



This article was originally published in a journal published by Elsevier, and the attached copy is provided by Elsevier for the author's benefit and for the benefit of the author's institution, for non-commercial research and educational use including without limitation use in instruction at your institution, sending it to specific colleagues that you know, and providing a copy to your institution's administrator.

All other uses, reproduction and distribution, including without limitation commercial reprints, selling or licensing copies or access, or posting on open internet sites, your personal or institution's website or repository, are prohibited. For exceptions, permission may be sought for such use through Elsevier's permissions site at:

<http://www.elsevier.com/locate/permissionusematerial>



Are the mixtures of homologous surfactants ideal?

Pablo C. Schulz^{*}, José L. Rodríguez, Rossana M. Minardi, María B. Sierra, Marcela A. Morini

Departamento de Química, Universidad Nacional del Sur, Bahía Blanca, Argentina

Received 10 May 2006; accepted 7 July 2006

Available online 11 July 2006

Abstract

The interaction between homologous surfactants in mixed micelles was studied by the Regular Solution Theory of mixed micelles. The interaction is independent of the nature of the polar head groups and attractive and the interaction parameter β_M depends linearly on the difference in chain length Δn_C . The interaction becomes ideal at $\Delta n_C = 0.75 \pm 0.06$. Above $\Delta n_C \approx 5$, the dependence remains linear but the slope increased 2.7 times. The phenomenon is explained as the effect of the reduction of the hydrocarbon/water micelle interface and a better packing of the chains in the micelle core, caused by the inclusion of a shorter homologous surfactants. This reduction can be more effective when $\Delta n_C \geq 5$.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Mixed micelles; Homologous surfactants; Critical micelle concentration; Cationic surfactants; Alkyltrimethylammonium bromides

1. Introduction

Research on surfactant mixtures is of considerable interest for numerous technical applications, because surfactant mixtures enhance the performance of applications when compared to the use of single surfactants. When mixing surfactants, not only the properties of components are combined, but in many cases new properties are found, such as in cationic–anionic surfactant mixtures. These properties are of both fundamental and commercial interest, since surfactants used in industrial applications (e.g., detergents, tertiary oil recovery, drug carrier systems, flotation) are often mixtures. In spite of their widespread use, surfactant mixtures are not well understood at a fundamental level. Surfactant mixtures for specific applications are often chosen based on experience, empirical evidence, or trial and error research. To optimize the applications of surfactant mixtures, it is important to understand the interplay of forces that govern the phase behavior. The main work in this sense was devoted to electrostatic interactions, while scarce attention has been put on the steric ones, mainly on the hydrophobic group geometry. Some work was devoted to the nature of molecular interactions in mixed micelles [1–7].

In the theory of mixed micelles formation the mixtures of surfactants belonging to the same homologous series are considered as ideal. This is commonly accepted in the theoretical treatment and the interpretation of the behavior of different surfactants mixtures, such as sodium octyl sulfate and sodium hexadecyl sulfate [8]. Along our research on mixed micelles, we have obtained results that suggested that this supposition is an oversimplification. This is an important point, because in studying the interactions in mixed micelles, all the possible sources of nonideality must be taken into account. To determine if the commonly accepted supposition of ideality is correct, it is necessary to obtain values of the micellar interaction parameter β_M for several mixtures of homologous surfactants and to verify if these values differ statistically from zero. Also, homologies of different kinds of surfactants must be compared, to ensure that the effect is due to the hydrophobic chains and not to modifications in the micelle Stern layer. We computed β_M data for several systems of different mixtures of homologous surfactants obtained from literature. The data were mainly from mixtures of soaps, but some mixtures of other anionic surfactants and some nonionic were also found. However, data for cationic homologous mixtures were almost inexistent. So we decided to determine the CMC of various mixtures of alkyltrimethylammonium bromides to compute the β_M values to complete the picture.

^{*} Corresponding author.

E-mail address: pschulz@criba.edu.ar (P.C. Schulz).

2. Theory

Regular solution theory has been very widely used to model the thermodynamic nonidealities of mixed micelles; it has been shown to accurately model critical micelle concentration (CMC) values [9] and monomer-micelle equilibrium compositions [10] in surfactant systems exhibiting negative deviations from ideality. However, it must be pointed out that the theoretical validity of using regular solution theory to describing non-ideal mixing in mixed surfactant micelles has been questioned [11]. Although this theory assumes that the excess entropy of mixing is zero, it has been demonstrated that in some surfactant mixtures this assumption is not true [12,13]. However, the pseudophase separation model and regular solution theory combination remains as a very widely used and convenient method for analyzing experimental data [14–16].

A mixture of two different surfactants 1 and 2 form micelles with composition X_1 and X_2 , in equilibrium with solution monomers of composition α_1 and α_2 . These mole fractions are on a surfactant-only basis, so that

$$X_1 + X_2 = 1, \quad (1)$$

$$\alpha_1 + \alpha_2 = 1. \quad (2)$$

At the CMC [14]:

$$\alpha_1 \gamma_{1,m} \text{CMC}_1 = X_1 \gamma_{1,M} \text{CMC}_M, \quad (3)$$

$$\alpha_2 \gamma_{2,m} \text{CMC}_2 = X_2 \gamma_{2,M} \text{CMC}_M, \quad (4)$$

where $\gamma_{i,m}$ and $\gamma_{i,M}$ are the activity coefficients of surfactant i in the intermicellar solution and in micelles, CMC_1 , CMC_2 and CMC_M are the CMC of pure surfactants 1 and 2, and the mixture. Each surfactant monomeric form is assumed to be dilute enough to obey Henry's law, i.e., based on the infinite dilution standard state, surfactant monomer activity coefficients are unity [17]. In applying regular solution theory to mixed micelles, the micellar activity coefficients are given by [18]:

$$\gamma_{1,M} = \exp(\beta_M X_2^2), \quad (5)$$

$$\gamma_{2,M} = \exp(\beta_M X_1^2), \quad (6)$$

where β_M is the dimensionless regular solution theory interaction parameter (in $k_B T$ units, where k_B is the Boltzmann constant and T the absolute temperature). Theoretically, β_M is independent on both temperature and the composition of the micelle. However, in practice β_M is temperature dependent [19–22] and it often depends on the micelle composition [22,23], so that an average value is commonly used. In spite of these limitations, the β_M parameter quantitatively captures the extent of nonideality in a single number that can be easily compared among different pairs of surfactants. The nature and strength of the interaction between two surfactants are measured by the value of the β_M parameter, which is a measure of the degree of nonideality of the interaction in a mixed micelle. The larger the negative value of β_M , the stronger the attractive interaction between the two different surfactant molecules, and the greater is the probability of the existence of synergism between them [24]. Repulsive interactions yield a positive β_M value and the

possibility of antagonism, whereas $\beta_M = 0$ indicates an ideal mixture. Positive β_M values occur in mixtures of fluorocarbon–hydrocarbon surfactants [25].

