Quantifying Critical Micelle Concentration and Nonidealities within Binary Mixed Micellar Systems: An Upper-Level Undergraduate Laboratory

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Received April 11, 2001. Accepted May 8, 2001

Abstract: Micelle-based systems have a long history in many areas, for instance, membrane mimics, reaction media, and food additives. All prior educational laboratory experiments dealing with micelle-based systems that have been published and utilized deal with unary surfactant systems. Unfortunately, most practical applications that use surfactants and micelles involve mixtures because these often exhibit behavior unlike the individual components. That is, surfactant mixtures deviate significantly from a regular solution approximation (i.e., there is synergism) when the individual surfactant structures differ significantly. In this laboratory experiment, we describe a simple method that exploits the unique behavior of the fluorophore pyrene to rapidly determine the critical micelle concentration (CMC) of mixed micelle systems. We also determine the dimensionless interaction parameter, β, that describes the net pairwise interaction between surfactant species within a binary micellar system. The binary system we chose to study is sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) dissolved in water. The β value recovered by students using our method is statistically equivalent to the value reported in the literature using more sophisticated and protracted methods. This laboratory experiment opens the door for students to explore regular solution theory, non-ideal mixing, micelle formation, and fluorescence spectroscopy within a single experiment.

Introduction and Background

Surfactants (surface-active agents) are amphiphiles consisting of long-chain hydrophobic tails and polar (often ionic) headgroups. By acting to lower interfacial tension, such amphiphilic molecules often aid in surface wetting, solubilization, emulsification, dispersion, and frothing [1–3]. In aqueous solutions above a narrow surfactant concentration range (the critical micelle concentration, CMC) surfactants can spontaneously self-associate to form thermodynamically stable molecular aggregates known as *micelles*. Micelles and their monomer constituents are of wide interest in colloidal chemistry because they are essential in industrial processes (e.g., the textile and semiconductor industries). Micelles and surfactants are also widely encountered in consumer products (e.g., detergents in cosmetics and soaps, emulsifiers in salad dressing). Biosurfactants are crucial for maintaining proper health [4] (e.g., proper prenatal lung development) and some surfactants even provide the necessary conditions for life itself (e.g., photosynthesis, intracellular processes). Micellar media also have a long history as rudimentary membrane mimics [1]; novel chemical reaction media [5–7]; and analytical agents to improve selectivity, particularly in the separation sciences [7]. Undergraduate laboratory experiments demonstrating the effects of micelles on physicochemical properties of a variety of substrates have appeared in the chemical education literature [8].

Abrupt changes in the physicochemical properties of a surfactant solution in proximity to the CMC signals the onset of micelle formation. Experimentally, the CMC is determined by monitoring a suitable physicochemical parameter (e.g., conductance, viscosity, surface tension, reaction rate, detergency, scattering) as a function of surfactant concentration [1–3]. Recently, a simplified undergraduate laboratory experiment based on surface tension measurements for the determination of CMC has appeared in the literature [9]. Fluorescence probe techniques are also widely used to study surfactant micellization, adsorption, and polymer interaction [10, 11]. Pyrene is a particularly popular fluorescent probe for the study of microheterogeneous media. The vibronic structure of the pyrene monomer emission spectrum is sensitive to solute–solvent dipole–dipole coupling, which is itself influenced by changes in the dipolarity of the environment surrounding the pyrene molecules [12, 13]. The pyrene fluorescence spectrum exhibits five vibronic bands numbered I through V. There is a significant enhancement in the forbidden 0–0 band intensity (peak I) in the presence of solvents of increasing dielectric constant at the expense of other bands [12]. Thus, the intensity ratio associated with the first (I at 373 ± 2 nm) and third peaks (III at 384 ± 2 nm) provides a sensitive measure of subtle changes in the pyrene local microenvironment [12, 13].

