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# Critical Micelle Concentration Determination in Binary Mixtures of Ionic Surfactants by Deconvolution of Conductivity/Concentration Curves

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A new method for the determination of critical micelle concentrations, cmc, of ionic surfactants from conductivity measurements has been developed. The method is based on deconvolution into Gaussians of the second derivative of the conductivity/concentration data, followed by two consecutive numerical integrations. In testing this procedure, aqueous decyl-, dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide solutions were used. The method has proved to be particularly useful for micellar systems formed of binary mixtures of these surfactants, in which the conductivity/concentration curves do not show any distinctive change in slope. The thermodynamic study of such binary mixtures can be carried out by using the mixture cmc vs composition data.

## Introduction

The phenomenon of micelle aggregation in mixtures of surfactants has aroused considerable interest in recent years.<sup>1</sup> This is because most surfactants used in daily applications are formed of mixtures of homologous ionic detergents or by mixtures of ionic and nonionic surfactants.

As in the case of other research on single-component micelle systems, when working with mixtures of surfactants it is essential to determine the critical micelle concentration, cmc, i.e., the concentration after which the process of micelle association begins, which in this particular case will strongly depend on the composition of the system.<sup>2-6</sup>

Experimentally, the usual way of finding the cmc is by plotting a graph of a suitable physical property (surface tension, electric conductivity, dye solubilization, etc.) as a function of concentration. An abrupt change of slope marks the cmc. In the case of ionic surfactants, one of the most often used physical properties has been electric conductivity. Its plot against the concentration of surfactant yields two straight lines from whose intersection the CMC is obtained. This procedure, which is perfectly applicable to single-component micelle systems, cannot be used successfully for the determination of the cmc of mixed micelle aggregates because the conductivity/concentration plot affords a curve that is not compatible with two straight lines.<sup>7</sup>

The aim of the present work was to develop a general method that would yield the cmc value of any kind of ionic micelle system from conductivity measurements. The work is structured in two parts. In the first, a model that interprets the variation of conductivity with the concentration of surfactant is developed, checking its validity in cationic micelle systems. In the second part, the

model is applied to six possible binary mixtures of surfactants (decyl-, dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromide), and the cmc of the mixed aggregate is then determined. The variation of this parameter with composition allows one to study the thermodynamic behavior of these systems.

## Description of the Algorithm

One the most successful thermodynamic models in the interpretation of the properties of micelle systems is the pseudophase separation model.<sup>5,8-10</sup> This model considers that, after a given concentration, cmc, the solution is formed of two pseudophases: the aqueous and the micelle phases. Accordingly, a sharp change in the physical behavior of the system is assumed. However, a more general empirical definition of the cmc that can be used to experimentally locate this concentration and that is taken as the starting point of the algorithm proposed here is the one reported by Phillips.<sup>11</sup> In this, the cmc is considered as the concentration at which the slope of the plot of a physical property of the solution,  $\phi$ , against concentration,  $C$ , is changing most rapidly:

$$(d^3\phi/dC^3) = 0; \quad C = \text{cmc} \quad (1)$$

This definition can be easily applied to any system as long as the measured physical property is a linear function of the concentration of all the species that take part in the micellization process. In the present work, this condition was applied to the value of electric conductivity of aqueous solutions of ionic surfactants,  $\kappa$ , assuming that this can be defined approximately as

$$\kappa = \lambda_{\text{I}}X + \lambda_{\text{D}}D + \lambda_{\text{M}}M \quad (2)$$