Typical values of β_M are $+2.2k_B T$ for lithium dodecyl sulfate–lithium perfluorooctanesulfonate [26], $-2.6k_B T$ in sodium dodecyl sulfate (SDS)–poly(oxyethylene)(23) dodecylether [27], $-3.9k_B T$ for the system SDS–poly(oxyethylene) (4) dodecylether [28] and $-13.2k_B T$ for sodium decyl sulfate–decyltrimethylammonium bromide [29].

The parameter β_M is related to the molecular interactions in the mixed micelle by [28]:

$$\beta_M = N_A(W_{11} + W_{22} - 2W_{12}), \quad (7)$$

where W_{11} and W_{22} are the energies of interaction between molecules in the pure micelle and W_{12} is the interaction between the two species in the mixed micelle. N_A is the Avogadro's number.

The parameter β_M reflects the two main contributions to the Gibbs free energy of mixed micellization. These are a free-energy contribution associated with the interactions between the hydrophobic groups of surfactants 1 and 2 in the micelle core, $\beta_{M,\text{core}}$, and an electrostatic contribution $\beta_{M,\text{elec}}$, associated with electrostatic interactions between the charged hydrophilic groups of surfactants 1 and 2 [30]:

$$\beta_M = \beta_{M,\text{core}} + \beta_{M,\text{elec}}. \quad (8)$$

It is commonly accepted that $\beta_{M,\text{core}}$ is typically equal to zero for mixtures of two hydrocarbon based (or fluorocarbon based) surfactants [31,32], but is larger than zero for a binary mixture of hydrocarbon and fluorocarbon surfactants due to the repulsive interactions in the micellar core [31–36].

The interaction parameter β_M is related to the excess chemical potential of mixing [15]:

$$\Delta\mu_{\text{mix}}^{\text{excess}} = \beta_M RT X_{1,M} X_{2,M} \quad (9)$$

where R is the gas constant and T is the absolute temperature. $\Delta\mu_{\text{mix}}^{\text{excess}}$ is the difference between the partial molar free energy of the mixed micelles and that calculated according to the ideal behavior, as a function of the mixture composition. This energy (and then the β_M value) is expected to depend much on the surface charge density of micelles and the ionic strength, and less on the size and shape of micelles [37,38]. The $\Delta\mu_{\text{mix}}^{\text{excess}}$ value does not take into account the change in the degree of association of the counterion upon surfactant mixing [19–21].

The value of the parameter β_M for the interactions in a mixed micelle was calculated from the equations [25]:

$$F = \frac{(X_1)^2 \ln(\alpha_1 \text{CMC}_M / X_1 \text{CMC}_1)}{(1 - X_1)^2 \ln[(1 - \alpha_1) \text{CMC}_M / (1 - X_1) \text{CMC}_2]} - 1 = 0, \quad (10)$$

$$\beta_M = \frac{\ln(\alpha_1 \text{CMC}_M / X_1 \text{CMC}_1)}{(1 - X_1)^2}. \quad (11)$$

Equation (10) is solved for X_1 , which is then replaced in Eq. (11) to obtain β_M . Hoffmann and Pössnecker [11] have demonstrated by error expansion of Eq. (11) that the minimum

error for β_M in a single determination is nearly $0.1k_B T$. The error is strongly increasing when one component in the micelle dominates.

The CMC_M value can be calculated as a function of the composition by the expression:

$$CMC_M = \left[\frac{\alpha_1}{\gamma_{1,M} CMC_1} + \frac{\alpha_2}{\gamma_{2,M} CMC_2} \right]^{-1}. \quad (12)$$

In the ideal approximation, $\gamma_{1,M} = \gamma_{2,M} = 1$, then Eq. (12) reduces to [37,39]:

$$CMC_M = \left[\frac{\alpha_1}{CMC_1} + \frac{\alpha_2}{CMC_2} \right]^{-1}. \quad (13)$$

This occurs mainly in mixtures of two homologous surfactants, such as sodium octyl sulfate and sodium decyl sulfate [40]. To determine if this supposition was correct, it is necessary to obtain β_M values for several mixtures and to verify if these values differ statistically from zero.

Since the hydrocarbon micelle core is of liquid nature, to study the thermodynamic effect of mixing homologous surfactants as a first approach it was considered that the micelle core may be compared with a mixture of two aliphatic hydrocarbons having different chain length. Mixtures of nonpolar components such as saturated hydrocarbons may be treated by the Scatchard–Hildebrand theory. This theory is also known as the regular solution theory, and gives a good semi-quantitative representation of activity coefficients for solutions containing nonpolar components. The activity coefficients in a two-component mixture are computed by [40]:

$$RT \ln \gamma_1 = v_1 \Phi_2^2 (\delta_1 - \delta_2)^2, \quad (14)$$

where v_i is the molar volume of component i , whose solubility parameter is δ_i , and Φ_2 the volume fraction of component 2 in the mixture, computed by:

$$\Phi_2 = \frac{v_2 x_2}{v_1 x_1 + v_2 x_2}, \quad (15)$$

where x_i being the mole fraction of component i .

To compute the micellar ionisation degree α the equation proposed by Evans [41] was employed:

$$1000 \left(\frac{d\kappa}{dC} \right)_2 = \frac{(n-m)^2}{n^{4/3}} \left[1000 \left(\frac{d\kappa}{dC} \right)_1 - \lambda_X \right] + \alpha \lambda_X, \quad (16)$$

where $(d\kappa/dC)_1$ and $(d\kappa/dC)_2$ are the slope of the specific conductivity curves before and after the CMC, n is the aggregation number, m the number of counterions attached to the micelle, and λ_X is the equivalent conductivity of the counterion ($\lambda_{Br^-} = 77.4 \text{ Scm}^2 \text{ mol}^{-1}$ [42]). Equation (16) is a quadratic function of α , because $(n-m) = n\alpha$. It is also dependent on n . However, this dependence is not strong and any reasonable value of n gives a good estimation of α [41]. We employed $n = 86$, which is an intermediate value for n in spherical micelles of surfactants having the used chain length range ($n = 52$ for $C_{10}TAB$ [43,44], $n = 80$ – 86 for $C_{12}TAB$ [45], $n = 107$ for $C_{14}TAB$ [43,44], $n = 127 \pm 3$ for $C_{16}TAB$ [46]).