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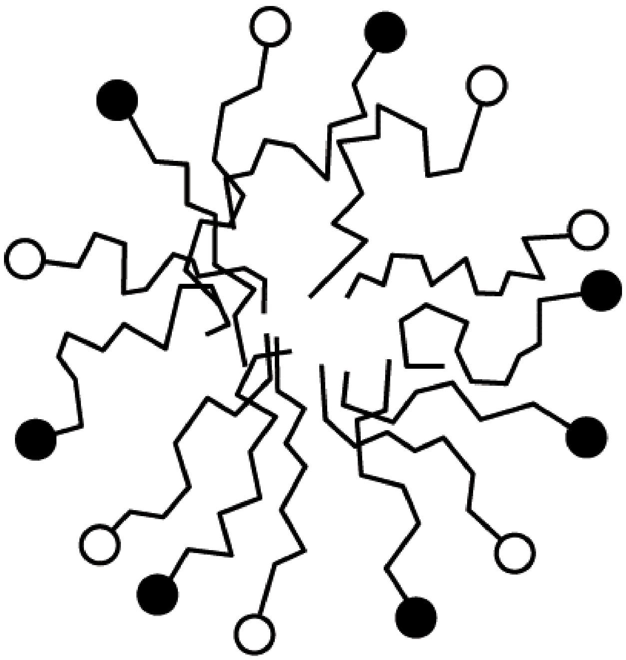

Figure 1. Simplified cartoon of a normal mixed micelle consisting of two surfactant types, illustrated by open and filled head groups.

Mixed Surfactant Systems. The important role(s) of microheterogeneous systems in nature, their increased use in industry, and their impact in the chemical sciences argue for their inclusion as part of a *complete* undergraduate chemical education. Nevertheless, these systems are afforded scant attention in traditional chemistry curricula. To address this shortfall, several excellent contributions have appeared in the literature [14–18]. Unfortunately, even though most practical surfactant systems consist of surfactant mixtures [19, 20], all prior reports appearing in the literature [14–18] have focused on unary surfactant systems.

Surfactant mixtures often exhibit features deviating significantly from individual surfactants [19, 20] (i.e., they exhibit substantial synergism). Mixed surfactant systems are also of significant theoretical interest because their propensity to form micelles in solution can differ substantially as compared to unary surfactant systems [19–21]. A simplified two-dimensional representation of a binary mixed micelle is presented in Figure 1. This model is highly schematic and intended only to depict the micelle disorder, nonlinearity, and fluctional nature. No absolute configuration, aggregate number, or distribution is implied [22].

Regular Solution Approximation/Nonideal Mixing Model. For the simplest case of a binary surfactant system without any significant net interaction between surfactant types, the mixture CMC (CMC_{Mix}) is given by [19, 20]

$$\frac{1}{CMC_{Mix}} = \frac{\alpha_1}{CMC_1} + \frac{1-\alpha_1}{CMC_2} \tag{1}$$

where α_1 is the solution mole fraction of the surfactant (solution composition) with critical micelle concentration CMC_1, and CMC_2 denotes the CMC for the second surfactant alone. Equation 1 can also be expressed in terms of the mole fraction of surfactant within the mixed micelle itself, x_i; here, CMC_{Mix} is simply the arithmetic mean of the CMCs of the individual surfactants, namely,

$$CMC_{\text{Mix}} = x_1\,CMC_1 + (1 - x_1)\,CMC_2 \tag{2}$$

The ideal mixing theory [19, 20] has been successful in explaining the properties of mixtures composed of surfactants with similar chemical structures; however, it fails for mixtures containing chemically dissimilar surfactants. For example, anionic–cationic surfactant mixtures exhibit striking deviations from ideal mixing and more elaborate analysis is required to gain molecular insight. In cases where the individual surfactant types interact strongly, eqs 1 and 2 can be recast to reflect the activity coefficients, f_i, of the individual surfactants within the mixed micelle:

$$\frac{1}{CMC_{\text{Mix}}} = \frac{\alpha_1}{f_1 CMC_1} + \frac{1-\alpha_1}{f_2 CMC_2} \tag{3}$$