Taking into account the mass balance of the surfactant

$$C = X + \beta M \quad (3)$$

$$C = D + M \quad (4)$$

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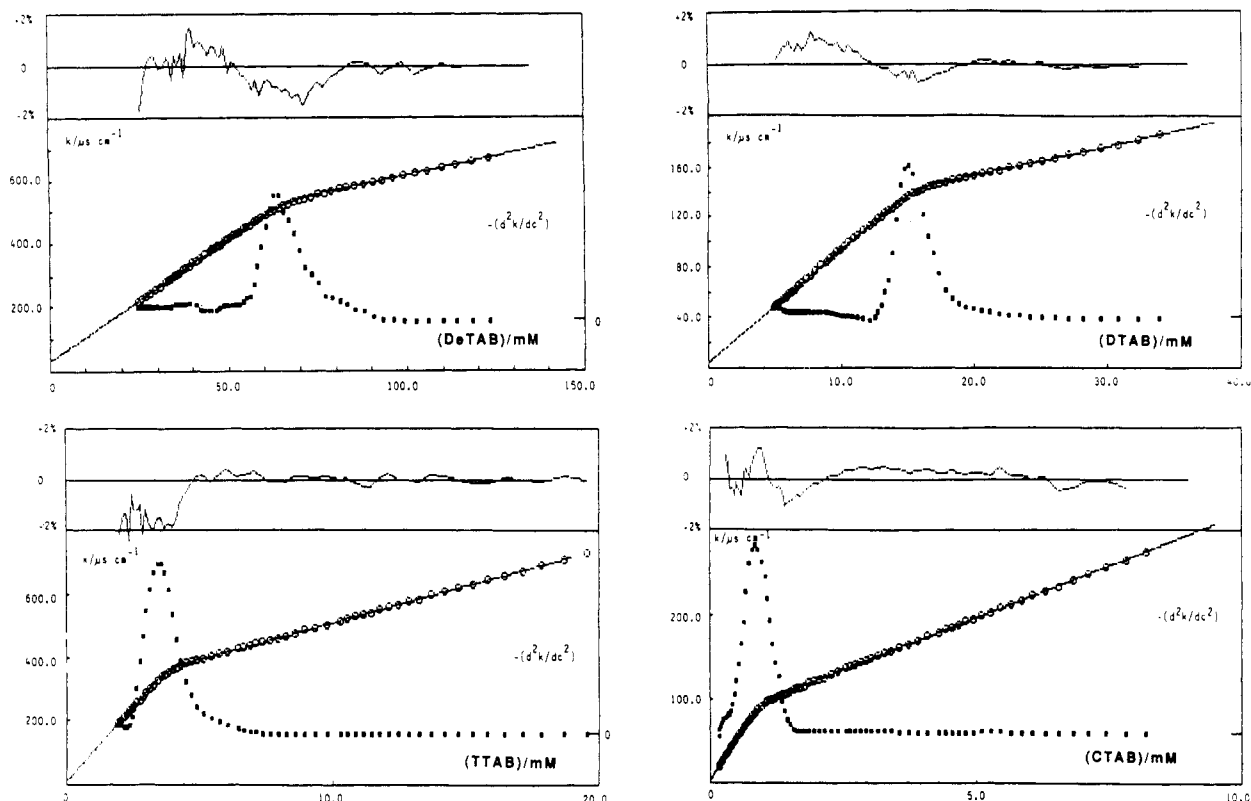
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**Figure 1.** Plots of the conductivity of unicomponent surfactant solutions vs total concentration. Open circles are experimental data, and the line is calculated according to eq 16 and the parameters of Table I. The upper line represents the percent deviation of experimental vs calculated data. For illustrative purposes, the second derivative of conductivity (full circles) is also shown.

this can then be written as

$$\kappa = A_X X + A_C C \quad (5)$$

where

$$A_X = \lambda_X + (\lambda_D/\beta) - (\lambda_M/\beta) \quad (6)$$

$$A_C = \lambda_D - (\lambda_D/\beta) + (\lambda_M/\beta) \quad (7)$$

These parameters are assumed to be independent of concentration for values close to the cmc. From eqs 3–5, one has

$$d^2\kappa/dc^2 = A_X(d^2X/dc^2) \quad (8)$$

$$d^3\kappa/dc^3 = A_X(d^3X/dc^3) \quad (9)$$

$$d^3X/dc^3 = \beta(d^3D/dc^3) = -\beta(d^3M/dc^3) \quad (10)$$

from which it can be deduced that the cmc is univocally defined with respect to the concentration of any of the three species considered.