3. Experimental

We computed β_M data for several systems by application of Eqs. (10) and (11) to CMC data of different mixtures of homologous surfactants obtained from literature. The data were mainly from mixtures of soaps, but some mixtures of other anionic surfactants and some nonionic were also found. However, data for cationic homologous mixtures were almost inexistent. So we decided to determine the CMC of various mixtures of alkyltrimethylammonium bromides to compute the β_M values.

Octadecyltrimethylammonium bromide ($C_{16}TAB$), hexadecyltrimethylammonium ($C_{18}TAB$), tetradecyltrimethylammonium ($C_{14}TAB$) and dodecyltrimethylammonium ($C_{12}TAB$) were from Fluka and decyltrimethylammonium ($C_{10}TAB$) bromide was from Kodak. All surfactants were of analytical grade and were used as purchased. To obtain different $\alpha_{C_{10}TAB}$ proportions, the concentrated solution of $C_{10}TAB$ was mixed with concentrated solution of other surfactant in the appropriate proportion. Here $\alpha_{C_{10}TAB}$ is the mole fraction of $C_{10}TAB$ in the $C_{10}TAB$ – C_xTAB mixture without considering water (i.e. $\alpha_{C_{10}TAB} + \alpha_{C_xTAB} = 1$). Only double-distilled water was used. Concentrated solutions of $\alpha_{C_{10}TAB} = 0, 0.25, 0.5, 0.75$ and 1 (pure $C_{10}TAB$). Conductivity measurements were made with an immersion cell and an automatic conductimeter, namely an Antares II of Instrumentalia, by titration of water with concentrated solution of each cationic mixture. The cell was calibrated as usually with KCl solutions, and the temperature was controlled with a thermostat and water circulation at $25 \pm 0.1 \text{ }^\circ\text{C}$.

To determine the critical micelle concentration from conductivity data, the excess specific conductivity $\Delta\kappa$ was employed, which is defined as $\Delta\kappa = \kappa - \kappa_{\text{extrap}}$ in which κ_{extrap} is the specific conductivity extrapolated from the pre-CMC straight line. The values of $\Delta\kappa$ are plotted against the total concentration. This representation was proposed by Miura and Kodama [47] to magnify the conductivity changes at the CMC.

Mean values and variances were computed by the minimum variance linear unbiased method [48] and the Student t function was employed to compute the error intervals. Confidence level was 0.90. Errors of derived data were computed with the error expansion method.

4. Results and discussion

There are some data in literature about mixtures of surfactants of the same homologous series (i.e., differing only in the alkyl chain length). These mixtures are potassium soaps [49–51], sodium alkyl sulfates [52,53], copper alkyl sulfates [53], sodium alkyl phosphates [54], alkyltrimethylammonium chlorides [55] and (alkylsulfanyl) ethanols [55]. These data comprise mainly anionic surfactants, with some examples of cationic and nonionic surfactant mixtures. In general these data were not studied with the regular solution theory of mixed micelles. When the parameter which measures the degree of nonideality of the mixture (β_M) was computed and ordered as a function of the difference in chain length Δn_C between the two components of the mixture (Table 1), it may be seen that the (negative)

Table 1
Values of the micellar interaction parameter β_M for several mixtures of homologous surfactants

Surfactant mixture	Δn_C	$\beta_M/k_B T$	Average value	Reference
C ₆ COOK–C ₇ COOK	1	-0.129 ± 0.088	-0.129 ± 0.088	[43]
C ₁₀ N(CH ₃) ₃ Br–C ₁₂ N(CH ₃) ₃ Br	2	-0.64 ± 0.21		This work
C ₁₀ SO ₄ Na–C ₁₂ SO ₄ Na	2	-0.63 ± 0.18		[45]
C ₁₂ SO ₄ Na–C ₁₄ SO ₄ Na	2	-0.40 ± 0.14		[46]
(C ₁₀ SO ₄) ₂ Cu–(C ₁₂ SO ₄) ₂ Cu	2	-0.59 ± 0.27		[46]
C ₁₂ SO ₄ Na–C ₁₄ SO ₄ Na	2	-0.84 ± 0.94		[45]
C ₁₁ COOK–C ₁₃ COOK	2	-0.685 ± 0.072		[44]
C ₇ COOK–C ₉ COOK	2	-0.64 ± 0.13		[42]
DeSE–OSE ^a	2	-0.12 ± 0.18		[48]
C ₁₀ N(CH ₃) ₃ Cl–C ₁₂ N(CH ₃) ₃ Cl	2	-0.43 ± 0.27		[48]
C ₁₀ N(CH ₃) ₃ Cl–C ₁₂ N(CH ₃) ₃ Cl	2	-0.11 ± 0.44	-0.519 ± 0.010	[48]
C ₆ COOK–C ₉ COOK	3	-1.13 ± 0.25		[43]
C ₇ COOK–C ₁₀ COOK	3	-1.26 ± 0.11	-1.24 ± 0.10	[42]
C ₁₀ N(CH ₃) ₃ Br–C ₁₄ N(CH ₃) ₃ Br	4	-2.868 ± 0.041		This work
C ₇ COOK–C ₁₁ COOK	4	-2.301 ± 0.042		[42]
C ₆ COOK–C ₁₀ COOK	4	-1.89 ± 0.32		[43]
C ₉ COOK–C ₁₃ COOK	4	-1.57 ± 0.24		[44]
C ₁₂ PO ₄ Na–C ₁₆ PO ₄ Na	4	-0.961 ± 0.043	-2.061 ± 0.024	[47]
C ₆ COOK–C ₁₁ COOK	5	-1.96 ± 0.27	-1.96 ± 0.27	[43]
C ₁₀ N(CH ₃) ₃ Br–C ₁₆ N(CH ₃) ₃ Br	6	-3.68 ± 0.58		This work
C ₇ COOK–C ₁₃ COOK	6	-3.20 ± 0.37	-3.34 ± 0.31	[42]
C ₆ COOK–C ₁₃ COOK	7	-2.6 ± 1.1	-2.6 ± 1.1	[43]
C ₁₀ N(CH ₃) ₃ Br–C ₁₈ N(CH ₃) ₃ Br	8	-5.4 ± 1.1		This work
C ₆ COOK–C ₁₄ COOK	8	-6.9 ± 1.0	-6.19 ± 0.74	[43]

^a (Decylsulfanyl)ethanol (DeSE) + (octylsulfanyl)ethanol (OSE).

