Determination of Critical Micelle Concentration of Some Surfactants by Three Techniques

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Surfactants, sometimes called *surface-active agents* or *detergents*, are among the most versatile chemicals available. They have applications in many areas, including chemistry (chemical kinetics or equilibria), biology (as membrane mimetics), and pharmacy (*1*). Surfactants are amphiphilic materials containing both apolar long-chain hydrocarbon "tail" and polar, usually ionic, "head" groups. In polar solvents, for example water, this dual character of the amphiphile leads to self-association or micellization: the surfactant molecules arrange themselves into organized molecular assemblies known as *micelles* (Fig. 1). The hydrophobic part of the aggregate forms the *core* of the micelle, while the polar head groups are located at the micelle–water interface in contact with and hydrated by a number of water molecules. Depending on the chemical structure of the surfactant, its micelle can be cationic, anionic, ampholitic (zwitterionic), or nonionic. This unique property of surfactants makes aqueous surfactant solutions microheterogeneous media; that is, they are heterogeneous on a microscopic scale, even though they are often homogeneous macroscopically. The concentration (actually an arbitrary concentration within a narrow range) above which micelles form is called the *critical micelle concentration* (CMC). Above the CMC, monomers and micelles exist in dynamic equilibrium.

Despite their growing importance, microheterogeneous media are not yet considered in most textbooks of general or experimental physical chemistry. Several reports illustrate the use of various techniques to measure the CMC (*2*–*5*). The experiments described in this article were designed to familiarize students of physical chemistry with micellar solutions and the basic structural parameters of micelles, and with some common techniques in physicochemical laboratories used to observe the changes in physical and chemical properties of surfactant solutions when micelles are formed. The paper presents the CMC determination of some surfactants by three methods. The advantages and disadvantages of each one are indicated.

In these experiments, undergraduate students in the fourth year in chemistry determined the CMC of a surfactant by measuring a change in (i) the UV-vis spectrum of benzoylacetone, (ii) the fluorescence emission spectrum of pyrene monomers, and (iii) the electrical conductivity of an ionic surfactant solution as the concentration of the amphiphile increases. There are several ways of organizing the laboratory experiments, depending on the time and equipment available. Each group of students could determine the CMC of a surfactant, for example sodium dodecyl sulfate, by using the three techniques under the same experimental conditions. The time required for determination of a CMC value by any of the techniques described here is no longer than two lab sessions; each one takes about four hours. The accuracy of students' results and response to the experiments were generally good.

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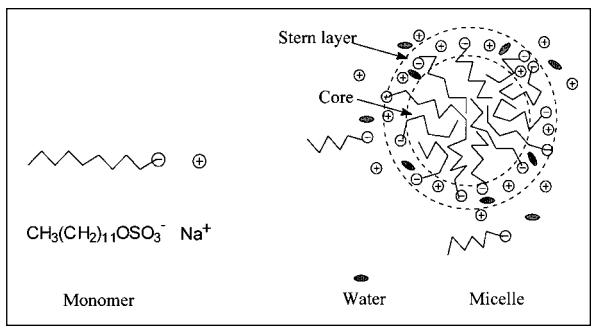


Figure 1. An idealized model for a spherical micelle of sodium dodecyl sulfate.

The Critical Micelle Concentration

Micelles are small colloidal particles, relative to the wavelength of light. When micelles form, the aqueous surfactant solution behaves as a microheterogeneous medium. The value of the CMC can be determined by the change in the physicochemical properties of the surfactant solution as the surfactant concentration increases.

Experimentally, the CMC is found by plotting a graph of a suitable physical property as a function of surfactant concentration. An abrupt change of slope marks the CMC. The choice of CMC is never unambiguous, since the change in slope occurs over a more or less narrow range of concentrations, whose magnitude depends on the physical property being measured and sometimes on the nature of the data and on the way they are plotted.

The CMC can be affected by many variables (*6*), temperature and pressure being of relatively minor importance. It decreases with increasing hydrocarbon chain-length of the apolar groups, and for ionic surfactants it also depends on the nature and concentration of counterions in solution. Added electrolytes decrease the CMC, and the effect increases with decreasing charge density of the counterion.