$$CMC_{\text{Mix}} = x_1 f_1\,CMC_1 + (1 - x_1) f_2\,CMC_2 \tag{4}$$

For convenience, one can describe the activity coefficients for the surfactants within the mixed micelle in terms of a dimensionless interaction parameter, β, that represents the net (pairwise) interaction between the different surfactant species within the micelle:

$$\ln f_1 = (1 - x_1)^2\,\beta \tag{5}$$

$$\ln f_2 = x_1^{\,2}\beta \tag{6}$$

Attractive interactions between two surfactant types result in a negative β value, positive β values imply a net repulsion, and the larger the absolute value of β the stronger the interaction, whether attractive or repulsive.

By combining the tenets of regular solution theory with a nonideal mixing model [19, 20], one can formulate the following relations for binary mixed micelles:

$$\alpha_1 CMC_{\text{Mix}} = x_1 CMC_1\,\exp[\beta(1 - x_1)^2] \tag{7}$$

$$(1 - \alpha_1)\,CMC_{\text{Mix}} = (1 - x_1)\,CMC_2\,\exp[\beta(x_1)^2] \tag{8}$$

Because α_1 is known, one can extract β and x_1 from a *single* measured value of CMC_{Mix}, if the pure surfactant component CMCs (i.e., CMC_1 and CMC_2) are known; however, eqs 7 and 8 cannot be solved analytically. In the supporting material we provide a simple QBASIC program for computing β [20].

In the experiment described here, sodium dodecyl sulfate (SDS) and dodecyl trimethylammonium bromide (DTAB) were selected as the surfactants. These inexpensive surfactants are easy to handle, widely used, exhibit well-defined properties, and are commercially available in high purity [23]. The SDS/DTAB binary system also has one of the largest known net attractions (β = –25.5) leading to a dramatic deviation from the regular solution theory prediction [20, 24].

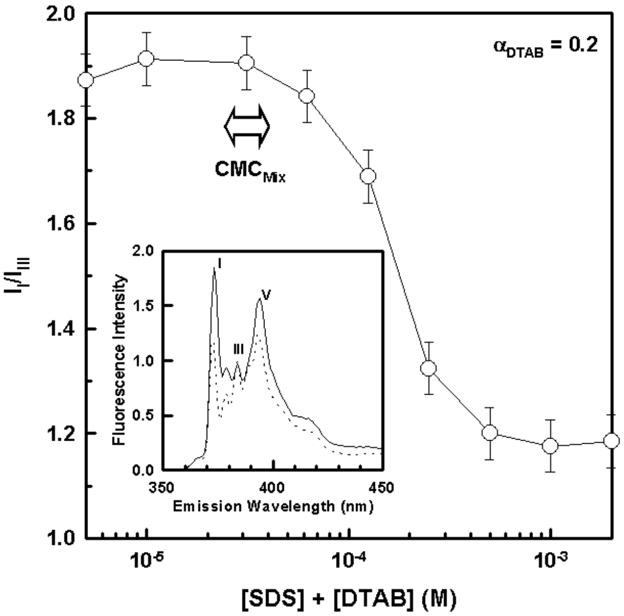

Figure 2. Ratio of pyrene vibrational-band intensities (I_I/I_{III}) as a function of total surfactant concentration (C_T = [SDS] + [DTAB]) at $\alpha_{DTAB} = 0.2$. In the inset, typical pyrene emission spectra (1×10^{-6} M) normalized at band III (384 nm) for $C_T = 10^{-5}$ M (CC) and 2×10^{-3} M (········) are shown.

