

Mixtures of Nonionic and Ionic Surfactants: Determination of Mixed Micelle Composition Using Cross-Differentiation Relations

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Cross-differentiation relations are used in thermodynamics to describe the behavior of cationic and nonionic surfactants in mixed micelles. This study uses dodecyltrimethylammonium bromide (DTABr) as cationic surfactant and dodecylpoly(oxyethylene glycol ether)₂₃, or BRIJ 35, as nonionic surfactant. One of these cross-differentiation relations allows us to connect the nonionic surfactant activity with that of the cationic surfactant by following the variations of DTABr molality with BRIJ 35 molality, at constant DTABr chemical potential. This was possible with a reliable DTA⁺-selective electrode. We show that this approach gives access to the activity of nonionic species in solution and into the micelle from potentiometric measurements.

Introduction

The aggregation conditions of mixed surfactants in aqueous or hydroorganic media have been the subject of recent studies whose objective is to define the parameters responsible for the micellization phenomenon and the mixed micelle constitution.^{1–11} Beyond its academic interest, this subject tackles the real problem of the use of surfactants in industry or in household applications. Surfactants are often mixed in water or hydro-organic media.

The analysis of micellar systems made of mixed surfactants requires experimental techniques that provide unambiguous determination of the distribution of different species in solution and their partition between solution and aggregates. For electrically charged amphiphiles, potentiometric methods⁶ can be considered, using selective electrodes. Recent extensive development of these electrodes permits their use in the study of different equilibrium reactions involving ionic surfactants (influence of the medium on critical micelle concentration (cmc),^{12,13} association equilibrium,^{13,14} adsorption of cationic surfactant onto clays,¹⁵ etc).

For nonionic species, there are, however, few ways to get this discrimination. Thus, most thermodynamic analyses of mixed surfactants in solution depend on an assumption about the behavior of the micelle constituents, introducing an additional condition that permits determination of the micelle composition if the cmc's of the two surfactants are known. This approach has been particularly developed by Rubingh¹¹ and used by other authors^{8–10} using the model of regular solution. This assumption is unnecessary for studies in which the activity of one of the two surfactants in solution is experimentally accessible, as is the case of mixtures containing at least one ionic surfactant.

Indeed, by using properties of cross-differentiation relations, the nonionic surfactant activity can be determined from variations of the ionic surfactant activity with different solution composition. This approach was particularly developed and applied by McKay.^{16–18} The method has also been used in the study of various mixtures of electrolytes and of electrolytes and molecules, in dilute and concentrated solutions.¹⁹

The aim of this article is to present these equations and to apply them in the particular case of mixtures, in aqueous

solution, of cationic surfactant dodecyltrimethylammonium bromide (DTA⁺Br[−]) and nonionic surfactant dodecylpoly(oxyethylene glycol ether)₂₃ (BRIJ 35, **2**) in variable proportions. We will show that this approach allows complete determination of the system and description of the behavior of each solution component as a function of composition.

Thermodynamic of Surfactant Mixtures

Consider a system constituted of n_1 moles of DTABr, n_2 moles of BRIJ 35, n_3 moles of water, and n_{NaBr} moles of NaBr to fix the Br[−] activity in the medium. Thus, the number of moles of Br[−] in solution can be supposed as constant during the different operations. In this case, the salt solution can be considered as a solvent. The molalities of solutes were calculated for 1 kg of water–NaBr (0.3 mol L^{−1}) mixtures.

The free energy of this system is a function of state parameters, i.e., T , P , and the macroscopic variables of composition

$$G = G(T, P, n_{\text{DTA}}, n_2, \mathcal{M}_{\text{solvent}}) \quad \text{with} \\ \mathcal{M}_{\text{solvent}} = n_{\text{Br}} M_{\text{Br}} + n_{\text{Na}} M_{\text{Na}} + n_3 M_3 = 1 \text{ kg}$$

and assuming that $n_{\text{Na}} \approx n_{\text{Br}} = \text{constant}$.