Materials

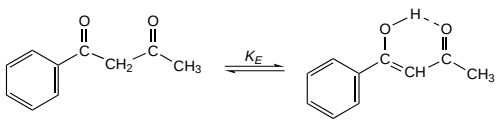
The surfactants sodium dodecyl sulfate (SDS), $CH_3(CH_2)_{11}OSO_3Na$; tetradecyl trimethyl ammonium bromide (TTABr), $CH_3(CH_2)_{13}N(CH_3)_3Br$; polyoxyethylene-9-lauryl ether ($C_{12}E_9$), $CH_3(CH_2)_{11}–(OCH_2CH_2)_9–OH$; the benzoylacetone (BZA); and the pyrene were Aldrich or Sigma products and were used as received. (If pyrene shows a yellow color it must be purified by column chromatography using silica gel as stationary phase and cyclohexane as eluent). The additives were all Merck products.

Caution: Benzoylacetone, pyrene, and the surfactants are harmful if ingested or inhaled or if they contact the skin; due precautions must be taken. (Stock solutions of BZA in dioxane and pyrene in methanol could be provided.)

Results

UV-Absorption Spectroscopy Method

This method is based on the tautomerism of benzoylacetone or 1-phenyl-1,3-butadione. Ketones and β-diketones, such as BZA, can exist in two tautomeric forms: the ketonic and the enolic forms. In solution, BZA enolizes practically exclusively to the *cis*-enolic form, which exists in a cyclic configuration stabilized by intramolecular hydrogen bonding:



This stabilization of the enol will be more pronounced when intermolecular hydrogen bonding with the solvent does not compete. Hence keto–enol equilibria of BZA are extremely solvent sensitive and the proportion of the enolic form is much greater in nonpolar solvents, such as cyclohexane, than in polar or hydrogen-bond donor solvents, such as water or alcohols.

BZA exists in water as a mixture of both tautomers (the percentage of the enol tautomer has been measured as 37.5% [*7*]). When a surfactant is added to a water solution of BZA, the amount of enol increases abruptly when the surfactant concentration rises above the CMC because the enolic form is taken up by the micelles, which provide a less polar solvent than the aqueous phase.

Figure 2a shows the effect of increasing surfactant concentration on the UV-absorption spectrum of aqueous BZA solutions of 7.0×10^{-5} mol L^{-1}. Below the CMC no changes are observed in the presence of surfactant monomers; above the CMC the absorption band centered at $\lambda = 312$ nm (due to the enolic form [*7*]) is augmented; and in parallel, the absorption band centered at $\lambda = 250$ nm (mainly due to the keto form) diminishes. The changes in the absorbance measurements at these two wavelengths with varying concentration of surfactant in aqueous solutions are shown in Figure 2b.

It is noticed that a remarkable enhancement of enolic absorption occurs just above the CMC. The concentrations corresponding to the break points observed for each surfactant, in the absence and presence of the indicated additive, are tabulated in Table 1.

Procedure. To obtain the data shown in Figure 2 and Table 1, prepare a concentrated solution (5 mg/mL) of BZA in dioxane (or another water-miscible nonpolar solvent). From this stock solution (~0.03 mol L^{-1}) prepare an aqueous BZA solution by pipetting 0.40 mL into 25-mL volumetric flasks and diluting to the mark with water. To draw each scan of the spectrum, 0.40 mL of the aqueous BZA solution is transferred with a pipet to a 1.0-cm quartz cell together with the appropriate amount of surfactant, the additive (if any), and the water volume necessary to give a 3-mL total volume in the cell ([BZA]~7×10^{-5} mol L^{-1}). The reference cell should contain the same concentrations of surfactant and additive as the sample. The spectrum of BZA in the presence of varying surfactant concentrations can be measured with any UV-vis spectrophotometer.

Fluorescence Spectroscopy Method

This method is based on the solvent dependence of vibrational band intensities in pyrene monomer fluorescence. Pyrene is one of the few condensed aromatic hydrocarbons that show significant fine structure (vibrational bands) in their monomer fluorescence spectra in solution. The intensities of the various vibrational bands of pyrene showed a strong dependence on solvent environment (*8*). Both solvent dipole moment and dielectric constants were found to be important in this effect.

