Thermodynamic Properties of Additive–Surfactant–Water Ternary Systems

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1 Introduction

Surfactants are often used in colloidal chemistry because of their amphiphilic nature. For example they stabilize naturally occurring dispersions of different types (emulsions, suspensions, foams) which are used in many technologies. Therefore, an understanding of surfactant systems is important from both theoretical and practical points of view.

In the last few years extensive structural, kinetic and thermodynamic studies have been performed on surfactant–water systems.[1] The thermodynamic properties investigated (volume, heat capacity, enthalpy, Gibbs energy, entropy, compressibility, *etc.*) have been interpreted using appropriate models.

In addition, thermodynamic studies have been devoted to water–surfactant–additive ternary systems so that a clear picture, even if not complete, of additive–surfactant interactions is available. In particular, the solubilization process of additives in micelles has been studied[2–15] by considering the nature of both the additive and the surfactant. Moreover, more attention has been paid to polar additives than to apolar ones because the latter have very low solubility in water. The effect of additives on the properties of micellization has been also studied.[5,6,13,16–22]

In this review thermodynamic results of water–additive–surfactant ternary systems are reported. Additives which essentially solubilize in the aqueous phase and additives which solubilize in the micellar phase are both briefly discussed. Among the former, compounds which can affect the properties of the surfactant through their interactions with the solvent (strong inorganic electrolytes, urea, *etc.*) are distinguished from β-cyclodextrin which interacts directly with the alkyl chain of the surfactant to form inclusion complexes.

As far as additives solubilizing in the micellar phase are concerned, homologous series of polar additives (alcohols, for instance) are discussed. Attention is also paid to crown ethers whose solubilization in micelles strongly depends on the nature of the surfactant counterion.

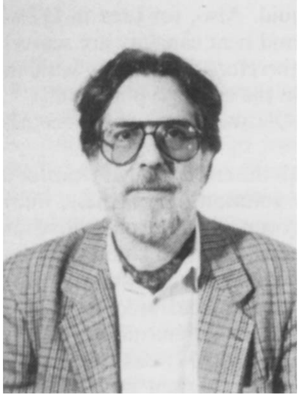
Finally, the importance of a given experimental thermodynamic approach as well as that of theoretical models is emphasized.

2 Water–Surfactant Systems

The thermodynamic characterization of water–additive–surfactant ternary systems often requires the knowledge of the water–additive and water–surfactant systems. In spite of the very wide literature of solutes in water, only in the last few years has interest grown in studies of surfactants in water.

The usual approach to surfactant solutions is that of studying a property as a function of surfactant concentration (m_S). At a given concentration, called the critical micelle concentration (cmc), the property shows a more or less abrupt change in slope (see Figure 1). This experimental evidence is consistent with the association of monomer surfactant molecules into aggregates, called micelles. The shape and the size of micelles depend on different parameters (temperature, pressure, concentration, nature of the surfactant, *etc.*). By assuming that the formation of the micelles corresponds to that of a new phase,[23] in the micellar region the increase in m_S leads to the increase in the concentration of the micellized surfactant while that of the unmicellized surfactant is constant and equal to the cmc. So, the cmc represents the solubility of monomeric surfactant in water and, therefore, it is easily correlated to the standard free energy of micellization ($\Delta_m G^\circ$). Other thermodynamic properties for the micellization process can be derived from the dependence of $\Delta_m G^\circ$ on temperature and/or pressure. However, since micellization is not a true phase-transition, it occurs in a more or less wide range of concentration around the cmc and the uncertainties which affect the cmc are reflected in the derived properties.

An accurate approach to the thermodynamics of surfactant solutions is based on the direct determination of surfactant properties as a function of m_S. In the pre-micellar region, the properties change almost linearly and give information on the solvent–monomer and monomer–monomer interactions. Just above the cmc, the properties change strongly with m_S owing to the transfer of the surfactant from water to the micelles. At high m_S, the properties tend to a constant value and deviations reflect micelle–micelle and monomer–micelle interactions. Examples are shown in Figure 1, where the apparent molar volume ($V_{\Phi,S}$)



Rosario De Lisi graduated in Chemistry in 1967 and was postdoctoral fellow until 1970 at the Institute of Physical Chemistry, University of Palermo. From 1970 to 1980 he taught Physics, Physical Chemistry, and Spectroscopy and since 1980 he has been Professor of Physical Chemistry of Interfaces. During 1977—1980 he was Invited Professor at the University of Sherbrooke, Canada. He worked on conductometric studies of interactions in solution and on anomalous proton mobility. Since 1977 his research activity has focused on the thermodynamics of surfactant solutions. He has published some 60 papers on this topic.

Stefania Milioto graduated in Chemistry in 1985 and received her Ph.D. degree in 1989 from the University of Palermo, Italy. She spent several months at the 'Centre des Recherche sur les Macromolecules (France), at the University of Saskatchewan (Canada), and at the Oak Ridge National Laboratory (USA) before taking up her present position as Research Assistant in the Department of Physical Chemistry, University of Palermo in 1991. She has collaborated with Professor R. De Lisi on research into the thermodynamics of surfactant solutions since 1985. She has more than 40 papers to her credit.