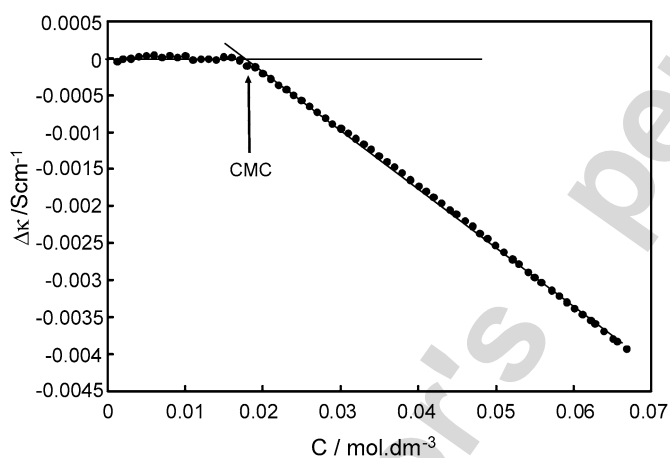


Fig. 1. The dependence of $\Delta\kappa$ on the mixed surfactant concentration for the C₁₀TAB:C₁₂TAB mixture with $\alpha_{C_{10}TAB} = 0.25$.

β_M values increase with increasing Δn_C , and that for the same Δn_C value, the β_M values obtained with different surfactant mixtures are similar.

To verify if the cationic surfactants follow the same trend, we have measured the CMC of mixtures of alkyltrimethylammonium bromides.

Fig. 1 shows an example of $\Delta\kappa$ vs surfactant concentration plot for the mixture C₁₀TAB:C₁₂TAB with $\alpha_{C_{10}TAB} = 0.25$. Plots for the other mixtures of cationic surfactants were similar. Fig. 2 shows the CMC of the cationic surfactant mixtures as a function of $\alpha_{C_{10}TAB}$. The values of β_M were included in Table 1. The mean values (computed taking into account their errors [48]) were then plotted as a function of Δn_C in Fig. 3. It may be seen that irrespective of the polar head group nature,

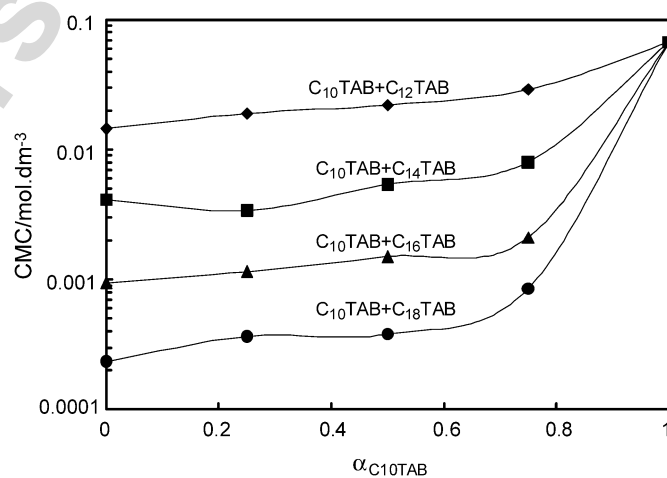


Fig. 2. Critical micelle concentration of cationic surfactant mixtures as a function of the mole fraction of dodecyltrimethylammonium bromide in the mixture, $\alpha_{C_{10}TAB}$.

the values of β_M fall on two straight lines. At low Δn_C values the equation of the straight line is

$$\beta_M = -(0.526 \pm 0.049)\Delta n_C + 0.403 \pm 0.021,$$

with $r = -0.9623$, giving $\beta_M = 0$ at $\Delta n_C = 0.75 \pm 0.06$, and the equation of the line at high Δn_C values is

$$\beta_M = -(1.426 \pm 0.044)\Delta n_C + 5.18 \pm 0.28,$$

with $r = -0.9986$. The intersection of both lines occurs at $\Delta n_C = 5.31 \pm 0.48$.

A glance on Fig. 3 shows that there is a change in the nature of the nonideal interaction between the two compo-

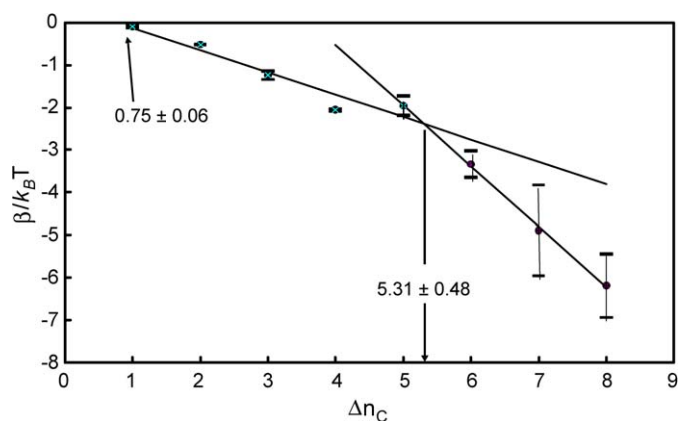


Fig. 3. Dependence of the average interaction parameter β_M on Δn_C .

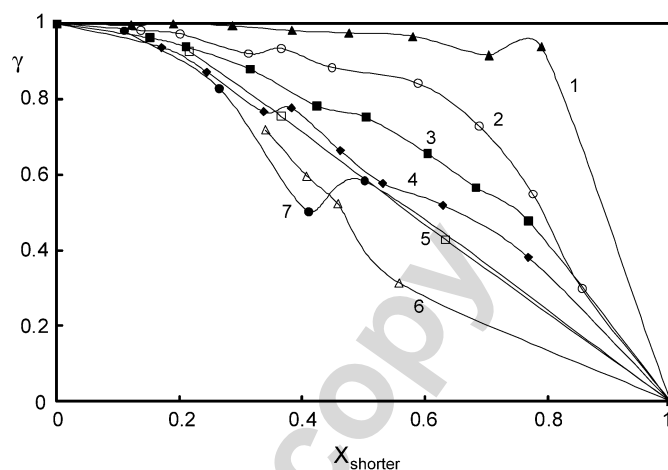


Fig. 5. Activity coefficients of the longest component in mixtures of potassium heptanoate with longer potassium soaps as a function of the mole fraction of the shortest component in micelles. The numbers are the values of Δn_C . Points obtained by elaboration of CMC data from Ref. [43].