At constant temperature and pressure, the free energy variation of this system leads to

$$dG = \mu_{\text{DTA}} dn_{\text{DTA}} + \mu_2 dn_2 + g'_{\mathcal{M}} d\mathcal{M} \quad (1)$$

in which μ_{DTA} , μ_2 , $g'_{\mathcal{M}}$ are the chemical potentials of DTA⁺, BRIJ 35, and the solvent, even if these different compounds can interact or react between them. We have chosen to associate with \mathcal{M} the thermodynamic magnitude $g'_{\mathcal{M}} = (\partial G / \partial \mathcal{M})_{n_{\text{DTA}}, n_2}$ and to conserve its mathematical form.

Properties of cross-differentiation relation can be expressed as

$$\left(\frac{\partial \mu_2}{\partial \mu_{\text{DTA}}} \right)_{m_2, \mathcal{M}} = - \left(\frac{\partial m_{\text{DTA}}}{\partial m_2} \right)_{\mu_{\text{DTA}}, \mathcal{M}} = - \left(\frac{\partial n_{\text{DTA}}}{\partial n_2} \right)_{\mu_{\text{DTA}}, \mathcal{M}} = -P_{(a_{\text{DTA}})} \quad (2)$$

Henceforth, constant terms of the medium will be omitted.

The first term of this equation describes the variations of the chemical potential of **2** when the chemical potential of DTA^+ is modified, maintaining the quantity of **2** constant in the solution. The right-hand term of this equation links up the variations of DTA^+ and BRIJ 35 molalities when the DTA^+ chemical potential (or the DTA^+ activity, a_{DTA}) is maintained constant. The value of $p_{(a_{\text{DTA}})}$ can be estimated experimentally by measuring DTA^+ activity by using a DTA^+ -selective electrode.

Knowing $p_{(a_{\text{DTA}})}$ (experimentally) and the variations of μ_{DTA} by measurement of DTA^+ activity gives access to the activity of **2** by calculation. We exploited this way to calculate the variations of the nonionic surfactant activity for different molalities of DTABr.

Experimental Section

Products. DTABr and BRIJ 35 were purchased from Aldrich. The technical form of BRIJ 35 gives a cmc of about $9.1 \times 10^{-5} \text{ mol L}^{-1}$ in water and an aggregation number of 40 monomers. The two surfactants were used without further purification.

The water used was filtered with an ELGA UHQ II system ($\chi = 18 \text{ M}\Omega$). Solutions of cationic and nonionic surfactants were sufficiently dilute in the saline medium so that the molality could be linked to the concentration through the density ($\rho = 1.02 \text{ kg dm}^{-3}$) of the water–NaBr saline solution.

$$C_{\text{DTA}} = \rho m_{\text{DTA}} \quad \text{and} \quad C_2 = \rho m_2$$

ρ is determined for each solution by a Picker electronic densimeter; its value is close to the density of the NaBr saline solution ($\rho \approx 1 \text{ kg dm}^{-3}$) so the concentration values are equal to the molality values.

Potentiometric Measurements. The reference electrode of the KCl-saturated calomel was protected from amphiphile diffusion by a saline agar–agar gel made of 2 mol L^{-1} KCl. To limit the diffusion speed of surfactant, the gel was contained in a Teflon capillary tube.¹⁴ The surfactant ion-selective electrode (ise) was produced in our laboratory as described in previous papers.^{12–15} The electrode response was determined to be Nernstian between the surfactant cmc and about $10^{-6} \text{ mol kg}^{-1}$. The emf was stable to $\pm 0.2 \text{ mV}$ within a few seconds and reproducible within $\pm 0.5 \text{ mV}$. We had verified that the presence of BRIJ 35 in solution did not change the electrode response. All measurements were carried out at $298.0 \pm 0.1 \text{ K}$.

Electrochemical Cell. The following electrochemical chain is present:

Cu (ΦI)	Calomel reference electrode	Aqueous solution of $\text{DTA}^+ (m_1)$, BRIJ 35 (m_2) NaBr 0.3 mol L^{-1}	$\text{DTA}^+ \text{ ise}$	Cu (ΦII)
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Assuming that the reference electrode potential remains constant during the nonionic surfactant addition in the solution, the emf of this cell can be written

$$\Delta E = \Phi \text{II} - \Phi \text{I} = \text{constant} + \frac{RT}{F} \ln a_{\text{DTA}} \quad (3)$$

Therefore, this electrochemical cell provides access to the cationic amphiphile activity as the solution composition changes.