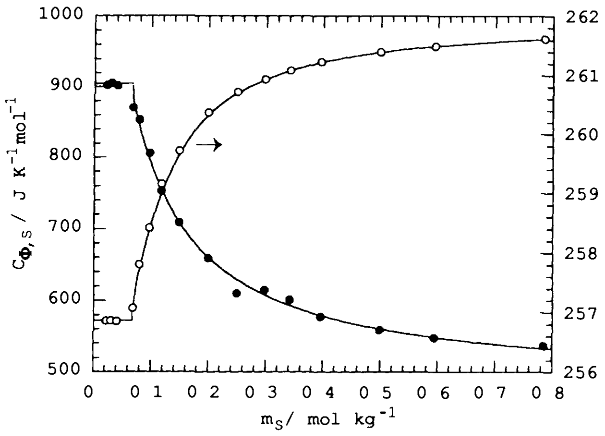


Figure 1 Apparent molar volume and heat capacity of decyltrimethylammonium bromide in water as a function of surfactant concentration at 298 K

and heat capacity ($C_{\Phi\,S}$) of decyltrimethylammonium bromide in water are plotted as a function of m_S [9]

To extract from the experimental data information on interactions within surfactant solutions, theoretical models are needed However, since the treatment of the water–surfactant system is outside the scope of this review, we will only briefly summarize the most used models and quote references where full details can be found

The pseudo-phase-transition model is currently used for surfactants with a low cmc According to this model,[17,24] the property of micellization is given by the difference between the partial molar property of the micellized and unmicellized surfactant at the cmc The two values are obtained by extrapolating at the cmc the trends in the post- and pre-micellar regions of a given thermodynamic property as a function of m_S

For surfactants having a high cmc value, a mass action model accounts more satisfactorily for the thermodynamic properties The simplest model is the two-step mass action model for non-ionic surfactants proposed by Desnoyers and co-workers [25] This model assumes that the monomers aggregate into monodisperse micelles The concentration of unmicellized and micellized surfactant depends on the stoichiometry through the micellization constant (K_M) and the aggregation number (N) From the fit of the resulting equation to the experimental data are derived K_M, N, and the corresponding property for the surfactant in the micellized and unmicellized form This model was applied also to ionic surfactants by taking into account the coulombic interactions [26]

For ionic surfactants, different thermodynamic properties have been treated[16] with a model valid for mixed electrolytes which uses the two-step mass action model and assumes that the aggregation number and the fraction of counterions bonded to the micelle are independent of temperature and pressure Another model[14] is based on the electrostatic cell approach in which the entire micellar solution is divided into spherical cells each containing one micellar aggregate and amounts of both water and electrolyte consistent with the overall composition As a consequence, the Gibbs energy is expressed in terms of hydrophobic and electrostatic interactions and of mixing of micelles

3 Water–Additive–Surfactant Systems

As we mentioned above, additives can solubilize in the micellar phase depending on their nature Therefore, it is useful to discuss the phenomena according to the following scheme

(i) Additives which do not penetrate micelles

Although a third component added to a micellar solution does not solubilize in the micellar phase, it can involve different interactions with surfactant which depend on the nature of the additive Therefore, thermodynamic properties are differently affected We can distinguish the following

(a) Strong inorganic electrolytes (KBr, KCl, *etc*) which interact with the micelles electrostatically

(b) Highly polar non-ionic additives (methanol, acetone, urea, acetonitrile, *etc*) which affect the micellization process through their effect on the physicochemical properties of the solvent

(c) Additives such as cyclodextrins – very different in nature and structure from the above additives – which can interact strongly with the surfactant alkyl chain because of the formation of inclusion complexes

(ii) Additives which penetrate micelles

In the micellar aggregates three sites of solubilization can be identified the micellar core (highly hydrophobic), the micellar surface (highly hydrophilic), and the palisade layer (the region between the head group and the core) Therefore, depending on the site of solubilization, there are three classes of compounds

(a) Apolar additives (*e g* alkanes) which are essentially solubilized in the micellar core Very few data are available[27] for these compounds because their low solubilities in water produce experimental problems

(b) Polar additives (medium alkyl chain-length alcohols, nitriles, nitroalkanes, *etc*) whose site of solubilization is the palisade layer

(c) Complexes with inorganic ions which can solubilize at the micellar surface depending on the nature of the surfactant and/or of the complexing molecule [5,7,19,27] Unfortunately, thermodynamic data are available only for crown ethers [5,19]

4 Additives which do not Penetrate Micelles

There is not an extensive literature reporting thermodynamic studies of additive–surfactant–water ternary systems where the additive is solubilized in the aqueous phase This is not fortuitous since the relevant importance of surfactant systems is the high solubilizing power that micelles show towards additives whose solubility in water is low

Properties of additives in surfactant aqueous solutions are quite scarce However data are available for the properties of surfactants in additive aqueous solutions