Figure 3a presents representative monomer fluorescence spectra for pyrene (in very dilute solutions, [pyrene] = 2×10^{-6} mol L^{-1}, so that complications due to excimers do not arise) in aqueous sodium dodecyl sulfate (SDS) solutions above and below the CMC. In the absence of micelles (below the CMC) pyrene senses the polar environment of water molecules; the ratio of fluorescence emission intensities cor-

Table 1. Values of the CMC of Some Surfactants

Surfactant	Method	Conditions[a]	CMC (mol L^{-1})	m_1 (Ω^{-1} cm^2 mol^{-1})	m_2 (Ω^{-1} cm^2 mol^{-1})	α
SDS	conductance	no additives	8.0×10^{-3}	73.5 ± 0.6	25.7 ± 0.2	0.35
SDS	conductance	[TMU] = 1 mol L^{-1}	$1.4–1.5 \times 10^{-2}$ [b]	52.5 ± 0.3	39.7 ± 0.6	0.76
SDS	conductance	[HCl] = 6 mmol L^{-1}	5.5×10^{-3}	60.5 ± 0.4	—	—
SDS	BZA-abs	no additives	7.8×10^{-3}	—	—	—
SDS	BZA-abs	[HCl] = 33 mmol L^{-1}	2.8×10^{-3}	—	—	—
SDS	fluorescence	no additives	7.4×10^{-3}	—	—	—
TTABr	conductance	no additives	3.9×10^{-3}	92.3 ± 0.3	22.6 ± 0.1	0.24
TTABr	BZA-abs	no additives	3.5×10^{-3}	—	—	—
TTABr	BZA-abs	[HCl] = 33 mmol L^{-1}	0.8×10^{-3}	—	—	—
TTABr	fluorescence	no additives	3.5×10^{-3}	—	—	—
TTABr	fluorescence	[NaBr] = 0.2 mol L^{-1}	2.3×10^{-4}	—	—	—
TTABr	fluorescence	[TMU] = 0.56 mol L^{-1}	5.9×10^{-3}	—	—	—
$C_{12}E_9$	BZA-abs	no additives	1.6×10^{-4}	—	—	—
$C_{12}E_9$	fluorescence	no additives	1.7×10^{-4}	—	—	—
$C_{12}E_9$	fluorescence	15% CH_3OH	3.4×10^{-4}	—	—	—

[a]All experiments were conducted at 25 °C.

[b]The value 1.5×10^{-2} was determined from the intercept of eq 3. In the other cases, the conductance technique yielded the same value of the CMC by both the cross point and the intercept method.

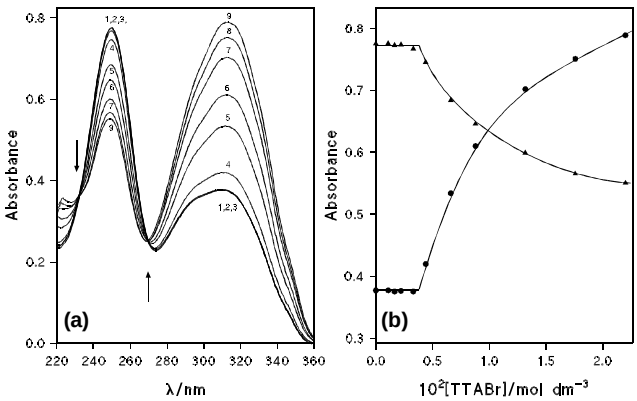


Figure 2. (a) Absorption spectrum of 7.0×10^{-5} mol L^{-1} BZA. 1, 2, 3: [TTABr] below the CMC are; 4: [TTABr] = 4.4 mmol L^{-1}; 5: [TTABr] = 6.6 mmol L^{-1}; 6: [TTABr] = 8.8 mmol L^{-1}; 7: [TTABr] = 13.2 mmol L^{-1}; 8: [TTABr] = 17.6 mmol L^{-1}; 9: [TTABr] = 22 mmol L^{-1}. Arrows indicate the isobestic points. (b) Absorbance of BZA as a function of [TTABr] at 312 nm (●) and at 250 nm (▲).