Procedure Measurement. In 0.3 mol L^{-1} NaBr aqueous solution, the DTABr cmc is $2.3 \times 10^{-3} \text{ mol kg}^{-1}$ (determined

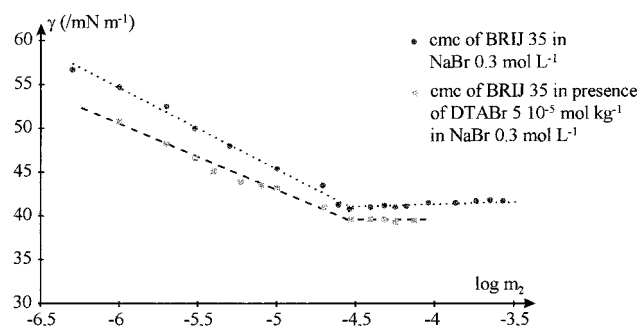


Figure 1. Surface tension variation with addition of nonionic surfactant. Determination of Brij 35 cmc ($2.88 \times 10^{-5} \text{ mol kg}^{-1}$) in 0.3 mol L^{-1} NaBr and in the presence of $5 \times 10^{-5} \text{ mol kg}^{-1}$ DTABr ($2.82 \times 10^{-5} \text{ mol kg}^{-1}$) in 0.3 mol L^{-1} NaBr.

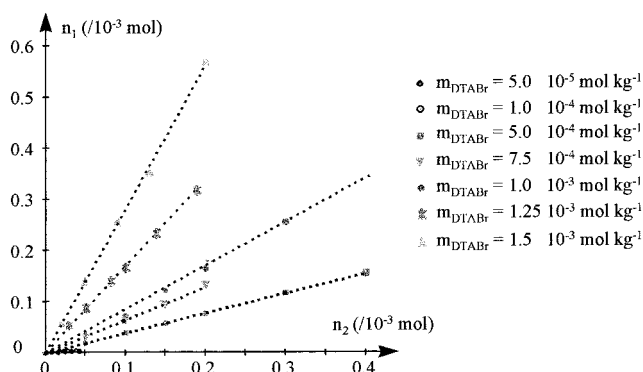


Figure 2. Variation of number of moles of DTABr added to the initial solution with total number of moles of BRIJ 35 for different initial DTABr molality in 0.3 mol L^{-1} NaBr solution.

potentiometrically) and the BRIJ 35 cmc is about $2.9 \times 10^{-5} \text{ mol kg}^{-1}$ (determined by surface tension measurements as described hereafter (Figure 1)).

Ten milliliters of DTABr solution at a molality m_{DTA}^0 below the cmc in this medium was introduced to the experimental vessel. The emf of the previously described cell was measured.

A small quantity of BRIJ 35 (δn_2), whose molality in final solution was higher than the pure nonionic surfactant cmc, was added to this solution. The result of this addition was a decrease in cationic surfactant activity and a decrease of cell emf, showing that cationic surfactants had combined with micellar aggregates. This variation was followed by the electrodes.

A quantity of DTABr (δn_{DTA}) was then added to the reaction medium to restore the DTA^+ activity to its initial value. To avoid any problem with dilution, molalities of DTABr and BRIJ 35 added ($10^{-1} \text{ mol kg}^{-1}$) are higher than the initial DTABr molality in solution.

This process was repeated for several nonionic surfactant quantities. Each time, the total quantities of cationic and nonionic surfactants expressed in molal scale ($M = 1 \text{ kg}$) in the reaction medium were calculated. Thus, a series of states was obtained, for each of these states, the DTA^+ chemical potential was constant and assigned to the initial value.

Plotting $\sum \delta n_{\text{DTA}}$ added versus $\sum \delta n_2$ at constant DTA^+ activity (Figure 2) gives a straight line whose gradient $p_{(a_{\text{DTA}})}$ gives the value of the partial differential $(\partial n_{\text{DTA}} / \partial n_2)_{a_{\text{DTA}}}$ as in eq 2. The $p_{(a_{\text{DTA}})}$ value depends on the DTA^+ activity.