4.1 Additives in Surfactant Solutions

For additives which do not penetrate micelles, if m_a is not high (in the molality scale), a small dependence of their properties is expected on the additive (m_a) and surfactant concentrations Accordingly, for methanol (MeOH), which is the most extensively studied additive, the apparent molar volume ($V_{\Phi\,a}$) in sodium dodecylsulfate (NaDS) micellar solutions does not change with m_a and m_S $V_{\Phi\,a}$ is practically equal to that in water as observed also in sodium decanoate (NaDec) [17] These values are smaller by 2 5 and 10 2 cm^3 mol^{-1} than the molar volume and the standard partial molar volume in octane, respectively [3] Similar results are obtained from the isoentropic compressibility In NaDec,[17] this property is close to that in water and smaller than that of the pure liquid Also, for urea in DTAB micellar solutions, both volume and heat capacity are scarcely dependent on m_S and m_a and, therefore, consistent with the additive–surfactant interactions in the aqueous phase only [18]

These findings confirm that MeOH and urea cannot penetrate micelles

More extensive studies deal with the enthalpies of transfer of additives from water to micellar solution From these, information on the effect of the head group of both the additive and the surfactant can be drawn MeOH has been studied in non-ionic (dodecyldimethylamine oxide, DDAO), cationic (dodecyltrimethylammonium bromide, DTAB), and anionic (NaDS) surfactant solutions [2] Experimental data confirm that micelle-additive interactions are absent and that weak hydrophilic interactions in the aqueous phase are present in NaDS and DTAB while negligible in DDAO A different behaviour[4] is observed when the −OH group is replaced by the −CN group In fact, while CH$_3$CN is a cosolvent in DDAO, it is a penetrating additive in DTAB because of the favoured interactions at the micellar surface This view is corroborated by data for nitromethane in DTAB[4] whose distribution constant is equal to that of the longer alkyl chain butanol

Cyclodextrins are cyclic carbohydrates consisting of six, seven or eight α-D-glucopyranose units called α-, β-, and γ-cyclodextrins, respectively Although the formation of inclusion complexes of cyclodextrins with unmicellized surfactants has been investigated,[20] their thermodynamic properties in micellar solutions are practically unknown As far as we know, only the apparent molar volumes and heat capacities of β-cyclodextrin (β-Cy) 0 005 *m* as a function of m_S in NaDS and DTAB are available[6] The $V_{\Phi\,a}$ *vs* m_S trends in both surfactants are practically the same $V_{\Phi\,a}$ increases strongly with m_S in the pre-micellar region, and slowly decreases in the micellar region An opposite behaviour is observed for $C_{\Phi\,a}$ In fact, by increasing m_S, $C_{\Phi\,a}$ sharply decreases up to the cmc beyond which it increases Also, for NaDS the $C_{\Phi\,a}$ *vs* m_S curve shows a jump at ≈0 1*m* due to the NaDS postmicellar transition[5] While it is easy to explain data in terms of the formation of inclusion complexes in the pre-micellar region, this is not the case for the micellar region

4.2 Surfactants in Water–Additive Mixtures

As a general rule, at a fixed m_a, apparent molar properties of the surfactant (Y_{Φ} s) as a function of m_S are similar to that in water, shown in Figure 1, and the same theoretical models can be used

A few thermodynamic properties of surfactants in inorganic strong electrolyte solutions are available Nevertheless, these studies offer insights into the effect of these additives on the interactions in micellar solutions For example, addition of NaBr to alkyltrimethylammonium bromide (aq) involves an increase in osmotic coefficients attributed to reduced repulsive interactions between the micelles[16] This effect is not evidenced by volume and compressibility data of sodium dodecanoate in NaCl solutions[21] In fact, addition of NaCl affects these properties for the unmicellized surfactant but not for the micellized surfactant This means that these properties are practically insensitive to micelle–micelle interactions

Attention has been paid to the effect of the electrolyte on the micellar structural transition which surfactants sometimes undergo For example, from volume and heat capacity data,[22] the hexadecyltrimethylammonium bromide postmicellar transition in KBr and KCl aqueous solutions was investigated An increase in the electrolyte content induces the transition which appears at low m_a for KBr and high m_a for KCl

As far as the non-ionic solutes are concerned, the water–DTAB–urea system has been extensively investigated at 298 K[18] At a given urea concentration, the profiles of Y_{Φ} s (volume, heat capacity, relative enthalpy) and the non-ideal contributions to the free energy and entropy as functions of m_S are similar to those for the corresponding properties in water From a quantitative point of view, by adding urea these profiles are progressively shifted (towards higher or lower values depending on the property) up to 3 *m*, beyond which they are virtually unaffected Figures 2 and 3 show examples of the effect of urea on the trend of the apparent molar relative enthalpy (L_{Φ} s) and the non-ideal Gibbs energy (G_2^{nl}) as a function of the 'normalized' concentration $\ln m_S$/cmc, respectively Since the increase in the urea content acts in the same direction as temperature, it was assumed that urea at 298 K breaks up the water molecules network in a similar manner as does temperature As the entropies of micellization as a function of urea concentration at different temperatures show (see Figure 4), this finding is still valid at lower temperatures but not at higher temperatures In fact, the slopes of these trends are negative at 288 and 298 K and positive at 308 K, the change in the sign occurring at about 300 K These results indicated that around 300 K there is a change in the urea effect on the water structure