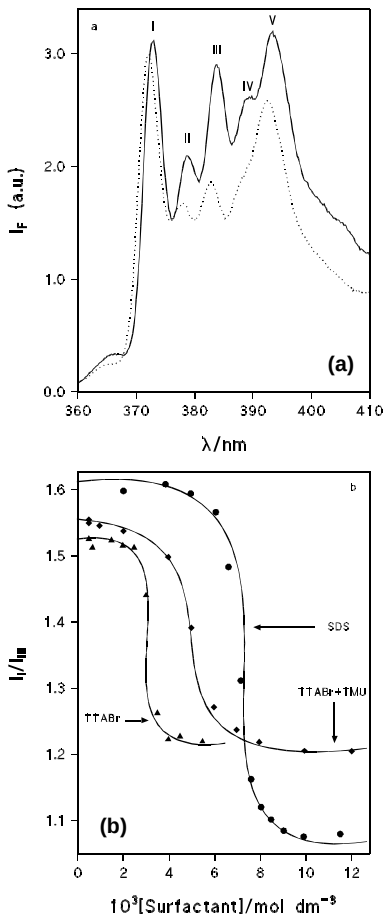


Figure 3. (a) Fluorescence emission spectrum of pyrene (2×10^{-6} mol L^{-1}) at [SDS] of 0.012 mol L^{-1} (—) (i.e., above the CMC) and 3×10^{-3} mol L^{-1} (···) (i.e., below the CMC). (b) Quotient of vibrational band intensities (I_I/I_{III}) as a function of [surfactant]. ([TMU] = 0.56 mol L^{-1}.)

responding to the first and third vibrational peaks (I_I/I_{III}) is high. Above the CMC, when micelles are present, and owing to the high hydrophobicity of pyrene molecules, these are solubilized in the interior micellar phase. This is a hydrocarbon-like solvent, so the environment sensed by pyrene is less polar; and therefore the ratio I_I/I_{III} decreases. Figure 3b shows the variation of the ratio of fluorescence emission intensities as a function of SDS concentration. The curves show a sharp decrease in the quotient intensities of both vibrational peaks when micelles are formed (i.e., at the CMC). The surfactant concentrations corresponding to the sharp decrease are listed in Table 1 as the CMC values.

Procedure. Prepare a pyrene solution by dissolving 5 mg in 10 mL of methanol. Dilute this solution 20 times (pipet 0.5 mL into 10-mL volumetric flasks). To prepare the working mixtures for fluorescence measurements, a small aliquot (50 μL) of the latter methanolic pyrene solution was transferred with an automatic pipet to a quartz fluorescence cell and mixed with the appropriate volumes of water, surfactant solution (~0.03 mol L^{-1}), and additive (if any) to give a total final volume of 3 mL, and to obtain the final surfactant concentrations shown in Figure 3. (If it is not possible to measure a small aliquot of the methanolic solution, the solvent should be allowed to evaporate before preparing the sample solutions.) The fluorescence emission was measured with an Aminco-Bowman spectrofluorimeter. Pyrene was excited at 334 nm and its emission was recorded at 373 and 384 nm, which correspond to the first and third vibrational peaks, respectively, and with the use of excitation and emission slits of 8 and 2 nm, respectively.

Electrical Conductivity Method

This method can only be applied to measure the CMC of ionic surfactants. The change in the electrical conductance of aqueous ionic surfactant solutions at the CMC is due to the different degree of surfactant ionization below (surfactant monomers behave as strong electrolytes) and above (micelles are partially ionized) the CMC. On the assumption that the aqueous surfactant solutions obey Kohlrausch's law (*9*), the specific conductivity, κ, of surfactant solutions can easily be calculated in terms of the molar ionic conductivities of ions ($\lambda_i = z_i u_i \mathcal{F}$, where z and u are the charge and mobility of the ion, and $\mathcal{F}$ the Faraday constant); ionic charges are omitted in the subscripts for the sake of simplicity.

Let us consider the case of SDS under two conditions:

1. *Below the CMC*, it is accepted that no micelles are formed; then the specific conductivity of aqueous SDS solution, in $mS \cdot cm^{-1}$ ($S = \Omega^{-1}$), is made up of independent contributions of anions $CH_3(CH_2)_{11}–OSO_3^-$, SD^- anions and Na^+ cations:

$$\kappa = (\lambda_{Na} + \lambda_{SD})\,[SDS]_t = m_1\,[SDS]_t \qquad (1)$$

where m_1 is the slope of the plot of κ vs. $[SDS]_t$ below the CMC.

2. *Above the CMC*, the conductivity of ionic surfactants such as SDS usually decreases. This is explained by the inclusion within the micelle of ions of opposite charge (counterions) to the long-chain ions. The percentage of counterions in relation to the number of long-chain ions in the micelle (the aggregation number, N_{agg} [*10*]) is called the fraction of micellar charge neutralized, β; then α (= 1 – β) is the degree of micellar ionization. Therefore the concentration of free counterions (Na^+, in the case of the SDS surfactant)

is given by $[Na^+]_f = CMC + \alpha[SDS]_m$, where $[SDS]_m = [SDS]_t - CMC$. The specific conductivity of an aqueous SDS solution at concentrations above the CMC may be regarded as divisible into three components: that due to the single ions (Na^+ and SD^-) at the CMC, that due to the micellar ions, and that due to the Na^+ ions in excess.