This process was repeated for different a_{DTA} values, i.e., several initial DTA^+ molalities, in order to have $(\partial n_{\text{DTA}} / \partial n_2)_{a_{\text{DTA}}}$ variations with a_{DTA} values. The two sets of results were necessary to make the integration to obtain the nonionic surfactant activity in the reaction medium. The partial dif-

TABLE 1: Values of the Term $p_{(a_{\text{DTA}})}$ versus the molality m_{DTA}° . A Theoretical Value of $p_{(a_{\text{DTA}})}$ was calculated from Eq 6

m_{DTA}° (mol kg ⁻¹)	5.0×10^{-5}	1.0×10^{-4}	5.0×10^{-4}	7.5×10^{-4}	1.0×10^{-3}	1.25×10^{-3}	1.5×10^{-3}
$p_{(a_{\text{DTA}})}$ experimental	0.05	0.12	0.39	0.64	0.86	1.69	2.81
$p_{(a_{\text{DTA}})}$ calculated	0.07	0.13	0.39	0.53	0.87	1.57	2.81

ferential equation

$$\left(\frac{\partial \mu_2}{\partial \mu_{\text{DTA}}} \right)_{m_2} = \frac{1}{RT} \left(\frac{\partial \mu_2}{\partial \ln a_{\text{DTA}}} \right)_{m_2} = -p_{(a_{\text{DTA}})}$$

in which a_{DTA} is the DTA^+ activity in molal scale, leads us to integrate the following expression at constant nonionic surfactant molality:

$$d \ln a_2 = -p_{(a_{\text{DTA}})} d \ln a_{\text{DTA}} \quad (4)$$

Use of dilute surfactant solutions permits use of molalities instead of activities. So,

$$\left(\frac{\partial \mu_2}{\partial \mu_{\text{DTA}}} \right)_{m_2} = - \left(\frac{\partial C_{\text{DTA}}}{\partial C_2} \right)_{a_{\text{DTA}}} = - \left(\frac{\partial m_{\text{DTA}}}{\partial m_2} \right)_{a_{\text{DTA}}} = - \left(\frac{\partial n_{\text{DTA}}}{\partial n_2} \right)_{a_{\text{DTA}}} = -p_{(a_{\text{DTA}})} \quad (5)$$

The choice of integration limits is problematic; it will be discussed in the next paragraph.

Results and Discussions

Results obtained for seven different DTABr molalities are shown in Figure 2. For each activity, plots of n_{DTA} added versus n_2 were linear and passed through the origin. $p_{(a_{\text{DTA}})}$ values varied with the molality m_{DTA}° and are given in Table 1.

Calculation of the Nonionic Surfactant Activity in Solution. Knowing the variation of $p_{(a_{\text{DTA}})}$ with a_{DTA} , we can access the nonionic surfactant activity. Before integrating, it is important to discuss the meaning of the different terms.

A simple model, assuming that the solution consists of mixed micelles of DTA^+ and BRIJ 35 dispersed in an aqueous intermicellar medium, can be used. DTA^+ activity is fixed with the help of a cationic amphiphile-selective electrode, calibrated in dilute medium, by following its potential response at different DTA^+ molalities in water–NaBr solution.

DTA^+ activity is maintained equal to the initial DTA^+ molality in solution. As nonionic surfactant is added, DTA^+ activity decreases, corresponding to partial DTA^+ fixing on BRIJ 35 micelles. DTA^+ is then added to the solution to restore the initial level, enabling the study of different systems at fixed DTA^+ cmc. It can be considered that the electrode measures the residual DTA^+ molality in the bulk. In this case, DTA^+ activity is equal to the cationic surfactant cmc in the presence of BRIJ 35 ($\text{cmc}_{\text{DTA}} = \omega_{\text{DTA}}$).

Similar arguments apply to the nonionic amphiphile. The activity a_2 is equal to free BRIJ 35 concentration in the bulk, i.e., to its cmc in the mixture (ω_2).