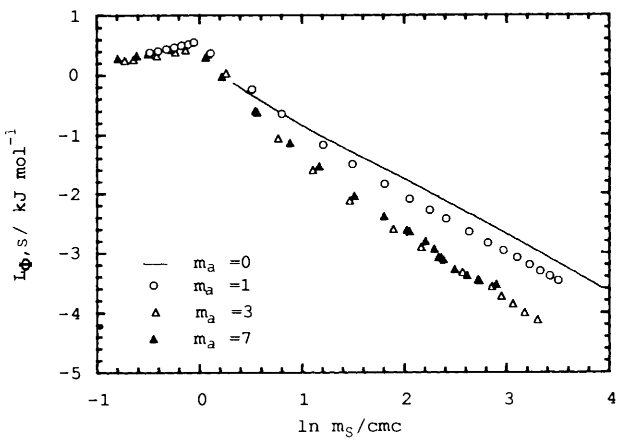


Figure 2 Effect of urea molality on apparent molar relative enthalpy *vs* surfactant concentration for dodecyltrimethylammonium bromide at 298 K

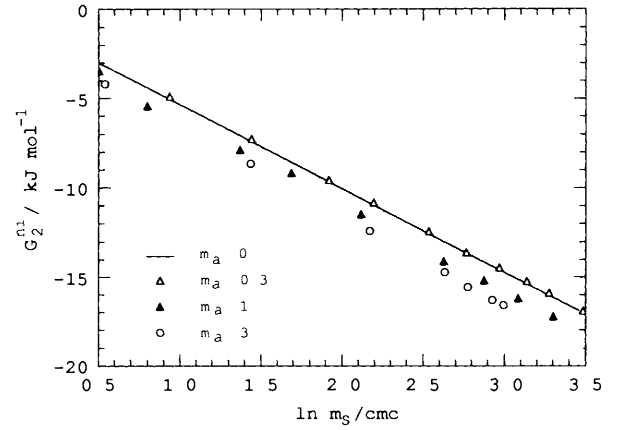


Figure 3 Effect of urea molality on non-ideal Gibbs energy *vs* surfactant concentration for dodecyltrimethylammonium bromide at 298 K

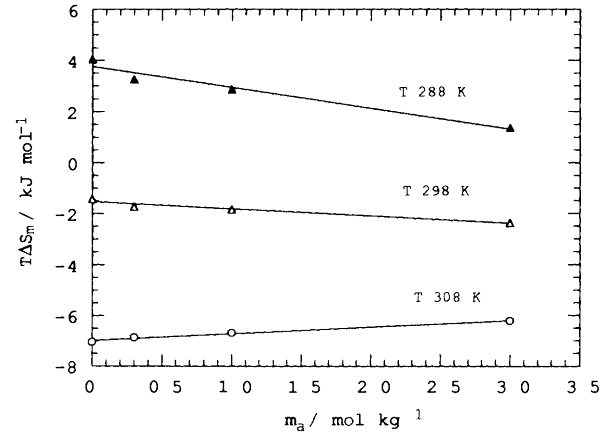


Figure 4 Effect of temperature on the dependence of the entropy of micellization of dodecyltrimethylammonium bromide on the urea molality

In contrast to what is observed for DTAB in urea solutions, for NaDec in water + MeOH mixtures,[17] by increasing alcohol concentration, V_{Φ} s of micellized surfactant increases regularly while that of unmicellized surfactant is a concave curve The former trend was ascribed to a decrease in the electrostriction of water molecules at the micellar surface The latter was assigned to concomitant effects due to (i) a maximum number of structure-promoted water molecules caused by the hydrophobic surfactant; (ii) the decrease in hydrophobic and hydrophilic hydration of the surfactant.

The effect of β-cyclodextrin on the $Y_{\Phi,S}$ *vs.* m_S profiles[6] is peculiar. In fact, $V_{\Phi,S}$ and $C_{\Phi,S}$ of NaDS and DTAB in water + β-Cy mixture are strongly affected in the premicellar region and hardly affected in the postmicellar one. However, these trends seem to be dependent on the nature of the surfactant. In fact, $V_{\Phi,S}$ of DTAB shows a maximum at ≈ 0.01 *m* beyond which it strongly decreases up to the cmc, and then slowly tends to the value in water. In the case of NaDS the maximum was not detected. $C_{\Phi,S}$ of DTAB and NaDS are very similar. In the premicellar region, they strongly decrease while those in water are essentially constant; in the post-micellar region, they are constant and practically equal to those in water. These results are consistent with the formation of inclusion complexes with the alkyl chain of monomeric surfactant in the pre-micellar region.

5 Additives which Penetrate Micelles

There are several ways for studying the solubilization of additives in the micellar phases. The choice of the experimental approach to use depends on the nature of the system to be investigated and the information required. If the study is aimed at determining the distribution constant of the additive between the aqueous and the micellar phases, different techniques (solubility, gas chromatography, vapour pressure, for instance) yield directly the amount of the additive in the two phases. Moreover, the distribution constant can be obtained from the dependence of the cmc on the additive concentration[8]

$$\ln\frac{\mathrm{cmc}}{\mathrm{cmc}_{w+a}} = \tfrac{1}{2}\left[2.3K_S + \frac{P}{55.5\ F}\right]m_a \tag{1}$$

where cmc_{w+a} represents the cmc in water + additive mixture. P is the partition constant in the mole fraction scale; K_S is the Setchenov constant and F is an 'activity coefficient'. The numerical coefficient 2 takes into account the dissociation of the 1:1 surfactant.