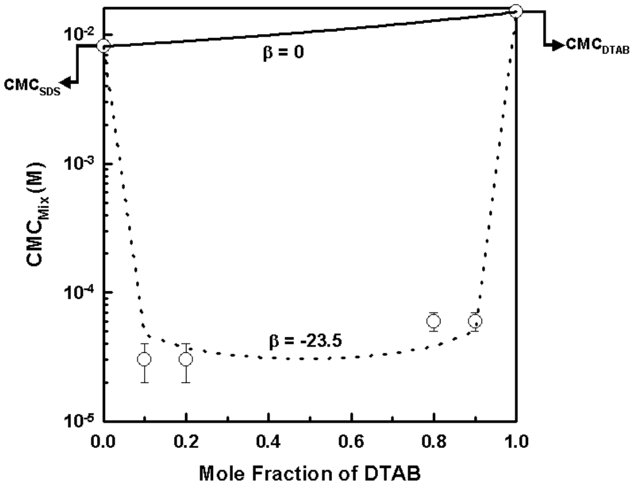

Figure 3. CMC_{Mix} for SDS + DTAB mixtures as a function of the DTAB solution mole fraction at 22 °C. The points are experimental results; the broken line is generated using the nonideal mixing model for $\beta = -23.5$, and the solid line assumes ideal mixing ($\beta = 0$).

Experimental Procedure

Materials. Pyrene [129-00-0] (Kodak) was twice recrystallized from absolute ethanol [64-17-5] (Pharmco). Sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}OSO_3Na$) [151-21-3] and dodecyl trimethylammonium bromide (DTAB, $CH_3(CH_2)_{11}N(CH_3)_3Br$) [1119-94-4] (Aldrich) were used as received and water was doubly distilled. Aqueous surfactant stock solutions were vortexed and allowed to equilibrate for at least 24 hours prior to spectroscopic study. All experimental results were reproducible at longer equilibration times.

Methods. Steady-state emission spectra were recorded using a SLM-AMINCO model 8100 and PTI model C60/2000 spectrofluorometer with Xe-arc lamp excitation. The excitation wavelength was set to 337 nm (pyrene) and the excitation and emission spectral bandwidths adjusted to 8 and 1 nm, respectively. All measurements were done at 22 °C (ambient room temperature) and the samples were placed in standard 1-cm^2 quartz cuvettes.

Working solutions for determining CMC_{Mix} were prepared as follows. From a stock solution of 10^{-3} M pyrene dissolved in ethanol, 10 µL aliquots were transferred with a micropipette into a series of clean, dry test tubes and the solvent allowed to evaporate under gentle nitrogen flow. Appropriate volumes of aqueous SDS and DTAB stock solutions (10^{-2} M) were then added to each test tube to achieve the desired surfactant mole fractions and the desired overall surfactant concentration (C_T = [SDS] + [DTAB]) upon dilution with water to a final volume of 10 mL. The final pyrene concentration within the surfactant mixture is 10^{-6} M. The final solutions were mixed gently and allowed to stand in the dark for 30 min before measurements were performed.

The pyrene I_I/I_{III} value for each binary surfactant mixture was determined as a function of C_T at constant solution mole fraction (α_i). The sharp decrease or break point in the I_I/I_{III} ratio with increasing surfactant concentration was taken as the CMC_{Mix}.

Results and Discussion

The results of a typical student experiment are presented in Figure 2 for $\alpha_{DTAB} = 0.2$. The curve shows a sharp decrease in I_I/I_{III} at CMC_{Mix} (indicated as a narrow range) due to partitioning of the pyrene probe molecules into the mixed micellar phase. As demonstrated by the pioneering work of Thomas and coworkers [12], the first observation of the decrease in the pyrene I_I/I_{III} value demonstrates the onset of the formation of micellar assemblies and thus indicates the CMC. The dramatic change in the microenvironment sensed by the pyrene molecule at the onset of micellization is illustrated in the inset, which shows pyrene emission spectra normalized at the solvent insensitive band (III) for overall surfactant concentrations of 10^{-5} M (CC) (i.e., $C_T < CMC_{Mix}$) and 2×10^{-3} M (········) (i.e., $C_T > CMC_{Mix}$). This same approach was used to determine the CMC_{Mix} values at several other α_{DTAB} values. Figure 3 summarizes the results of this exercise.