A priori, the function $p_{(a_{\text{DTA}})} = p(\omega_{\text{DTA}})$ describing the surfactant association has no thermodynamically predetermined form. So, we have developed a polynomial form:

$$p_{(a_{\text{DTA}})} = 1570\omega_{\text{DTA}} - 2.5 \times 10^6 \omega_{\text{DTA}}^2 + 1.8 \times 10^9 \omega_{\text{DTA}}^3 \quad (6)$$

provides a good fit to experimental results, as is shown in Table 1, in which we have reported calculated and measured values

of p . This expression remains valid at all nonionic surfactant concentrations.

Equation 5 is $d \ln a_2 = -p_{(a_{\text{DTA}})} d \ln a_{\text{DTA}}$. Thus, the following differential equation must be integrated:

$$d \ln a_2 = -(1570\omega_{\text{DTA}} - 2.5 \times 10^6 \omega_{\text{DTA}}^2 + 1.8 \times 10^9 \omega_{\text{DTA}}^3) \frac{1}{\omega_{\text{DTA}}} d\omega_{\text{DTA}}$$

so

$$d \ln a_2 = -(1570\omega_{\text{DTA}} - 2.5 \times 10^6 \omega_{\text{DTA}}^2 + 1.8 \times 10^9 \omega_{\text{DTA}}^3) d\omega_{\text{DTA}}$$

The choice of limits of integration is important. We have chosen to take as first limit the value of the nonionic surfactant activity (or ω_2) in the presence of the lower DTA^+ molality in NaBr aqueous solution. This value can be determined by surface tension measurements (Figure 1). The curve $\gamma = f(\log m_2)$ at fixed DTA^+ molality shows the presence of a minimum which corresponds to the cmc of BRIJ 35 in the presence of 5×10^{-5} mol kg⁻¹ $\text{DTA}^+(\omega_2)$.

Therefore, the first limit of integration is defined by the data pair ($\omega_{\text{DTA}} = 5 \times 10^{-5}$ mol kg⁻¹; $\omega_2 = 2.82 \times 10^{-5}$ mol kg⁻¹). The second limit of integration corresponds to some DTA^+ molality leading to the activity a_2 , i.e., the nonionic surfactant cmc in the presence of DTA^+ .

Integration of the previous equation gives

$$\ln a_2 = -10.401 - 1570\omega_{\text{DTA}} + 1.25 \times 10^6 \omega_{\text{DTA}}^2 - 6 \times 10^8 \omega_{\text{DTA}}^3 \quad (7)$$

Results of this equation are given in Table 2. The cationic surfactant cmc (ω_{DTA}) increases as the nonionic surfactant activity in the solution decreases. Knowing the molalities of the two surfactants free in the intermicellar medium, we can determine the composition of micelles. Since the total quantities of the two surfactants are known, the molality of cationic surfactant free in solution is measured by the electrode and the nonionic surfactant molality has been calculated; the micellar phase composition is given by the difference.

$$x = \frac{n_{2,\text{micelle}}}{n_{2,\text{micelle}} + n_{\text{DTA},\text{micelle}}}$$

Table 3 shows results of this study. BRIJ 35 is a peculiar nonionic surfactant because its cmc is so low that it can be considered as entirely under micelle form. So $n_{2,\text{total}} \approx n_{2,\text{micelle}}$, and an approximate value of the molar fraction could be calculated.

$$x_{\text{app}} = \frac{n_{2,\text{total}}}{n_{2,\text{total}} + n_{\text{DTA},\text{total}}}$$

The values of the molar fraction calculated from the results of the cross-differentiation relation were very close to those of the approximate molar fraction. Thus, this particular case shows

TABLE 2: Values of BRIJ 35 Activity (a_2) for Different DTA⁺ Molalities. a_2 Is Equal to the Value of ω_2

ω_{DTA} (mol kg ⁻¹)	5.0×10^{-5}	1.0×10^{-4}	5.0×10^{-4}	7.5×10^{-4}	1.0×10^{-3}	1.25×10^{-3}	1.5×10^{-3}
$a_2 = \{\omega_2\}$	2.8×10^{-5}	2.6×10^{-5}	1.8×10^{-5}	1.5×10^{-5}	1.2×10^{-5}	9.3×10^{-6}	6.3×10^{-6}