If the distribution constant is determined as a function of temperature and/or pressure, several thermodynamic properties of transfer (enthalpy, heat capacity, volume, compressibility, expansibility, *etc.*) of the additive from the aqueous to the micellar phases can be calculated. However, the uncertainty in the determination of the distribution constant and the small change in the intensive variables lead to unreliable derived properties and, consequently, only qualitative conclusions can be drawn. In addition, even precisely determined, properties of transfer cannot yield information on the additive–surfactant interactions in the aqueous and micellar phases. Standard thermodynamic properties are sensitive to solute–solvent interactions and, by comparing a given property in different solvents, insights into the nature of the interactions involved in the solubilization process can be obtained. For example,[15] at 298 K the standard partial molar heat capacity of pentanol is 532 J K^{-1} mol^{-1} in water, 191 J K^{-1} mol^{-1} in dimethylformamide, 208 J K^{-1} mol^{-1} in ethylene glycol, 136 J K^{-1} mol^{-1} in octane while its molar value is 208 J K^{-1} mol^{-1}. Consequently, since a given property of the additive is expected to be different in the micellar and aqueous phases, the extraction of the additive from the aqueous phase (obtained by increasing m_S) affects the bulk property (Figure 5). Therefore, a better approach to the thermodynamics of solubilization of an additive in micellar solutions is based on the determination of a given standard partial molar property as a function of m_S. By fitting the bulk experimental data using an appropriate model, both the distribution constant and the property of the additive in the micellar phase can be obtained. Often, the apparent molar property at low additive concentration is analysed instead of the standard one since they are very close in value. In addition, the study is less time-consuming since, for a given m_S, measurements as a function of the additive concentration are not needed.

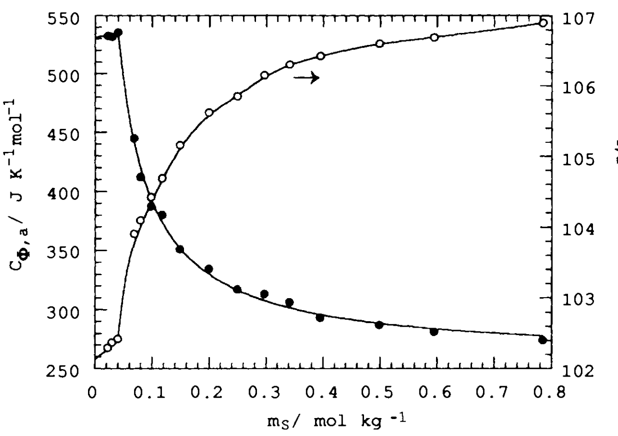


Figure 5 Apparent molar volume and heat capacity of pentanol 0.05 *m* in decyltrimethylammonium bromide aqueous solutions as a function of the surfactant concentration at 298 K.

5.1 Basic Models

If the additive can be considered in a state of infinite dilution, it behaves as a probe unaffecting the physicochemical properties of the micelles. Therefore, to rationalize the investigated property as a function of m_S, the following contributions are almost sufficient.

(i) Additive–surfactant interactions in the aqueous phase.
(ii) Additive–surfactant interactions in the micellar phase.
(iii) Distribution constant of the additive between the aqueous and the micellar phases.
(iv) Shift of the micellization equilibrium due to the presence of the additive.
(v) Structural variations (shape, aggregation number, degree of ionization changes) of the micelles.

At present, no models taking into account structural variations (point v) have been proposed.

The simplest approach considers the points (i) through (iii) and is based on the pseudo-phase-transition model for both the micellization and the additive distribution processes.[8] Consequently, the property of the additive in the aqueous (Y_f) and micellar (Y_b) phases contribute to the bulk property (Y_a) through the fraction of the additive in the corresponding phases (N_f and N_b)

$$Y_a = N_bY_b + N_fY_f \tag{2}$$

where N_b and N_f are given by

$$N_b = \frac{K(m_S - \mathrm{cmc})}{1 + K(m_S - \mathrm{cmc})} \qquad N_f = \frac{1}{1 + K(m_S - \mathrm{cmc})} \tag{3}$$

In equation 3 K is the distribution constant of the additive between the aqueous and the micellar phases. If the cmc is sufficiently low, then Y_f can be considered to be equal to the value in water (Y_w). From equation 2 Y_b can be obtained provided that K and Y_w are known. The model has been applied to enthalpies of solution of various alcohols in hexadecyltrimethylammonium bromide micellar solutions.[8] From these data the standard enthalpy of transfer of the additive from water to the micellar phases has been derived.