Inspection of the results presented in Figure 3 shows that the SDS/DTAB mixture exhibits significant deviation from ideality (solid line between neat SDS and neat DTAB) with CMC_{Mix} values that are two orders of magnitude or more (points) lower than those expected for ideal mixing. By using the data presented in Figure 3 in concert with eqs 7 and 8 we determined β (Table 1, dashed curve in Figure 3). We can describe the entire DTAB/SDS system well at all compositions with a single β parameter (–23.5), and this value agrees within our measurement precision with the β value from the literature [20, 24]. Inspection of Table 1 also shows that the apparent micelle composition (x_i) is largely unaffected by changes in solution composition ($x_{SDS} \sim x_{DTAB}$) suggesting that Coulombic attraction between SDS and DTAB is the dominant driving force controlling micellization in this particular binary system.

It is important to mention that the DTAB/SDS system shows one of the strongest deviations from ideality, which is manifested via a very large negative value of the interaction parameter (β). Binary mixtures of similarly charged ionic as well as nonionic and combination of ionic + nonionic surfactants, however, do not show such strong nonidealities. The magnitude of the interaction parameter for a binary mixture of surfactants usually increases in the following order:

Table 1. Representative student results obtained from nonideal mixing model for the SDS-DTAB mixed micellar system[a]

$\alpha_{SDS}/\alpha_{DTAB}$	CMC_{Mix}(M)		β^{c}	$\underline{\mathbf{x}}_{SDS}/\underline{\mathbf{x}}_{DTAB}$	
	This Report	Liturature		This Report	Liturature
1.0/0.0	—	8.1×10^{-3} [b]	—	1.0/0.0	1.0/0.0
0.9/0.1	$(3 \pm 1) \times 10^{-5}$	2.91×10^{-5}	-25	0.55/0.45	0.551/0.449
0.8/0.2	$(3 \pm 1) \times 10^{-5}$	2.26×10^{-5}	-24	0.54/0.46	0.538/0.462
0.2/0.8	$(6 \pm 1) \times 10^{-5}$	2.33×10^{-5}	-22	0.48/0.52	0.486/0.514
0.1/0.9	$(6 \pm 1) \times 10^{-5}$	3.06×10^{-5}	-23	0.47/0.53	0.472/0.528
0.0/1.0	—	1.5×10^{-2} [b]	—	0.0/1.0	0.0/1.0

[a] All experiments were conducted at 22 °C

[b] Reference 23; provided as a priori information to the students

[c] The literature value reported for ß is -25.5 [24]

nonionic–nonionic < anionic–anionic/cationic–cationic < nonionic–anionic/nonionic–cationic < anionic–cationic [20]. The values of the interaction parameter for a variety of binary surfactant mixtures are readily available in literature (interaction parameters for some binary mixed-micellar systems are collected and tabulated in reference 20). Similar laboratory exercises can easily be developed using different sets of surfactant mixtures showing different degrees of interaction between the two surfactants in the mixture.

Conclusion

In spite of their considerable practical importance and the challenging theoretical issues associated with the description of these complex fluids, solutions of surfactant mixtures have yet to receive the full attention they deserve in the undergraduate chemistry curriculum. We approach this problem by describing a simple means of measuring and assessing nonideality within binary surfactant mixtures within the regular solution approximation and nonideal mixing frameworks.

Implementation. The use of fluorescence techniques to investigate mixed-micellar media affords an opportunity to introduce surface and colloidal chemistry, photophysics, spectroscopy, and thermodynamics to chemistry students. These procedures have been tested by the authors who found that students can generate 8–12 point titration curves at several different surfactant mole fractions within a typical four-hour laboratory period. The methodology that we describe can be extended to include other surfactant pairs as well as investigations of temperature, cosolvent, electrolyte, and organic-additive effects.

Supporting Material. The student laboratory handout and QBASIC program are available as an Adobe Acrobat PDF file (http://dx.doi.org/ 10.1007/s00897010487b).

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