TABLE 3: For Different Compositions of the Mixed Surfactants Solution, the Molar Fraction (x) of Nonionic Surfactant in the Mixed Micelle Is Calculated. x_{app} Is the Approximate Molar Fraction Calculated by Assuming That All the Nonionic Surfactant Is Micellized

ω_{DTA} (mol kg ⁻¹)	5.0×10^{-5}	1.0×10^{-4}	5.0×10^{-4}	7.5×10^{-4}	1.0×10^{-3}	1.25×10^{-3}	1.5×10^{-3}
ω_2 (mol kg ⁻¹)	2.8×10^{-5}	2.6×10^{-5}	1.8×10^{-5}	1.5×10^{-5}	1.2×10^{-5}	9.3×10^{-6}	6.3×10^{-6}
$p_{(\omega_{\text{DTA}})}$	0.07	0.13	0.39	0.53	0.87	1.57	2.81
x	0.954	0.905	0.725	0.622	0.554	0.366	0.264
x_{app}	0.955	0.906	0.725	0.622	0.555	0.367	0.265

that our thermodynamic approach is quite valid. Afterward, this method can be applied to nonionic surfactant with a higher cmc value.

However, knowing the nonionic surfactant activity in the medium allows the description of the characteristics of the equilibrium between surfactants in micelles and surfactants free in solution.

Micelle Equilibrium. Within a very simple model of diphasic medium, the mixed micelle can be considered as consisting of a phase in equilibrium with the intermicellar medium.

The nonionic surfactant possesses the same chemical potential throughout the solution, allowing us to write the equality

$$\mu_2 = \mu_2^\ominus + RT \ln a_2 = \mu_2^* + RT \ln a_2^* \quad (8)$$

in which μ_2^\ominus is the BRIJ 35 standard potential at infinite dilution in aqueous solution and a_2 is the nonionic surfactant activity in solution in this same model; as shown previously, this magnitude is equal to ω_2 .

To write the chemical potential of compound **2** in the micelle, it is necessary to adopt a simple reference system which takes into account the particular case of pure BRIJ 35 micelle free from cationic surfactant. By referring to this state, we can write, in the case of a pure **2** micelle

$$\mu_2 = \mu_2^\ominus + RT \ln \text{cmc}_2^\ominus = \mu_2^* \quad (9)$$

cmc_2^\ominus is the BRIJ 35 cmc in 0.3 mol L⁻¹ NaBr aqueous solution. This value, about 2.88×10^{-5} mol kg⁻¹, was determined by surface tension measurements (Figure 1).

Equations 15 and 16 link the nonionic surfactant activity in the micelle according to cmc:

$$\frac{\omega_2}{\text{cmc}_2^\ominus} = a_2^* \quad (10)$$

The introduction of the molar fraction of the considered micelle as for a mixed solvent allows us to introduce the nonionic amphiphile activity coefficient, γ_2^* :

$$\gamma_2^* = \frac{\omega_2}{\text{cmc}_2^\ominus} \frac{1}{x} \quad (10')$$

γ_2^* values were calculated for each experiment and are reported in Table 4. These values do not depend on the determination of the cmc_2^\ominus value but only on the fit of the function $p_{(\omega_{\text{DTA}})} = f(\omega_{\text{DTA}})$. This is the weak spot of this method and demands many experimental measurements for a good definition of this function.

As is shown in Table 4, the behavior of the mixed micelle BRIJ 35-DTABr in 0.3 mol L⁻¹ NaBr solution can be well-

TABLE 4: Variations of Nonionic Surfactant Activity and Activity Coefficients in the Micelle with cmc_2 Values

$a_2^* = \omega_2/\text{cmc}_2^\ominus$	x	γ_2^*
0.977	0.954	1.02
0.911	0.905	1.02
0.610	0.725	0.84
0.509	0.622	0.82
0.420	0.554	0.76
0.323	0.366	0.88
0.220	0.264	0.83

described by an ideal solution model. Indeed, in this large range of composition ($0.265 < x < 1$), γ_2^* varies only between 1 and 0.76.