Since the property of the surfactant in the micellized and unmicellized form are generally different, the change of the cmc with the additive affects the property of the water + surfactant binary solvent. This effect is reflected in the bulk property of the additive. It is to be stressed that for a ternary system at fixed m_a, by increasing m_S, the monomer concentration is not constant even in the hypothesis of the pseudo-phase-transition model. Consequently, the micellization shift contribution depends on m_S and, by neglecting it, the quantities derived from equation 2 are more or less reliable, depending on the nature of both the additive and the surfactant

This contribution was taken into account in the model proposed by Desnoyers and co-workers,[10] who assumed a mass-action model for the micellization process and the pseudo-phase-transition model for the additive distribution, and by De Lisi *et al* ,[2] who considered the pseudo-phase-transition model for the micellization and a mass-action model for the distribution

In spite of the difference in the models, the resulting equations for Y_a as a function of m_S are very similar

$$Y_a = N_b Y_b + N_f Y_f + \frac{([m_0] - [m])\Delta Y_m}{m_a} \tag{4}$$

where $[m_0]$ and $[m]$ are the unmicellized surfactant concentrations in the absence and in the presence of the additive, respectively, m_a is the additive concentration and ΔY_m is the property of micellization Following the approach discussed by De Lisi *et al* ,[2] in the limit the additive concentration tends to zero, the shift of the micellization equilibrium can be expressed as

$$\begin{aligned}\lim_{m_a \to 0} \frac{([m_0] - [m])\Delta Y_m}{m_a} &= \frac{\mathrm{cmc}\ \Delta Y_m}{(1+\nu)}\{2\ 3K_S + (1+\beta)K\} \\ &= A_{cdc}\ \Delta Y_m\end{aligned} \tag{5}$$

By introducing equations 3 and 5 into equation 4, the following equation is obtained

$$Y_a = Y_b - (Y_b - Y_f - A_{cdc}\Delta Y_m)N_f \tag{6}$$

from which Y_b, Y_f, and K can be obtained through non-linear regression By converting K into the partition constant, the standard Gibbs energy of transfer (ΔG_t°) of the additive from the aqueous to the micellar phases can be calculated

In order to solve equation 4, Desnoyers and co-workers[10] evaluate $[m_0]$, ΔY_m, the aggregation number, and the constant of micellization (K_M) from the water–surfactant binary system (see Section 2) Then, K_M and the distribution constant have been correlated with m_S and with the additive concentration in the aqueous and micellar phases From the resulting equations, the distribution constant and Y_b are calculated by successive approximations

These models have been applied to different thermodynamic properties (volume, heat capacity, enthalpy, compressibility) for various additives and surfactants [2–4 9 10 13]

Other models from which it is difficult to extract the property of the additive in the micellar phase, have been proposed by Johnson *et al* [14] and by Christian *et al* [11] The first one is based on the electrostatic cell model for water + surfactant systems expanded in order to take into account the presence of the additive In other words, one additional contribution to the Gibbs energy due to the distribution of the additive was considered The second one is based on a two-step mass-action model for the micellization and a multi-step model for the distribution of the additive By assuming that the micelles are monodisperse and that the equilibrium constants of the different steps are equal (with the exception of that of the solubilization of the first molecule in the micelle), an equation correlating the aggregation number, the constant of micellization, and the various distribution constants was obtained

5.2 Examples of Applications

In this paragraph some examples of properties derived from equation 4 applied to the experimental bulk properties of the additive in surfactant solutions are reported in order to show that information on additive–micelle interactions in connection with the nature of both the additive and the surfactant can be obtained In addition, the above models can be also used for a quantitative treatment of the transfer properties of the surfactant from water to water + additive mixtures

5 2 1 Polar Additives

Polar additives in micellar solutions have been extensively explored However, these studies are essentially limited to the determination of the distribution constant and are not systematic Data reported here were chosen to show the effect of the hydrophobic and hydrophilic moieties of both the additive and the surfactant on the thermodynamics of solubilization of additives in the micellar phase For this reason, complete sets of thermodynamic properties of homologous series are needed In this review, we refer essentially to medium alkyl chain length alcohols

Comparisons between a given standard thermodynamic property of an additive in micellar phase (Y_b) and that in different solvents give information on the nature of the additive–micelle interactions and, therefore, on the site of solubilization of the additive in the micelle For a homologous series of additives, Y_b generally changes linearly with the alkyl chain length (n_c) of the additive

$$Y_b = A + Bn_c \tag{7}$$

where A and B represent the hydrophilic and the CH_2 hydrophobic contributions to Y_b, respectively The validity of equation 7 implies that an additional CH_2 group does not affect the hydrophilic interactions and that it is equivalent to the other methylene groups

Figure 6 shows molar volumes (V^*) and standard partial molar volumes in DTAB micellar phase (V_b), in water (V_w) and in octane (V_{oct}) for some primary alcohols as functions of n_c [9] As can be seen, equation 7 is always satisfied, the intercept and slope depending on the medium solvent The CH_2 group contribution to volume in the micellar phase (16 7 cm^3 mol^{-1}) is practically equal to that in pure liquid alcohols (16 9 cm^3 mol^{-1}) and in octane (16 5 cm^3 mol^{-1}) but different from that in water (16 0 cm^3 mol^{-1}) If these results indicate that the environment of the CH_2 group is hydrophobic in nature, they do not indicate if the alcohol is solubilized in either the core or the palisade layer of the micelle The hydrophilic contribution in the micellar phase (23 9 cm^3 mol^{-1}) is equal to that in pure liquids (24 4 cm^3 mol^{-1}), close to that in water (22 5 cm^3 mol^{-1}) and smaller than that in octane (33 2 cm^3 mol^{-1}) These findings suggest that alcohol solubilizes in the palisade layer of the micelle being involved in both hydrophilic and hydrophobic interactions A different behaviour is observed for alkanes[12] since V_b values in sodium