Furthermore, from eqs 3 and 4, the following expression is obtained for the degree of aggregation of counterions or of monomers,  $\gamma$ :

$$\gamma = dM/dC = (1/\beta)[d(C - X)/dC] = d(C - D)/dC \quad (11)$$

Defined in this way, this parameter can take values from 0 to 1 as the concentration of surfactant increases, changing according to a sigmoidal profile.<sup>12</sup>

From a probabilistic point of view, the distribution of counterions or of monomers in the aqueous and micelle phases could be interpreted with the aid of a binomial distribution model, in which each counterion or monomer can occupy two possible states, aggregated or free, and where the degree of aggregation,  $\gamma$ , would represent the distribution function of the model. When the num-

**Table I.** cmc and Gaussian Fitting Parameters of Eq 16 for Unicomponent Aqueous Cationic Surfactants

surfactant	cmc, mM	$\sigma$ , mM	$H$ , $\mu S cm^{-1} mM^{-2}$	cmc, <sup>a</sup> mM
DETAB	66.00	6.00	-3.4	68.00
DTAB	15.60	1.00	-16.0	16.00
TTAB	3.80	0.32	-89.5	3.50
CTAB	0.92	0.26	-120.0	0.92

<sup>a</sup> Reference 18.

ber of aggregates is large enough, this would become a continuous distribution corresponding to the Gauss function:<sup>13</sup>

$$\gamma = 1/2 + \text{erf}[(C - \langle C \rangle)/\sigma] \quad (12)$$

where  $\langle C \rangle$  and  $\sigma$  represent the mean and the standard deviation, respectively.

Taking into account that the degree of aggregation is also defined by eq 11, one has

$$\gamma = (1/\beta)[d(C - X)/dC] = d(C - D)/dC = 1/2 + \text{erf}[(C - \langle C \rangle)/\sigma] \quad (13)$$

$$d\gamma/dC = -(1/\beta)(d^2X/dc^2) = -d^2D/dc^2 = (1/\sigma(2\pi)^{1/2}) \exp[-(C - \langle C \rangle)^2/2\sigma^2] \quad (14)$$

Considering eqs 8 and 14, one obtains

$$d^2\kappa/dc^2 = -[A_X\beta/\sigma(2\pi)^{1/2}] \exp[-(C - \langle C \rangle)^2/2\sigma^2] \quad (15)$$

and according to the definition of the cmc adopted, one has that the third derivative of conductivity with respect to the concentration of the surfactant vanishes for a concentration value coinciding with the mean of the distri-

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**Table II. Mixture cmc Values and Gaussian Fitting Parameters of Eq 17 for Binary Mixtures of Aqueous Cationic Surfactants**

x	i = 1			i = 2			i = 3			%RMS <sup>a</sup>
	cmc, mM	σ, mM	H, μS cm <sup>-1</sup> mM <sup>-2</sup>	cmc, mM	σ, mM	H, μS cm <sup>-1</sup> mM <sup>-2</sup>	cmc, mM	σ, mM	H, μS cm <sup>-1</sup> mM <sup>-2</sup>	
DTAB/DeTAB										
0.103	43.90	5.00	-3.50							0.91
0.198	35.00	5.05	-3.60							1.04
0.294	29.40	2.50	-7.20							0.84
0.450	23.80	1.83	-10.0							0.85
0.584	20.70	1.53	-12.90							0.77
0.789	17.50	1.40	-17.30							0.93
TTAB/DeTAB										
0.212	9.00	1.20	-9.50							0.37
0.285	7.40	0.92	-13.95							0.40
0.450	5.84	0.90	-18.50							0.41
0.614	5.90	0.60	-34.05							0.44
0.778	4.32	0.40	-57.90							0.39
CTAB/DeTAB										
0.106	3.40	0.45	-10.45							0.24
0.210	2.11	0.39	-20.50							0.35
0.305	1.84	0.30	-41.00							0.42
0.448	1.42	0.28	-50.05							0.38
0.602	1.30	0.27	-70.40							0.41
0.809	1.10	0.26	-101.80							0.79
TTAB/DTAB										
0.093	3.55	0.60	-2.20	10.90	3.35	-7.50				0.43
0.166	8.90	1.85	-10.00	14.30	1.00	-3.90				0.51
0.219	8.40	2.80	-8.10	15.50	0.38	-5.00				0.44
0.347	6.50	1.20	-16.50	12.80	0.70	-7.00				0.58
0.494	5.55	1.00	-23.50	14.00	0.99	-4.00				0.45
0.776	4.20	0.65	-41.00	9.80	0.50	-4.00				0.52
0.925	3.90	0.52	-55.50							
CTAB/DTAB										
0.114	3.22	0.90	-9.00	8.90	1.20	-5.00				0.55
0.299	1.98	0.65	-21.13	7.00	0.40	-9.00				0.54
0.399	1.55	0.31	-100.00	6.90	0.04	-47.00				0.51
0.499	1.30	0.18	-95.00	8.10	0.20	-15.80				0.62
0.657	1.20	0.30	-75.00	7.00	0.30	-6.90				0.64
0.801	1.02	0.19	-120.00							0.58
CTAB/TTAB										
0.122	1.20	0.50	-8.77	2.40	0.49	-29.04	3.45	0.39	-27.04	0.44
0.320	1.62	0.38	-52.00	3.45	0.39	-27.00	3.60	0.17	-30.00	0.58
0.501	1.39	0.34	-65.32	3.60	0.80	-6.60				0.45
0.660	1.19	0.34	-73.18	3.70	1.15	-2.57				0.50
0.772	1.08	0.34	-130.00	3.65	0.17	-17.50				0.75
0.833	1.01	0.18	-130.00	3.70	0.17	-22.00				0.89
0.925	0.98	0.26	-114.00							0.89

