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Determination of micellar characteristics by measuring quantities related to the surfactant chemical potential

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A simple method of finding the critical micelle concentration (cmc) and the degree of counterion binding of surfactant micelles from the experimental dependence of the activity coefficient, the osmotic coefficient and the vapour-pressure lowering of a surfactant solution on concentration is described.

Partial molal (molar) quantities of micellar solutions have been widely discussed in the literature.[1–5] It is of special interest that such data can be used to determine the aggregation number[4] and other micellar characteristics. However, the evaluation of the degree of counterion binding in ionic micellar systems was not considered. Recently, new methods for determining the aggregation number and the degree of counterion binding found from the surface tension isotherm have been proposed by comparing the isotherm slopes below and above the critical micelle concentration (cmc).[6–8] The rule has recently been verified by experiment.[9–11] However, there should be a more direct way of finding the degree of counterion binding from the bulk properties of a micellar solution. We discuss this problem in the present communication using some quantities related to the surfactant chemical potential: the activity coefficient, the osmotic coefficient and the lowering of the vapour pressure of a surfactant solution.

Let us consider the case of an ionic surfactant producing a surface-active ion of stoichiometric coefficient ν_1 and a counterion with the stoichiometric coefficient ν_2 (subscripts 1 and 2 refer to the surface-active ion and the counterion, respectively). The chemical potentials of the electrolyte, μ, and of the single ions, μ_1 and μ_2, are related by the condition of ionic equilibrium:

$$\mu = \nu_1\mu_1 + \nu_2\mu_2 \tag{1}$$

Equalising the chemical potentials of the ions to the chemical potentials, μ_{11} and μ_{21}, of their monomeric forms (the additional subscript 1 refers to the monomeric form of an ion), equation (1) may be written:

$$\mu = \nu_1\mu_{11} + \nu_2\mu_{21} \tag{2}$$

For the sake of simplicity, we consider the case of low ionic strength and assume ideal behaviour of the monomeric ions and ionic micelles, bearing in mind that the mean electrolyte activity coefficients are well known and can be easily introduced into the theory if necessary. Then we may write:

$$\mathrm{d}\mu/\mathrm{d}\ln c = \nu_1 kT\mathrm{d}\ln c_{11}/\mathrm{d}\ln c + \nu_2 kT\mathrm{d}\ln c_{21}/\mathrm{d}\ln c \tag{3}$$

Here $c = c_1/\nu_1 = c_2/\nu_2$ is the electrolyte concentration (c_1 and c_2 are the total concentrations of the surface-active ion and the counterion and c_{11} and c_{21} are the concentrations of their monomeric forms, respectively) and kT is of convenional meaning. The expressions for the derivatives on the right-hand side of equation (3) are given by the mass-action-law theory of micellization:[6–9]

$$\frac{\mathrm{d}\ln c_{11}}{\mathrm{d}\ln c} = \frac{1-(\nu_2/\nu_1)n_1\alpha\beta(1-\beta)/(1-\alpha\beta)}{1-\alpha+n_1\alpha[1+(\nu_2/\nu_1)(1-\alpha)\beta^2/(1-\alpha\beta)]} \tag{4}$$

$$\frac{\mathrm{d}\ln c_{21}}{\mathrm{d}\ln c} = \frac{1}{1-\alpha\beta}\left[1-\beta+\beta(1-\alpha)\frac{\mathrm{d}\ln c_{11}}{\mathrm{d}\ln c}\right] \tag{5}$$

where $\alpha \equiv (c\nu_1 - c_{11})/c\nu_1$ is the degree of micellization of the surface-active ion and $\beta = n_2\nu_1/n_1\nu_2$ is the degree of counterion binding (n_1 and n_2 are the aggregation numbers of the surface-active ion and the counterion, respectively). Putting (4) and (5) in equation (3) yields:

$$\mathrm{d}\mu/\mathrm{d}\ln c = kT\,\{\nu_2\,(1-\beta)/(1-\alpha\beta) + [\nu_1 + \nu_2\beta(1-\alpha)/(1-\alpha\beta)]\,\mathrm{d}\ln c_{11}/\mathrm{d}\ln c\} \tag{6}$$

where the derivative $\mathrm{d}\ln c_{11}/\mathrm{d}\ln c$ is given by equation (4).