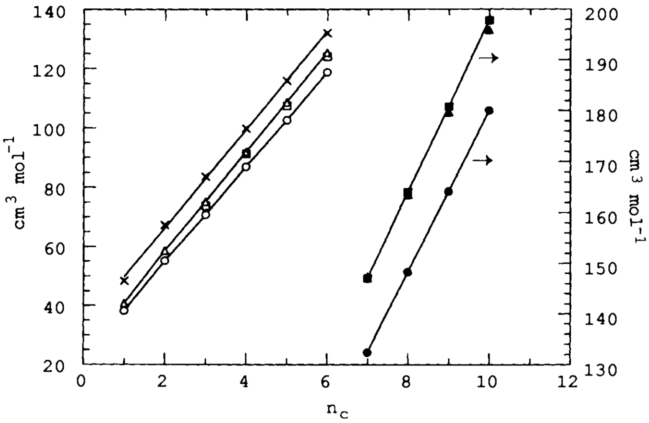


Figure 6 Molar volumes (triangles) and standard partial molar volumes of alkanes (filled symbols) and alcohols (open symbols) in the micellar phase (squares), in water (circles) and in octane (cross) as a function of the additive tail at 298 **K** The micellar phase refers to sodium dodecanoate for alkanes and to dodecyltrimethylammonium bromide for primary alcohols

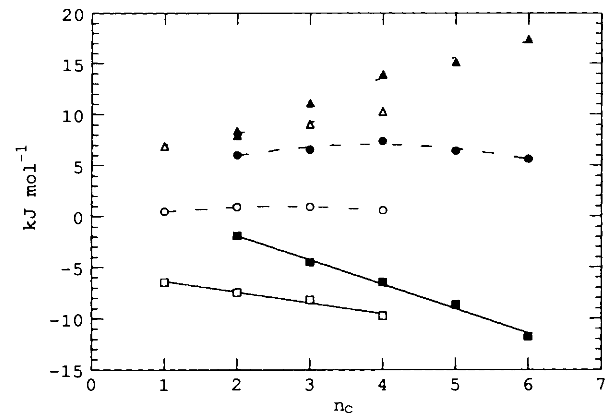


Figure 7 Standard Gibbs energy (squares), enthalpy (circles), and entropy (triangles) of transfer of nitroalkanes (open symbols) and primary alcohols (filled symbols) from the aqueous to the micellar phases of dodecyltrimethylammonium bromide at 298 K

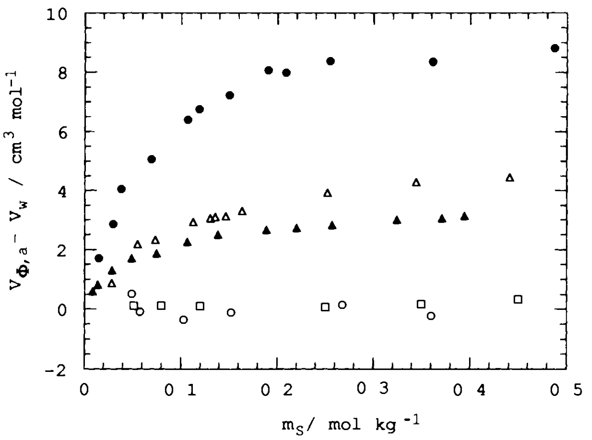


Figure 8 Apparent molar volume, corrected for that in water, of pentanol (triangles), 18-crown-6 (circles), and urea (squares) in surfactant solutions as a function of the surfactant concentration Filled symbols, sodium dodecylsulfate, open symbols, dodecyltrimethylammonium bromide

dodecanoate micelles are equal to V^* and higher than those in water (Figure 6) This pattern indicates that the site of solubilization of alkanes in micelles is the hydrocarbon liquid core The same information was derived from heat capacity data [15]

As far as other thermodynamic properties are concerned, Gibbs energy, enthalpy, and entropy of transfer of alcohols from the aqueous to the micellar phases are available [28] The additivity rule (equation 7) for these properties is not expected to be valid because the aqueous phase is not a pure phase Of course, if additive–surfactant interactions in the aqueous phase can be neglected, then equation 7 can be used This is the case for Gibbs energy, the CH_2 group contribution to this property is $-2\ 3$ kJ mol^{-1} for all surfactants [2–4] In the case of enthalpy and entropy (Figure 7), their plots *vs* n_c curves show maxima at $n_c \approx 5$ or 6, depending on the nature of the system [2 8] The same profiles are obtained if the properties of transfer are corrected for the additive–surfactant interactions in the aqueous phase, *i e* if the transfer from water to micelle is considered [8]

More direct information on the additive–micelle interactions are obtained through the solvation properties These were calculated for primary alcohols and alkanes in NaDS micelles[2] and compared with those in water and octane These properties were interpreted in the same manner as those of transfer, and the information obtained was consistent with that derived from other thermodynamic properties