<sup>a</sup> Percent root mean square deviation.

bution, i.e.,  $\text{cmc} = \langle C \rangle$ , such that the second derivative of conductivity with respect to the concentration of the surfactant can be written as

$$d^2\kappa/dC^2 = -H \exp[-(C - \text{cmc})^2/2\sigma^2] \quad (16)$$

By integration of this differential equation, the conductivity in terms of total surfactant concentration can be obtained with the following three fitting parameters: the mean of the Gauss distribution, cmc; the width of the Gauss band,  $\sigma$ ; and the height of the curve at the mean value, or preexponential factor,  $H = A_x\beta/\sigma(2\pi)^{1/2}$ .

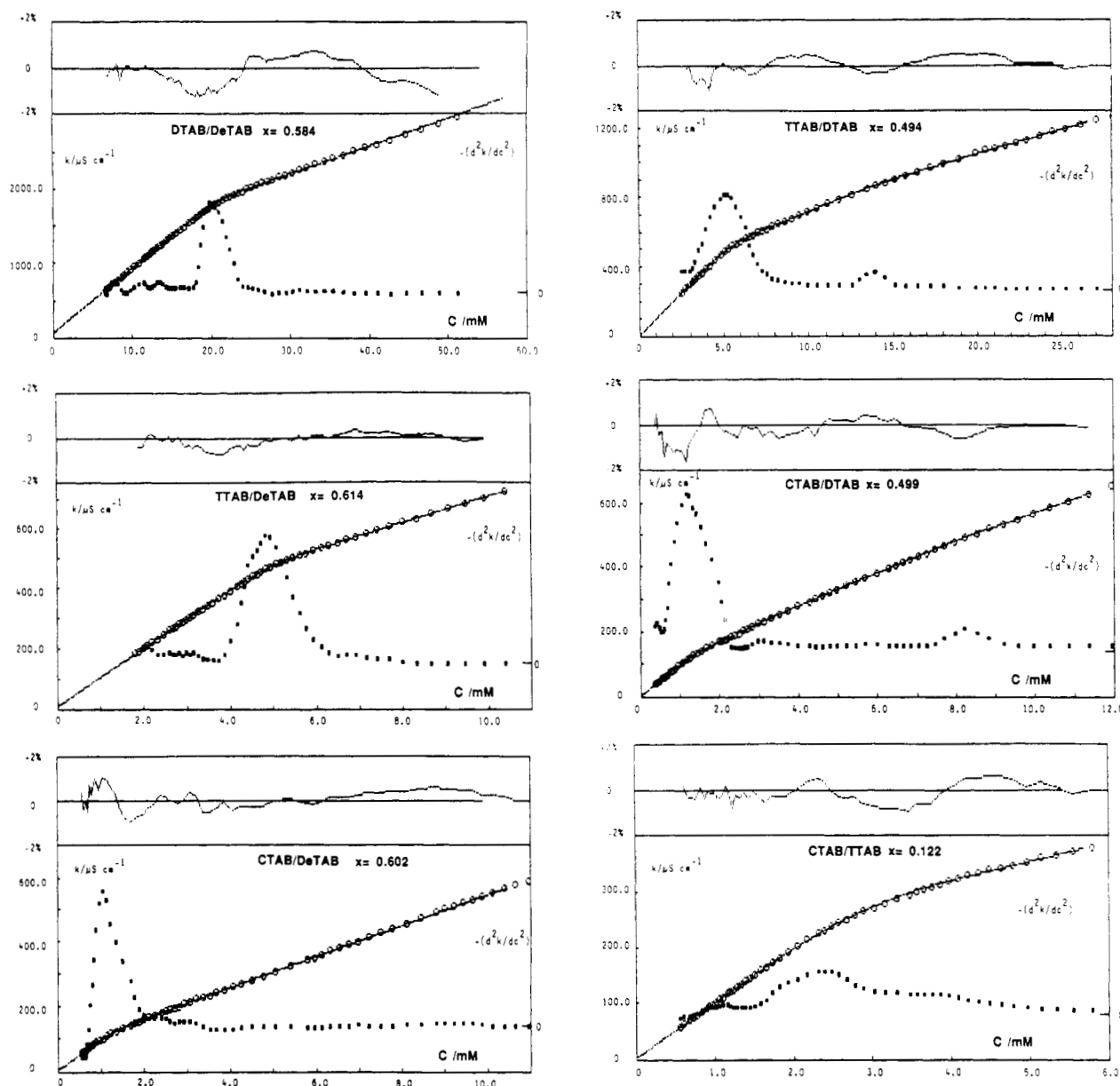
The two consecutive integrations were carried out numerically by using a Euler method.<sup>13</sup> As the first integration constant, i.e., the first derivative of conductivity with respect to the concentration at zero surfactant concentration, the initial slope of the experimental data determined by a linear least-squares fit, was used. The second integration constant, i.e., the value of the conductivity of the solution at zero surfactant concentration, was taken as the one of the solvent. The results of this integration were accompanied by a fitting procedure to the experimental data, based on a least-squares iterative grid

search of the best-fitting parameters (cmc,  $\sigma$ , and  $H$ ). The execution of this iterative procedure requires starting values for the Gaussian fitting parameters close to the optimum ones, since in the opposite case the procedure converges very slowly. This becomes more evident on analyzing the conductivity/concentration curves in systems comprising mixtures of surfactants in which several processes of micelle aggregation can occur within the working concentration range.