Conclusion

The aim of this paper was to demonstrate in a simple case the use of cross-differentiation relations in thermodynamics to describe the behavior of ionic and nonionic surfactants in mixed micelles. The validity of this approach had been checked using a nonionic surfactant with a low cmc value. This thermodynamic method is possible with a reliable DTA⁺-selective electrode which allows us to obtain a series of reactions occurring at constant chemical potential of the amphiphilic cation in solution.

Determination of nonionic surfactant activity requires a great number of experiments. Firstly, this is important to define the parameters of the variations of the gradient with cationic surfactant molality. Secondly, the nonionic surfactant activity is calculated from an integration, so a limit of integration must be known with another method such as surface tension that allows one to determine the cmc of mixed micelle. Thus, we can envisage obtaining the composition of a mixed micelle with a nonionic surfactant having a higher cmc.

On the other hand, this approach allows access to the activities of nonionic species in solution by potentiometric methods. The technique used in this work can be generalized to other molecules which can interact with ionic amphiphiles.

In this study, we used a background salt (NaBr) in solution, but we have checked that it was possible to work in pure water using the same junctionless cell described in this paper. This cell gives access to the DTABr activity in solution and to the nonionic surfactant activity, by the same approach.

Systems illustrating these different cases are under study at our laboratory, as are mixtures involving anionic amphiphiles and nonionic surfactants.

References and Notes

- (1) Nishikido, N. In *Mixed Surfactant Systems*; Ogino, K.; Abe, M., Eds.; Surf. Sci. Series 44; Marcel Dekker, Inc.: New York, 1993; p 23.
- (2) Graciaa, A. P.; Lachaise, J.; Schechter, R. S. In *Mixed Surfactant Systems*; Ogino, K.; Abe, M., Eds.; Surf. Sci. Series 44; Marcel Dekker, Inc.: New York, 1993; p 63.
- (3) Makayssi, A.; Lemordant, D.; Treiner, C. *Langmuir* **1993**, *9*, 2808.

- (4) Takasawa, Y.; Ueno, M.; Meguro, K. *J. Colloid Interface Sci.* **1980**, 78, 207.
- (5) Gorski, N.; Gradzielski, M.; Hoffmann, H. *Langmuir* **1994**, 10, 2594.
- (6) Das Gupta, P. K.; Moulik, S. P. *Colloid Polym. Sci.* **1989**, 267, 246.
- (7) Yu, Z.; Zhao, G. *J. Colloid Interface Sci.* **1989**, 130, 414.
- (8) Treiner, C.; Nortz, M.; Vaution, C. *Langmuir* **1990**, 6, 1211.
- (9) Treiner, C.; Amar Kodja, A.; Fromon, M. *Langmuir* **1987**, 3, 729.
- (10) Furuya, H.; Moroi, Y.; Sugihara, G. *Langmuir* **1995**, 11, 774.
- (11) Rubingh, D. N. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum: New York, 1979; p 337.
- (12) Jezequel, D.; Mayaffre, A.; Letellier, P. *J. Chim. Phys.* **1991**, 88, 391.
- (13) Martin, J. V.; Turmine, M.; Letellier, P.; Hemery, P. *Electrochim. Acta* **1995**, 40, 2749.
- (14) Jezequel, D.; Mayaffre, A.; Letellier, P. *Can. J. Chem.* **1991**, 69, 1865.
- (15) Gloton, M. P.; Mayaffre, A.; Turmine, M.; Letellier, P.; Suquet, H. *J. Colloid Interface Sci.* **1995**, 172, 56.
- (16) McKay, H. A. C. *Nature* **1952**, 169, 464.
- (17) McKay, H. A. C.; Perring, J. K. *Trans. Faraday Soc.* **1953**, 49, 163.
- (18) McKay, H. A. C. *Trans. Faraday Soc.* **1953**, 49, 237.
- (19) Lewis, G. N.; Randal, M. In *Thermodynamics* McGraw-Hill Book Co.: New York, 1961; p 551.