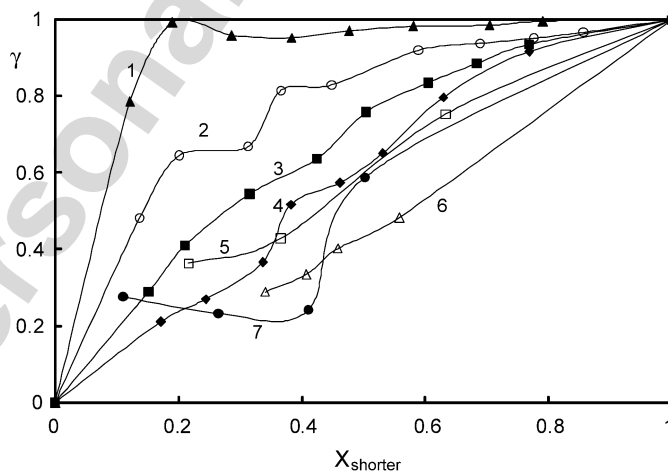


Fig. 6. Activity coefficients of the shortest component in mixtures of potassium heptanoate with longer potassium soaps as a function of the mole fraction of the shortest component in micelles. The numbers are the values of Δn_C . Points obtained by elaboration of CMC data from Ref. [43].

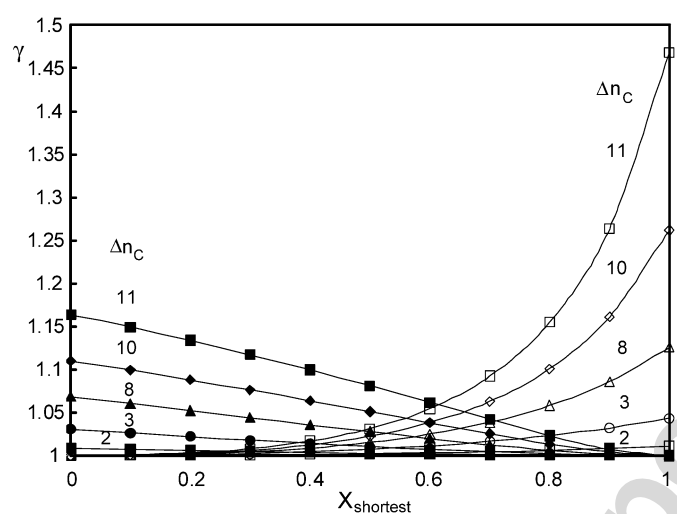


Fig. 4. Activity coefficients of liquid binary saturated linear hydrocarbon mixtures as a function of the mole fraction of the shorter component, computed by the Scatchard–Hildebrand theory. Full symbols correspond to the shorter component and open symbols to the longest one in the mixture.

nents below and above $\Delta n_C = 5.31 \pm 0.48$. Below this value, $\partial\beta_M/\partial\Delta n_C = -0.526k_B T$ (i.e., $-(1.30 \pm 0.12)$ kJ mol at 25 °C), and above the intersection, $\partial\beta_M/\partial\Delta n_C = -1.43k_B T$ ($-(3.55 \pm 0.11)$ kJ mol at 25 °C).

Using the values of v and δ for *n*-pentane ($116 \text{ cm}^3 \text{ mol}^{-1}$, $14.5 \text{ (J cm}^3)^{1/2}$), *n*-hexane ($132 \text{ cm}^3 \text{ mol}^{-1}$, $14.9 \text{ (J cm}^3)^{1/2}$), *n*-octane ($164 \text{ cm}^3 \text{ mol}^{-1}$, $15.3 \text{ (J cm}^3)^{1/2}$) and *n*-hexadecane ($294 \text{ cm}^3 \text{ mol}^{-1}$, $16.3 \text{ (J cm}^3)^{1/2}$) [40], the activity coefficients of their mixtures were computed using the Scatchard–Hildebrand theory. Fig. 4 shows the activity coefficients of the components as a function of composition and the difference in chain length between them (Δn_C). Firstly, all activity coefficients are ≥ 1 , which is a characteristic of the Scatchard–Hildebrand theory. It can also be seen that the dependence on composition of the activity coefficient of the longest component of the mixture (open symbols) is different to that of the shortest one (full symbols).

Fig. 5 shows the activity coefficient of the longer component in the mixed micelle for one of the homologous series as a function of the mixed micelle composition and Δn_C . Fig. 6 depicts the activity coefficient of the shorter component in the mixed

micelle (similar plots were found with the other surfactant homologous series). It may be seen that even though if $\Delta n_C = 1$ the mixture in micelles is not ideal, but the nonideality is small. In all cases, both components affect each other. Strictly speaking, no one of the components can be considered as the solvent or the solute.

When comparing Fig. 4 with Figs. 5 and 6, the first difference is that in mixtures of aliphatic hydrocarbons $\gamma \geq 1$, whilst for the surfactant mixtures $\gamma \leq 1$, i.e., the interaction between aliphatic hydrocarbons of different chain length is repulsive, while that between homologous surfactants are attractive. The second difference is that the dependence of γ on concentration is different for the shorter component to that for the longer component in mixtures of aliphatic hydrocarbons, while in the homologous surfactant mixtures there is no significant difference between the two components. Moreover, the effect is of larger magnitude in surfactant mixtures than in hydrocarbon ones. This situation may be seen when the activity of surfactants

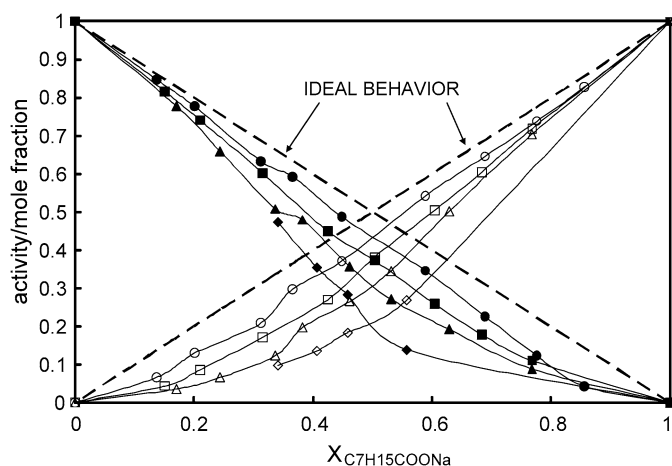


Fig. 7. Activity of micellised surfactants versus micelle composition. Full symbols correspond to the longest component, open symbols to the shortest one. Mixtures of potassium octanoate with (○, ●) potassium decanoate; (□, ■) potassium undecanoate; (△, ▲) potassium dodecanoate; and (◇, ◆) potassium tetradecanoate. Points obtained by elaboration of CMC data from Ref. [42].