<sup>14,15</sup> In this later case, the curves will be formed of several Gaussians. Accordingly, before starting the fitting procedure, the experimental values of the conductivity were subjected to a double numerical derivation with respect to the total concentration ( $d^2\kappa/dC^2$ ) from which first estimates of the fitting parameters (cmc,  $\sigma$ , and  $H$ ) for every observed micellization process were obtained. A simplified least-squares procedure for smoothing and differentiation of data was used.<sup>16</sup>

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**Figure 2.** Plots of the conductivity of binary mixtures of aqueous surfactant solutions vs total concentration. Open circles are experimental data, and the line is calculated according to eq 17 and the parameters of Table II. The upper line represents the percent deviation of experimental vs calculated data. For illustrative purposes, the second derivative of conductivity (full circles) is also shown.

### Experimental Section

The reagents dodecyltrimethylammonium bromide, DeTAB (Tokyo); dodecyltrimethylammonium bromide, DTAB (Sigma); tetradecyltrimethylammonium bromide, TTAB (Sigma); and hexadecyltrimethylammonium bromide, CTAB (Merck) were purified by recrystallization with ethanol.

The solutions were prepared with water obtained after treatment with a Milli Q system from Millipore.

Application of eq 1 for the determination of the cmc requires a large number of experimental results, so a technique of conductimetric titration was employed. Thus, each curve has more than 50 conductivity/concentration values.