The specific conductivity of an SDS micellar solution may be written in the form

$$\kappa = (\lambda_{Na} + \lambda_{SD})\,CMC + \lambda_{Na}\alpha[SDS]_m + \lambda_{mic}[micelles] \quad (2)$$

Taking into account that $[micelles] = ([SDS]_t - CMC)/N_{agg}$ and assuming that the contribution of the micelle to the conductance is the same as that of an equivalent number of monomeric ions, the sum of whose charges equals the micellar charge, then $\lambda_{mic} = \alpha N_{agg}\lambda_{SD}$ and eq 2 becomes eq 3:

$$\kappa = (\lambda_{Na} + \lambda_{SD})CMC(1 - \alpha) + (\lambda_{Na} + \lambda_{SD})\alpha[SDS]_t = \kappa_o + m_2[SDS]_t \quad (3)$$

where m_2 ($= m_1\alpha$) is the slope of the linear plot of κ vs. $[SDS]_t$ above the CMC, and κ_o is the corresponding intercept.

The CMC value can then be determined either as the cross point of the two straight lines defined by eqs 1 and 3, or from the intercept of the straight line obtained above the CMC (eq 3) together with the values of the slope m_1 and the fractional micellar ionization α, which can be obtained as the ratio of the slopes of conductance vs. $[SDS]_t$ above and below the CMC; that is, $\alpha = m_2/m_1$.

Figure 4a shows results obtained working with aqueous solutions of SDS in the presence and absence of 1 mol L^{-1} of tetramethylurea (TMU). The following parameter values were obtained: in the absence of TMU, $m_1 = 73.5 \pm 0.6$ and $m_2 = 25.7 \pm 0.2$ $\Omega^{-1}cm^2mol^{-1}$, and $\alpha = 0.35$; in the presence of TMU, $m_1 = 52.5 \pm 0.3$ and $m_2 = 39.7 \pm 0.6$ $\Omega^{-1}cm^2mol^{-1}$ and $\alpha = 0.76$. The CMC values obtained in each case are listed in Table 1. Both CMC and α values increase in the presence of TMU. This is because, in the first case, TMU decreases the dielectric constant of water mixtures, and thus the solubility in water of the hydrophobic monomers of SDS increases. In the second case, the inclusion of TMU molecules within the micelle decreases the electrical repulsions between the ionic head groups ($-OSO_3^-$ in SDS) and the degree of micellar ionization, α, increases.

The same treatment can be applied to any other ionic surfactant to determine CMC and α values.

Figure 4b shows the specific conductivity of aqueous SDS solutions in the presence of a constant concentration of HCl. Below the CMC the conductivity increases, owing to the independent contributions of Na^+, SD^-, H^+, and Cl^- ions:

$$\kappa = (\lambda_H + \lambda_{Cl})[HCl] + (\lambda_{Na} + \lambda_{SD})[SDS]_t \quad (4)$$

Above the CMC part of the Na^+ ions included within the micelle are exchanged with H^+ ions: $Na_m^+ + H_w^+ \rightleftharpoons Na_w^+ + H_m^+$, with K_I being the corresponding equilibrium constant whose value are in the range of 0.7–1.0. The subscripts m and w refer to micelle and aqueous pseudophases, respectively. Then the specific conductivity of the solution is given by

$$\kappa = \kappa_o + (\lambda_H + \lambda_{Cl})[HCl] + (\lambda_{Na} - \lambda_H)[H^+]_m + \alpha(\lambda_{Na} + \lambda_{SD})[SDS]_t \quad (5)$$

but as $\lambda_H = 349.8$ $\Omega^{-1}cm^2mol^{-1}$ and $\lambda_{Na} = 50.1$ $\Omega^{-1}cm^2$ mol^{-1} (*11*) the observed specific conductivity of the solution decreases at low [SDS] because the third (and negative) term predominates over the fourth.

Procedure. To obtain the data shown in Figure 4, a surfactant solution of the higher concentration (0.05 mol L^{-1}) was prepared. To measure the specific conductivity at each [surfactant] we followed the step-by-step dilution–extraction method (*12*). The conductivity measurements were carried out in a jacketed beaker thermostated at 25 °C by circulating water, and by using a Knick microprocessor conductimeter provided with a four-pole measuring cell (factor cell 1.1 cm^{-1}).

