It is clear from Table 1 that binary mixtures are more surface active than ternary systems.

The area per molecule at the interface provides the information on the degree of packing and orientation of the adsorbed surfactant molecule when compared with the dimensions of the molecule as obtained by use of molecular models. For the surface excess concentration, the

Table 1
Interfacial and Thermodynamic Parameters of Pure, Binary and Ternary Combinations of CPC, SDS and BRIJ-56 at 298 K[a].

System	γ_{CMC} (mN/m)	10^6 Γ_{max} (mol/m^2)	A_{min} (nm^2/molecule)	$-\Delta G_m$ (kj/mol)	$-\Delta G_{ad}$ (kj/mol)	$-\Delta G_{ex}$ (kj/mol)
CPC	37.468	4.982	0.333	27.538	34.068	–
SDS	27.749	2.581	0.643	24.969	41.337	–
BRIJ 56	33.679	1.048	1.583	38.107	72.741	–
CPC + SDS	41.998	1.146	1.448	27.538	51.968	6.597
SDS + BRIJ-56	37.433	1.204	1.378	39.302	66.331	5.303
CPC + BRIJ-56	35.696	1.563	1.062	39.018	60.960	4.377
0.5 CPC/0.25 SDS/0.25 BRIJ-56	30.860	0.767	2.164	46.329	97.335	–
0.25 CPC/0.5 SDS/0.25 BRIJ-56	29.416	0.930	1.783	38.708	82.304	–
0.25 CPC/0.25 SDS/0.5 BRIJ-56	29.519	0.410	4.048	38.791	137.475	–
0.33 CPC/0.33 SDS/0.33 BRIJ-56	29.133	0.445	3.723	38.576	130.204	–

[a]Standard uncertainties (*u*) are $u(T) = 0.20$ K and $u(p) = 10$ kPa. Relative standard uncertainties (u_r) are $u_r(\Gamma_{max}) = \pm 5\%$, $u_r(A_{min}) = \pm 5\%$, $u_r(\Delta G_m) = \pm 3\%$, $u_r(\Delta G_{ad}) = \pm 4\%$ and $u_r(\Delta G_{ex}) = \pm 4\%$.