Conductivity was measured with a Crison 522 conductivity bridge with an Ingold cell of  $0.991 \pm 0.001 \text{ cm}^{-1}$  cell constant calibrated with solution of KCl of known concentration.<sup>17</sup> All measurements were performed at  $25.0 \pm 0.1^\circ \text{C}$ .

### Results and Discussion

The conductivity/concentration results for the homomeric solutions of the surfactants DeTAB, DTAB, TTAB,

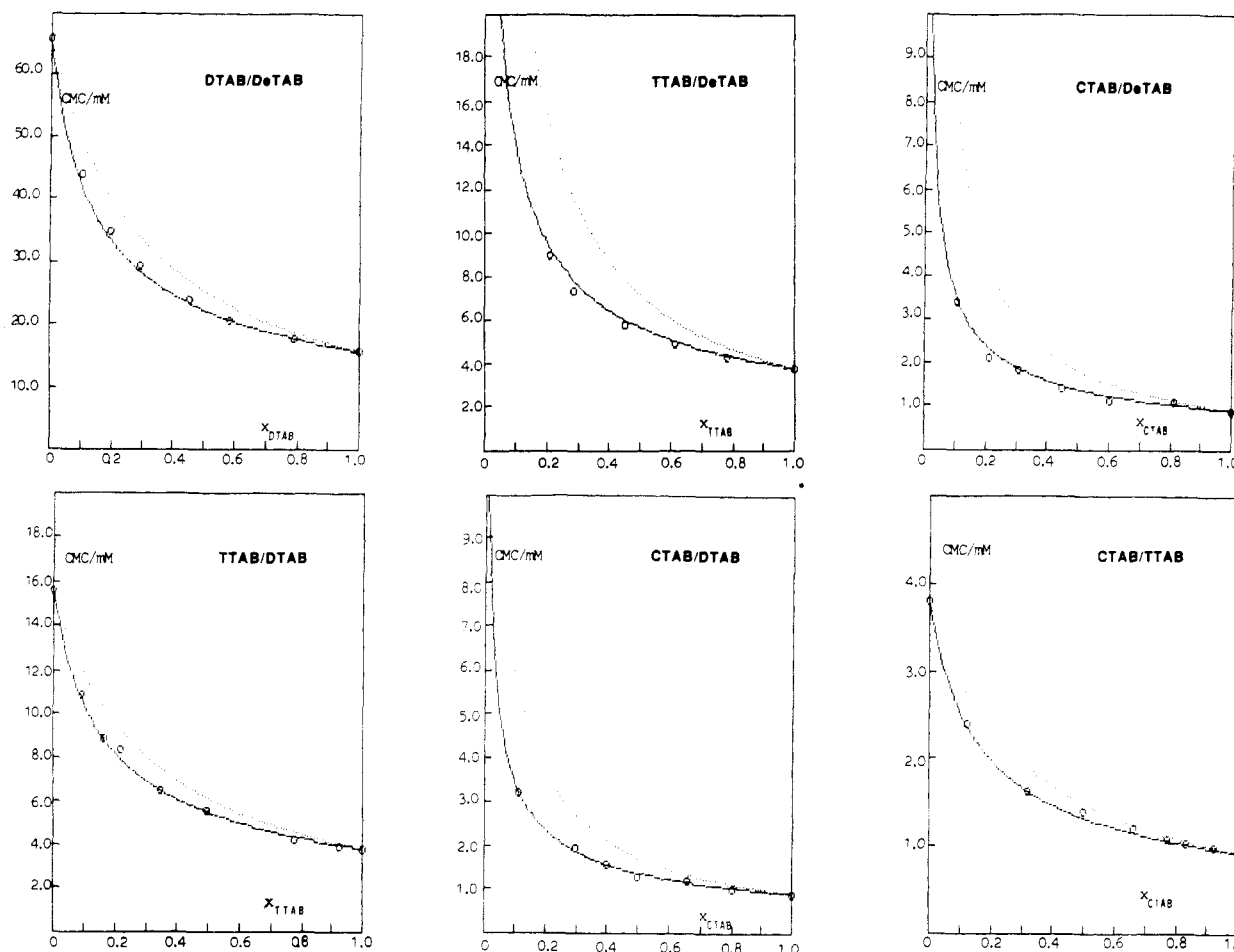
and CTAB are shown in Figure 1. These plots show the good concordance between the experimental values of conductivity and those calculated by the two consecutive integrations of eq 16, obtained by using the fitting parameters (cmc,  $\sigma$ , and  $H$ ) for each system, as presented in Table I. The percentage of deviation between the calculated and experimental values and the second derivative of the conductivity with respect to the concentration are also shown.