As mentioned above, the nature of the polar head of the additive in the solubilization process in the micelle has a relevant effect since MeOH behaves like a co-solvent, while nitromethane penetrates the micelles From homologous series of nitriles, nitroalkanes, and alcohols in DTAB[4] the affinity of the micelles towards −CN and $-NO_2$ groups is higher than that towards the −OH group while opposite behaviour was found for the methylene group While the transfer of the CH_2 group from the aqueous to the micellar phases is always governed by the entropy, that of the polar groups depends on their nature The transfer of $-NO_2$ and −CN groups is governed by the entropy and that of the −OH group by the enthalpy

5 2 2 Crown Ethers

Crown ethers are macrocyclic polyethers which with inorganic cations form stable complexes having mostly 1 1 stoichiometry, the result of strong ion-dipole interactions They show a high degree of selectivity towards specific cations which depends on the radius of both the cation and the cavity of the crown ether [19] For example, 18-crown-6 and 15-crown-5 form stable complexes with sodium ions whereas 12-crown-4 does not Studies of these additives in micellar solutions gave insights into the effect of the complexes' formation on their solubilization in micelles

The apparent molar volume and heat capacity of 18-crown-6 0 04 *m* as a function of NaDS concentration are typically trends of distribution [5] Accordingly, the $V_{\Phi\,a}$ *vs* m_S trend is similar to that of pentanol in NaDS (Figure 8) The distribution of crown was ascribed to the formation of a complex which can be adsorbed at the micellar surface In fact, in DTAB micellar solutions, where crown ethers cannot be complexed, both $V_{\Phi\,a}$ and $C_{\Phi\,a}$ are independent of m_S, such as it occurs for urea The properties for pentanol possess again the feature of a distributing additive Therefore, in order to obtain the distribution constant and the property of the complexed crown in the micellar phase, equation 6 was modified to take into account the complexation equilibrium in the aqueous phase The *K* value agreed with that obtained from NMR techniques [7] The V_b value is smaller than that in the aqueous phase, counter to what is observed for other additives This pattern is consistent with the substitution at the micellar surface of uncomplexed sodium ion with the complexed one This process involves the formation of free sodium ions which causes a decrease in the volume

5 2 3 Transfer of Surfactants from Water to Water + Additives Mixtures

The transfer properties

$$\Delta Y_{\Phi\,S}(w \rightarrow w + a) = Y_{\Phi\,S}(w + a) - Y_{\Phi\,S}(w) \qquad (8)$$

of surfactants from water to aqueous solutions of alcohols and crown ethers as a function of m_S are available [5 13 17]

The shapes of these curves are characteristic of the system investigated For example, for NaDec in water + propanol mixtures, $\Delta V_{\Phi\,S}(w \rightarrow w + a)$ monotonically increases with m_S at low m_a, whereas it shows a maximum at higher m_a [17] Maxima are present also in the $\Delta V_{\Phi\,S}(w \rightarrow w + a)$ and in the isoentropic compressibility of transfer of DTAB in water + pentanol mixture at different temperatures [13] As a general feature, by increasing the hydrophobicity of the alcohol the maximum is shifted towards lower m_S values and its amplitude increases [9] A similar behaviour was observed for the volume of transfer of NaDS from water to water + 18-crown-6 mixtures, for DTAB, $\Delta V_{\Phi\,S}(w \rightarrow w + a)$ is negative in the pre-micellar region and null in the post-micellar region (Figure 9) The effect of the size of the cavity of crown ethers was also investigated by studying NaDec in 12-crown-4, 15-crown-5, and 18-crown-6 [19] Both the volume and the isoentropic compressibility of monomeric and micellized surfactant increase with crown concentration These results were quantitatively explained in terms of the extraction of the additive from the aqueous phase to the micelle which depends on the distribution constant In the case of crown ethers

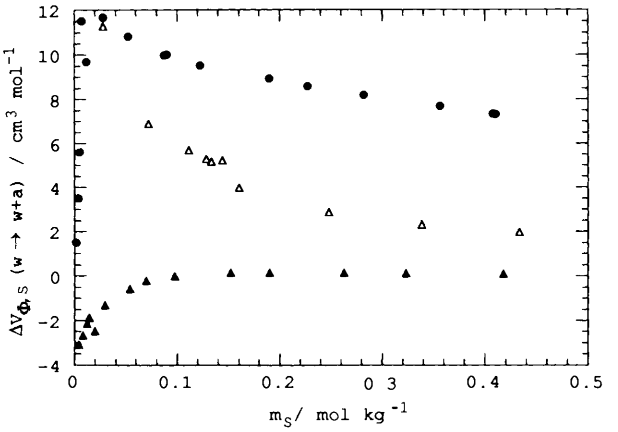


Figure 9 Volume of transfer of sodium dodecylsulfate (circles) and dodecyltrimethylammonium bromide (triangles) from water to water + 18-crown-6 (filled symbols) and water + pentanol (open symbols) as a function of the surfactant concentration at 298 K

the distribution constant is related also to the complexation constant which for Na$^+$ is known to increase in the order 12-crown-4, 15-crown-5, 18-crown-6

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