Discussion

From Figure 2a it can be seen that BZA shows two absorption bands in the UV region: one centered around 250 nm (due mainly to the ketonic form) and the other centered at 312 nm (due to the enolic form). Also seen is the presence of two well-defined isosbestic points in the absorption spectrum of BZA as a function of [surfactant]. The students are required to relate the two absorption bands with the possible electronic transitions ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) in both keto and enol tautomers of BZA, and to explain the meaning of the isosbestic points in terms of the keto–enol equilibrium.

It is seen that λ_{max} in the case of BZA (see Fig. 2a) does not change in the presence of micelles, whereas in the fluorescence spectrum of pyrene (see Fig. 3a) λ_{max} shifts toward

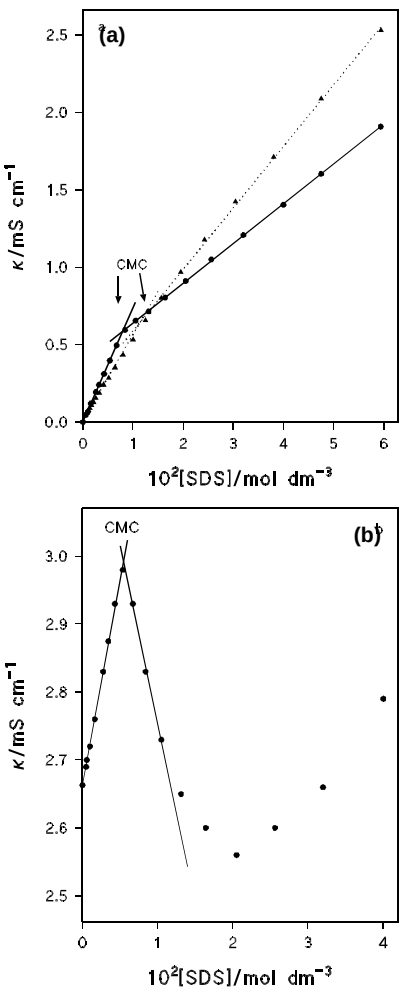


Figure 4. Electrical conductivity, in mS cm^{-1} ($S = \Omega^{-1}$). (a) As a function of [SDS] with no additives (●), and [TMU] = 1 mol/dm^3 (▲). (b) In the presence of [HCl] = 6.0×10^{-3} mol L^{-1}.

red in the presence of micelles. Again, the students are required to relate these effects with the possible location of both probes (BZA and pyrene) within the micelle and to draw conclusions about the polarity of the different regions in a micelle.

In Table 1 one can observe the opposite effects on the CMC of electrolytes (NaCl, HCl) and nonelectrolytes (tetramethylurea, methanol), which are a consequence of the polarity of the water–electrolyte and water–nonelectrolyte media. The presence of TMU increases the degree of ionization of SDS micelles. This is due to the solubilization of TMU in the Stern layer of the micelle, which separates the ionic head groups and consequently decreases the repulsion between them.

Finally, it is important to recognize that there may be systematic differences among methods for determining the CMC. The solubilization of a dye (or any hydrophobic species, such as BZA) in micelles depends mainly on the total amount of micelles in a system. Therefore, in general, the method of keto–enol tautomerism of BZA is not applicable to determine the CMC of surfactants with low CMC values (less than $\sim 5 \times 10^{-4}$ mol L^{-1}). Nevertheless, this method is satisfactory for the determination of CMC of anionic, cationic, or nonionic surfactant under any experimental conditions of electrolyte or nonelectrolyte concentration. The fluorescence method is the most versatile and precise. A variety of probe molecules have been used to determine the CMC of micelles, most of which have fluorescence parameters sensitive to solvent polarity, such as pyrene. To determine correct values for the CMC, the probes employed must be mostly solubilized in the micellar phase (high partitioning coefficient) and special care must be taken to ensure that no aggregation between the probe and surfactant monomers occurs below the CMC. The method of the vibrational emission spectrum of pyrene reported here can also be applied to test for polarity in micelles. The electrical conductance method, obviously, can only be applied to ionic surfactants. The results obtained in the presence of high electrolyte concentrations are not good, as a consequence of the residual conductance by the electrolyte. Another problem arises when an ion of the salt can exchange with surfactant counterions, as is the case of SDS in the presence of H^+ ions or of TTABr in the presence of OH^- ions.

Acknowledgment

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