In Table I, it may be seen that the cmc values for these cationic surfactants are in perfect agreement with those reported in the literature,<sup>18</sup> showing that the method can be applied for the interpretation of the conductivity/concentration curves, thus obtaining the cmc.

**Determination of the cmc in Binary Systems.** Having checked the validity of this method in the determination of the cmc values of homomeric systems, it was applied to the following mixtures of surfactants: DTAB/DeTAB, TTAB/DeTAB, CTAB/DeTAB, TTAB/

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**Figure 3.** Mixture cmc values vs mole fraction for binary mixtures of aqueous cationic surfactants. The plotted points are experimental results, and the solid line is calculated according to the ideal model of eqs 18 and 19, including the dependence on added electrolyte of the cmc for pure surfactants. The dashed line is the prediction for ideal mixing not including this correction.

DTAB, CTAB/DTAB, and CTAB/TTAB. In all cases, a constant mole fraction of the surfactant was maintained, varying the total surfactant concentration, in order to study the micellization process as a function of the molar composition of each mixture.

On applying this method to the foregoing cationic mixtures, the conductivity/concentration results were seen to fit an equation of the type

$$d^2\kappa/dC^2 = -\Sigma H_i \exp[-(C - \text{cmc}_i)^2/2\sigma_i^2] \quad (17)$$

where the number of Gaussians involved was one to three, depending on the nature of the system. Table II summarizes the fitting parameters obtained for each mixture at different mole fractions. In the table, the mole fraction is referred to the surfactant with the longest chain. For illustrative purposes, Figure 2 shows some selected conductivity/concentration curves for these systems and their calculated curves.

In all cases, an intense Gaussian that shows a great degree of dependence of the mole fraction can be observed. It may be assigned to the formation of the mixed micelle aggregate. In some cases, when the surfactants in the mixture permit one to work in a sufficiently large total concentration range, as in the case of CTAB/TTAB, the conductivity/concentration curves show two more Gaussians of lower intensity than the previous one. These are centered at a total surfactant concentration close to the cmc of each pure component, although it seems not to be possible to ascertain whether they indicate the formation of the respective homomicelles or whether they are associated with structural changes in the micelles which

affect counterion binding and thereby conductance. In the other binary mixtures (DTAB/DeTAB, TTAB/DeTAB, and CTAB/DeTAB), the cmc values of each pure surfactant employed are very different from one another, which experimentally prevents one from working in a sufficiently large total concentration range as to be able to observe similar effects. In the case of the mixtures of TTAB/DTAB and CTAB/DTAB, apart from the formation of the mixed micelle, it is also possible to detect one of the two additional Gaussians.

The foregoing results unequivocally afford, at least, the cmc values for each of the binary mixtures studied. From these values, it is possible to obtain a quantitative description of the micelle aggregates formed, using the pseudophase thermodynamic model,<sup>19,20</sup> which relates the cmc of a mixed aggregate to those of the pure components:

$$1/\text{cmc}^* = x_1/(\text{cmc}_1) + (1 - x_1)/(\text{cmc}_2) \quad (18)$$

For binary mixtures formed, as in the present case, by surfactants with similar structures, ideal behavior will be expected, because the interactions between monomers in the mixed micelle are similar to those in the homomicelle.<sup>1</sup> Therefore, the activity coefficients should be taken as unity. However, as is shown in Figure 3, the variation of the  $\text{cmc}^*$  with the mole fraction cannot entirely be interpreted from eq 18, probably because it does not account for the variation of the solution ionic strength