in micelles (i.e., $a_i = X_i \gamma_i$) is plotted against the micelle composition (Fig. 7) and the activity of the components in hydrocarbon mixtures. We have computed the deviations from Raoult's law for mixtures of hydrocarbons having chain length from C₁₀ to C₁₈ with Eq. (14) and found that the mixture of surfactants with $\Delta n_C = 1$ was almost ideal, but the nonideality augmented as Δn_C became larger. Moreover, all deviations were positive. When the activity of each surfactant in the micelle is plotted as a function of micelle composition (Fig. 7), the behavior is similar to that of a nonideal mixture of two completely miscible liquids, i.e., when the mole fraction of one component approaches unity, the activity approaches the concentration. In both components at all micelle compositions the activity is less than the mole fraction. This confirms the miscibility of both components and the attractive interaction between them. Since in the mixed surfactant model the activity coefficient of each component in micelles tends to unity when the mole fraction of the component approaches unity, the standard state in mixed micelles is related to the Raoult's law. In mixtures of homologous hydrocarbons it is common that positive deviations to the Raoult's law be found [56]. This means that the activity of both components is higher than their respective concentration. Actually, the behavior of the homologous surfactant mixtures seems that of mixtures having negative deviations to the Raoult's law. When this situation occurs, it is accepted that the partial formation of compounds involving both components may occur in the condensed phase [56].

In view of the above discussion, the origin of this nonideality in mixed micelles composed of homologous surfactants must arise from the difference between liquid hydrocarbon mixtures and liquid hydrocarbon tails in micelles. The main difference is that the hydrocarbon chains in micelles are anchored by one of their ends to the Stern layer in a spherical structure, whilst the hydrocarbon molecules are free to move without restrictions. Spherical micelles are formed by a mixture of molecules having stretched chains and other having their chains folded to fill the spaces near the surface created by the radial disposition

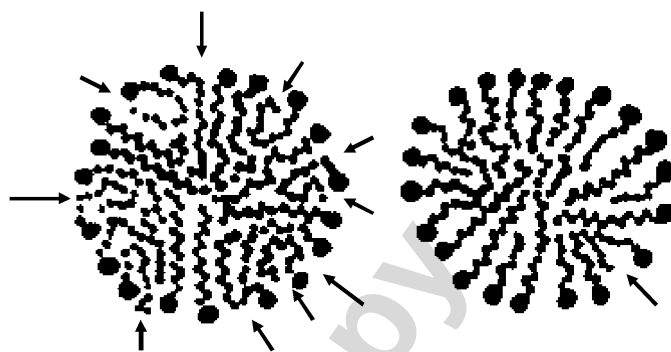


Fig. 8. Left: proposed scheme of a pure surfactant micelle of a surfactant having 13 carbon atoms in the hydrocarbon chain showing by arrows the hydrocarbon surface exposed to water; right: mixed micelle composed by two homologous surfactants, one of them having 13 and the other 6 carbon atoms in the alkyl chain, i.e., with $\Delta n_C = 7$. The amount of hydrocarbon surface exposed to water was substantially reduced.

of the stretched molecules. This packing reduces the hydrocarbon/water contact at the micelle surface. Then, the inclusion of a shorter surfactant into a micelle of a longer homologous surfactants may produce stabilization because the shorter surfactant may fill these spaces with a reduced folding. The advantage must be small if Δn_C is small, but must increase with increasing Δn_C . This is the behavior observed in Fig. 3. The structuring of solvent molecules around other solvent molecule is in principle no different from that of solvent molecules at a surface, and is primarily determined by the molecule geometry and how they can pack around a constraining boundary. Linear chain molecules such as *n*-octane and *n*-tetradecane exhibit similar oscillatory force laws, with a period of about 0.4 nm that corresponds to the molecular width and indicates that the molecular axes are oriented parallel to each other [57]. This means that the most favorable ordering of the long chain molecules is with their axes parallel in average. This situation is not possible in micelles composed by only one kind of surfactant molecules, because of the constraint produced by the spherical geometry of the micelle. Some of the surfactant chains must be folded to fulfill the spaces between the other molecules. This also produces some water–hydrocarbon contact. The inclusion of a short homologous surfactant in a micelle produces a reduction in the folding of the longer component, as it can be seen in Fig. 8 (right). In the difference in chain length is not high; the shorter surfactant must also fold to fulfill the spaces left by the longer surfactant. The increase in stabilization above $\Delta n_C = 5.31$ probably reflects that the need of folding of the shorter surfactant is reduced when the difference in chain length exceeds this value. Since the micelle core is of liquid nature [58] the folding of a chain must reduce its freedom of motion in comparison with the stretched ones.

In the light of this interpretation, both components are affected by the inclusion in the mixed micelles. As said above, in a pure surfactant micelle some of the chains are extended while other must be folded to fulfill the spaces between the extended surfactant molecules in order to reduce the hydrocarbon/water interface (Fig. 8, left). However, some part of the chain, about 3–4 methylene groups by each micellised surfac-

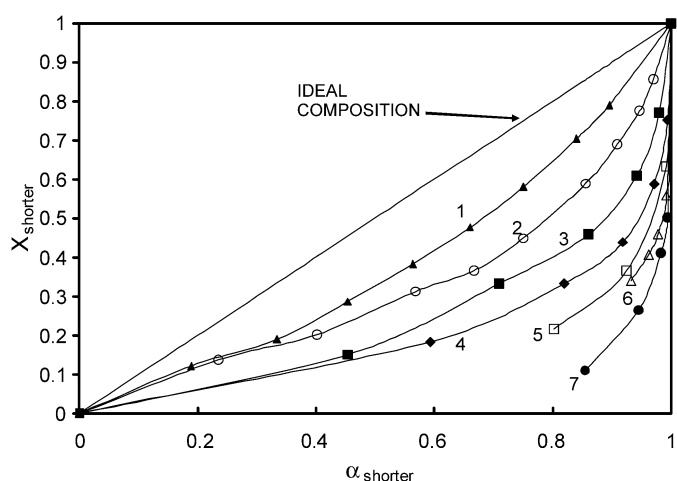


Fig. 9. Composition of micelles formed by potassium heptanoate and higher homologous surfactants, as a function of the composition of the surfactant mixture. Numbers are values of Δn_C . Points obtained by elaboration of CMC data from Ref. [43].

tant molecule remains in contact with water [56,58–67]. This is because it is impossible to cover the entire micelle surface with the polar headgroups. The inclusion of a shorter molecule may be intercalated between the extreme of the folded chain of the longest component and the micelle surface, replacing part of the hydrocarbon/water interface by a polar headgroup. This situation reduces the surface free energy of micelles (see Fig. 8, right). The energetic advantage must increase with Δn_C , because when Δn_C is large, the longest component can fold its distal end more easily in the space within the centre of the micelle and the end of the shorter component chain. This situation must be more favorable when that space is of five methylene groups or more (i.e., about 0.66 nm length or more). Both the longer and the shorter chains in the mixed micelle expose less hydrocarbon surface to water than in the respective pure surfactant micelles and can be less folded. This is reflected in the respective activity coefficient in micelles, as it can be seen in Figs. 5 and 6.

Fig. 9 shows the dependence of the micelle composition (X_{shorter} = mole fraction of the shorter component in the micelle) as a function of the total surfactant mixture composition (α_{shorter} = mole fraction of the shorter surfactant in the mixture); and the difference in length of the hydrocarbon chains between the two surfactants of the mixture, Δn_C . It may be seen that the larger Δn_C , the lower the proportion of the shorter surfactant in the mixed micelle. The same behavior was shown by the other homologous mixtures. This means that the inclusion of the longer surfactant molecules in the mixed micelles is favored by the presence of a shorter homologous surfactant, and that effect increase with the difference in chain length.

The micelle ionization degree (α) of mixed micelles of the alkyltrimethylammonium bromides were computed with the Evans equation (16) and plotted as a function of the micelle composition in Fig. 10. Two factors govern the value of α , if the polar head group and the counterion are the same: the ionic strength (I) in the intermicellar solution and the electrostatic surface potential of micelles (Ψ). An increase in I or Ψ must

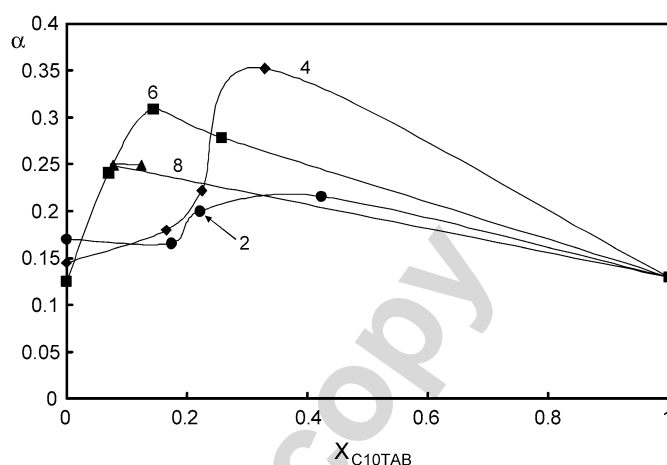


Fig. 10. Micelle ionization degree of mixtures of dodecyltrimethylammonium bromide with higher homologous surfactants as a function of the micelle composition. Numbers correspond to Δn_C .

reduce the value of α . Since the values of α were computed at the CMC, a reduction of that concentration is equivalent to a reduction in I and then α must increase. However, the inclusion of the shorter molecule replaces micelle hydrocarbon surface by polar head groups, and then the surface charge density of micelles must increase, producing an increase of Ψ which in turn captures more counterions in the micelle Stern layer. As a consequence, the inclusion of the shorter component must produce an increase of α by reduction of the CMC, but an increase in the efficiency in the accommodation of the components must work in the opposite direction reducing the value of the micelle ionization degree. A more efficient packing of the components produces a more high Ψ and a reduction of α . In the light of the preceding results, the values of α in mixed micelles must increase with Δn_C between 1 and 5, and then α must decrease for $\Delta n_C > 5$, as it can be seen in Fig. 10.

5. Concluding remarks

- Previous work suggested that the supposition that mixed micelles of homologous surfactant do not behave ideally, as supposed in the Regular Solution Theory. This is an important point, because in studying the interactions in mixed micelles, all the possible sources of nonideality must be taken into account, and caused the present research.
- The interaction between homologous surfactants in mixed micelles is not ideal, on the contrary as supposed in the Regular Solution Theory of mixed micelles.
- The interaction is attractive and the interaction parameter β_M depends linearly on the difference in chain length Δn_C . The value of β_M becomes zero (i.e., the interaction becomes ideal) at $\Delta n_C = 0.75 \pm 0.06$. When $\Delta n_C \approx 5$, the dependence remains linear but the slope increased 2.7 times. This dependence is independent of the nature of the polar head groups.
- This phenomenon can be understood as the effect of the reduction of the hydrocarbon/water micelle interface by inclusion of a shorter homologous surfactant, and a better packing of the chains in micelles caused by a reduction

in the chain folding. This reduction can be more effective when $\Delta n_C \geq 5$.

Acknowledgments

M.B.S. has a fellowship of the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC). M.A.M. is an adjunct researcher of the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET). This work was supported by a grant of the Universidad Nacional del Sur and the grant BID 1201 OCAR PICT No 10-14560 from the Agencia Nacional de Promoción Científica y Tecnológica de la República Argentina (ANPCyT).