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with changing composition. The values for  $\text{cmc}_i$  (the cmc of the single surfactants in water) are independent of composition only if the ionic strength is constant, as would be the case for solutions with an excess of an added (swamping) electrolyte. This condition has not been considered in the present study, because it would invalidate the conductance method used for determining the mixture  $\text{cmc}^*$ . Therefore, the values of  $\text{cmc}_i$  to be used in eq 18 will strictly be defined as the cmc of unicomponent surfactants at the same conditions ( $T$ ,  $p$ , ionic strength) as the mixture at the mixture  $\text{cmc}^*$ .<sup>21</sup> The effect of counterion concentration on the cmc of a pure ionic surfactant is well established<sup>12</sup> and can be expressed quantitatively

$$\text{cmc}_i = (\text{cmc}^\circ)_i [X_0 / (\text{cmc}^\circ)_i]^{-b_i} \quad (19)$$

where  $X_0$  represents total concentration of counterion and  $(\text{cmc}^\circ)_i$  is the cmc for the pure surfactant with no excess of added electrolyte. For the exponent,  $b_i$ , the following values can be found in the literature for the surfactants used: 0.67 (CTAB),<sup>22</sup> 0.65 (TTAB),<sup>22</sup> 0.62 (DTAB),<sup>23</sup> and 0.35 (DeTAB).<sup>24</sup> The combined relation that results from eqs 18 and 19, using the mixture  $\text{cmc}^*$  as the concentration of total added electrolyte,  $X_0$ , in eq 19 leads to an acceptable description of the experimen-

tal  $\text{cmc}^*$  for all binary mixtures studied, as can be seen in Figure 3.

The obtained results may confirm not only the expected ideal behavior of the considered binary mixtures but also the usefulness of the newly developed conductivity method in a more precise determination of the  $\text{cmc}^*$  in mixtures of ionic surfactants. Whether its application would also be extensible to other kind of mixtures, such as those formed by ionic/nonionic surfactants, would depend on the assignment of the correct meaning of the Gaussian maxima concentrations for the conductivity/concentration second derivative in these systems, as well as on its development for physical quantities other than conductivity.

### Symbols

$C$	total concentration of surfactants
$X$	concentration of free counterion
$D$	total surfactant monomer concentration
$M$	total micellized surfactant concentration
$\kappa$	conductivity
$\lambda$	ionic conductance
$\beta$	micelle counterion binding parameter
$\text{cmc}^*$	cmc of mixed system
$x_i$	mole fraction of surfactant in total mixed solution

(21) We acknowledge a reviewer for this suggestion.

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**Registry No.** DeTAB, 2082-84-0; DTAB, 1119-94-4; TTAB, 1119-97-7; CTAB, 57-09-0.

## Effect of Nonionic Surfactant on Ion Adsorption and Hydration Forces

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Measurements have been carried out of the force between mica surfaces immersed in aqueous micellar solutions of the nonionic surfactant penta(oxyethylene) *n*-dodecyl ether with sodium sulfate as a background electrolyte. At surfactant concentrations below about  $5 \times 10^{-3}$  M ( $\approx 100 \times \text{cmc}$ ), adsorption to the mica surface is weak and can only be indirectly inferred from a reduction in the surface potential in dilute electrolyte solution. Further evidence for adsorption is provided by a decrease in the measured adhesion between the surfaces and an enhanced viscous drag at small ( $< 5.0$  nm) separations. In more concentrated salt solution, there is a decrease in the magnitude of the hydration force due to surfactant adsorption. Unlike the case with cationic surfactants, the adsorbed surfactants do not give rise to any steric force; they are easily pushed out as the surfaces are brought together. At high surfactant concentrations ( $> 100 \times \text{cmc}$ ), extensive aggregation occurs between the surfaces, and this gives rise to very long-range, repulsive forces. We speculate that the reduction in surface potential may be a more general feature of nonionic adsorbates and rationalize some earlier results on the adsorption of dextran.

### Introduction

The adsorption of ionic surfactants to solid surfaces from aqueous solution depends, in general, upon electrostatic attachment of the headgroups to surface sites, sup-

ported by a favorable reduction in hydrophobic tail-water contact. In systems of nonionic surfactants, the adsorption mechanism is less well defined. For surfactants of the poly(oxyethylene) alkyl ether type (and related species), the adsorption process seems quite well under-