References

- [1] R.M. Minardi, P.C. Schulz, B. Vuano, *Colloid Polym. Sci.* 274 (1996) 669.
- [2] P.C. Schulz, R.M. Minardi, B. Vuano, *Colloid Polym. Sci.* 276 (1998) 278.
- [3] R.M. Minardi, P.C. Schulz, B. Vuano, *Colloid Polym. Sci.* 276 (1998) 589.
- [4] N. El-Kadi, N.F. Martins, D. Clausse, P.C. Schulz, *Colloid Polym. Sci.* 281 (2003) 353.
- [5] M.B. Sierra, P.V. Messina, M.A. Morini, J.M. Ruso, G. Prieto, P.C. Schulz, F. Sarmiento, *Colloids Surf. A Phys. Eng. Aspects* 277 (2006).
- [6] Z.E. Proverbio, P.C. Schulz, *Colloid Polym. Sci.* 280 (2002) 1045.
- [7] Q. Zhou, M.J. Rosen, *Langmuir* 19 (2003) 4555.
- [8] C.-H. Cheng, *J. Chin. Chem. Soc.* 42 (1994) 33.
- [9] A.V. Barzykin, M. Almgren, *Langmuir* 12 (1996) 4672.
- [10] J.C. Eriksson, S. Ljunggren, U. Henriksson, *J. Chem. Soc. Faraday Trans. 2* (81) (1985) 833.
- [11] H. Hoffmann, G. Possnecker, *Langmuir* 10 (1994) 381.
- [12] T. Forster, W. von Rybinski, M.J. Schwuger, *Tenside Surf. Deterg.* 27 (1990) 254.
- [13] I.W. Osborne-Lee, R.S. Schechter, in: J.F. Scamehorn (Ed.), *Phenomena in Mixed Surfactant Systems*, in: ACS Symp. Series, vol. 311, Am. Chem. Soc., Washington, DC, 1986, p. 30.
- [14] R. Zhang, L. Zhang, P. Somasundaran, *J. Colloid Interface Sci.* 278 (2004) 453.
- [15] M. Prasad, S.P. Moulik, R. Palepu, *J. Colloid Interface Sci.* 284 (2005) 658.
- [16] M.S. Bakshi, S. Sachar, T. Yoshimura, K. Esumi, *J. Colloid Interface Sci.* 278 (2004) 224.
- [17] J.F. Scamehorn, R.S. Schechter, W.H. Wade, *J. Dispersion Sci. Technol.* 3 (1982) 261.
- [18] R.E. Balzhiser, M.R. Samuels, J.D. Eliassen, *Chemical Engineering Thermodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1972, chap. 9.
- [19] R. Crisantino, R. De Lisi, S. Miloto, *J. Solution Chem.* 23 (1994) 639.
- [20] M.J. Hey, J.W. Mac Taggart, *J. Chem. Soc. Faraday Trans. 1* (81) (1985) 207.
- [21] M.J. Rosen, F. Zhao, *J. Colloid Interface Sci.* 95 (1983) 443.
- [22] C. Treiner, A. Amar Khodja, M. Fromon, *Langmuir* 3 (1987) 729.
- [23] A. Shiloach, D. Blankschtein, *Langmuir* 14 (1998) 1618, and references therein.
- [24] M.J. Rosen, T. Gao, Y. Nakatsuji, A. Masuyama, *Colloids Surf. A* 88 (1994) 1.
- [25] P. Mukerjee, A. Yang, *J. Phys. Chem.* 89 (1976) 1388.
- [26] J.H. Miyagishi, Y. Ishibai, T. Asakawa, M. Nishida, *J. Colloid Interface Sci.* 103 (1985) 164.
- [27] C. Treiner, C. Vaution, E. Miralles, F. Puiseux, *Colloids Surf.* 14 (1985) 285.
- [28] D.N. Rubingh, in: K.L. Mittal (Ed.), *Solution Chemistry of Surfactants*, vol. 1, Plenum Press, New York, 1979, p. 337.
- [29] P.M. Holland, D.N. Rubingh, *J. Phys. Chem.* 87 (1983) 1984.
- [30] C. Sarmoria, S. Puvvada, D. Blankschtein, *Langmuir* 8 (1992) 2690.
- [31] J.F. Scamehorn, in: J.F. Scamehorn (Ed.), *Phenomena in Mixed Surfactant Systems*, in: ACS Symp. Series, vol. 311, Am. Chem. Soc., Washington, DC, 1986.
- [32] M. Ghogomu, M. Bourouka, J. Dellacherie, D. Balesdent, M. Dirand, *Thermochim. Acta* 306 (1997) 69.
- [33] P. Mukerjee, T. Handa, *J. Phys. Chem.* 85 (1981) 2298.
- [34] T. Handa, P. Mukerjee, *J. Phys. Chem.* 85 (1981) 3916.
- [35] R.M. Clapperton, R.H. Ottewill, B.T. Ingram, *Langmuir* 10 (1994) 51.
- [36] S.J. Burkitt, B.T. Ingram, R.H. Ottewill, *Progr. Colloid Polym. Sci.* 76 (1988) 247.
- [37] H. Lange, K.H. Beck, *Kolloid Z.U.Z. Polym.* 251 (1973) 424.
- [38] N. Funasaki, S. Hada, *J. Phys. Chem.* 83 (1979) 2471.
- [39] J. Clint, *J. Chem. Soc.* 71 (1975) 1327.
- [40] J.M. Prausnitz, R.N. Lichtenthaler, E. Gomes de Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, third ed., Prentice-Hall, Englewood Cliffs, NJ, 1999 pp. 313–317.
- [41] H.C. Evans, *J. Chem. Soc. Pt. 1* (1956) 579.
- [42] *Handbook of Chemistry and Physics*, 56th ed., CRS Press, Cleveland, 1975–1976.
- [43] H.J.L. Trap, Thesis, Groningen, 1953.
- [44] H.J.L. Trap, J.J. Hermans, *Proc. Kon. Ned. Akad. Wetensch.* 58 (1955) 97.
- [45] E.W. Anacker, A.E. Westwell, *J. Phys. Chem.* 68 (1964) 3490.
- [46] L.J. Magid, *Colloids Surf.* 19 (1986) 129.
- [47] M. Miura, M. Kodama, *Bull. Chem. Soc. Jpn.* 45 (1972) 428.
- [48] J. Mandel, *Statistical Analysis of Experimental Data*, Interscience, New York, 1964, pp. 134–137.
- [49] K. Shinoda, *J. Phys. Chem.* 58 (1954) 1136.
- [50] K. Shinoda, *J. Phys. Chem.* 58 (1954) 541.
- [51] H.B. Klevens, *J. Phys. Colloid Chem.* 52 (1948) 100.
- [52] H. Lange, *Kolloid Z.* 131 (1953) 90.
- [53] Y. Moroi, N. Nishikido, R. Matuura, *J. Colloid Interface Sci.* 50 (2) (1975) 344.
- [54] M. Nakagaki, T. Handa, *Bull. Chem. Soc. Jpn.* 48 (2) (1975) 630.
- [55] K. Motomura, M. Aratono, in: K. Ogino, M. Abe (Eds.), *Mixed Surfactant Systems*, Dekker, New York, 1993, pp. 99–142, chap. 4.
- [56] S. Glasstone, *Tratado de Química Física*, Aguilar, Madrid, 1966, p. 644–645.
- [57] J.N. Israelachvili, *Intermolecular and Surface Forces*, second ed., Academic Press, London, 1992, pp. 261, 271.
- [58] D.J. Stigter, *Colloid Interface Sci.* 23 (1967) 379.
- [59] D. Stigter, *J. Phys. Chem.* 78 (1974) 2480.
- [60] J. Clifford, B.A. Pethica, *Trans. Faraday Soc.* 61 (1965) 182.
- [61] J. Clifford, *Trans. Faraday Soc.* 61 (1965) 1276.
- [62] M. Muller, J.M. Pellerin, W.W. Chen, *J. Phys. Chem.* 76 (1972) 3012.
- [63] T. Drakenberg, B. Lindman, *J. Colloid Interface Sci.* 44 (1973) 184.
- [64] J. Clifford, B.A. Pethica, *Trans. Faraday Soc.* 61 (1965) 182.
- [65] T. Walker, *J. Colloid Interface Sci.* 45 (1973) 372.
- [66] G.H. Griffith, P.H. Dehlinger, S.P. Van, *J. Membr. Biol.* 15 (1974) 159.
- [67] P. Ekwall, L. Mandell, P. Solyom, *J. Colloid Interface Sci.* 35 (1971) 519.