The left-hand side of (6) can be expressed through the mean activity coefficient, $f_\pm$, or through the molal osmotic coefficient, ϕ, or through the lowering of the vapour pressure, p, of the surfactant solution according to the following relationships:

$$\mathrm{d}\mu/\mathrm{d}\ln c = kT\nu\,(1 + \mathrm{d}\ln f_\pm/\mathrm{d}\ln c) \tag{7}$$

$$d\mu/d\ln c = d\mu/d\ln m = kTv\, d(\phi m)/dm \qquad (8)$$

$$d\mu/d\ln c = -kTc_3\, d\ln p/dc \qquad (9)$$

where $v \equiv v_1 + v_2$ is the total number of ions produced at dissociation by one molecule of the surfactant, m is the molality and c_3 is the concentration of a solvent. Equations (7)–(9) are examples showing how the derivative $d\mu/d\ln c$ can be determined from experiment. On obtaining experimental values of this derivative and of the degree of micellization of the surface-active ion α, we have equation (6) as an equation with two unknowns, n_1 and β, so that one of them can be found from equation (6) if the other is given. Since both n_1 and β are only slightly dependent on concentration, it is also possible to assume both of them to be constant and to calculate, with the aid of equation (6), their average values using experimental data for two different concentrations (then we have two equations with two unknowns). The third (and some other) concentration can be used to verify whether or not n_1 and β are constant within a chosen concentration range.

In the limit $\alpha = 0$, we have $d\ln c_{11}/d\ln c = 1$, and equation (6) becomes:

$$(d\mu/d\ln c)_{\alpha=0} = kTv \qquad (10)$$

This is a result for an ideal solution which we consider here in the sense that we neglect interactions between the particles of the solute (micelles and ions). Our activity coefficient, as well as the osmotic coefficient in (8), reflects only aggregation in solution. Strictly speaking, we should write, in place of (10), the same equation (7) with the Debye–Hückel activity coefficient, but the latter would be very close to unity in the case under consideration (say, 0.98 as for the concentration of 0.35 mol m^{-3} for a 1-1 electrolyte[9]).

In the opposite limit $\alpha = 1$, we have

$$d\ln c_{11}/d\ln c = 1/n_1 - (v_2/v_1)\beta \approx -(v_2/v_1)\beta \qquad (11)$$

$$(d\mu/d\ln c)_{\alpha=1} \approx kTv_2\,(1-\beta) \qquad (12)$$

where the obvious condition $1/n_1 \ll (v_2/v_1)\beta$ has been used for typically large n_1. By comparing (10) and (12), the theory predicts a considerable decrease [about $v/v_2\,(1-\beta)$ times] in a positive slope of the surfactant chemical potential or $\ln f_\pm$ *versus* $\ln c$ or ϕm *versus* m or $\ln p$ *versus* c when passing the cmc. This provides a basis for the experimental determination of the cmc by using the above dependencies. To illustrate the experimental confirmation of this trend, we present in Figure 1 the dependence of ϕm on m for an aqueous solution of *N*-dodecylnicotinamide chloride at 25 °C calculated from the experimental data of DeLisi *et al.*[5] The transition point determined in this way correlates well with the transition point for the heat capacity,[5] which confirms the reliability of the method. If the above dependences are close to linearity (Figure 1), it is also possible to determine the degree of counterion binding by comparing the slopes below and above the cmc, or, since the slope below the cmc is known from theory [*e.g.*, $d(\phi m)/dm = 1$], simply by measuring the slope above the cmc (the slope decrease in Figure 1 is about 10 times, which gives β about 0.8 at $v/v_2 = 2$). The corresponding formulaes for this purpose are derived by putting (7)–(9) into (12):

$$\beta \approx 1 - (v/v_2)\,(1 + d\ln f_\pm/d\ln c)_{\alpha_1=1} \qquad (13)$$

$$\beta \approx 1 - (v/v_2)[d(\phi m)/dm]_{\alpha_1=1} \qquad (14)$$

$$\beta \approx 1 + (c_3/v_2)d\ln p/dc = 1 + [(1 - x)/v_2 x]\, d\ln p/d\ln c = 1 + [(1 - x)/v_2 x]\, d\ln p/d\ln m \qquad (15)$$

where $x = c/(c + c_3)$ is the mole fraction of the ionic surfactant as a whole in solution.

Let us illustrate the practical utilisation of equations (6)–(15) by using the data on the lowering of the vapour pressure in a micellar solution. Fineman and McBain[12] were first to measure the osmotic coefficient and the lowering of the vapour pressure for micellar solutions of a number of surfactants. The data on the vapour-pressure lowering are convenient to use because of the linear character of the dependence of the vapour-pressure lowering on concentration.[12] A rather pronounced change in the slope of the straight line describing the vapour-pressure lowering close to the cmc was observed, as should be expected on comparing equations (10) and (12). Using the slope values given by Fineman and McBain and setting $c_3 = 55.51$ for water, equation (15) permits the calculation of the degree of counterion binding. The results are given in Table 1.

The values obtained look reasonable, although one might expect higher values of the degree of counterion binding for the soaps investigated by Fineman and McBain at excess additional electrolyte. This is in agreement with the fact that they applied the evaporation-rate method which should give higher values for $-d\ln p/dc$ and lower values for β because of the influence of surfactant adsorption on the evaporation rate. However, such an influence was not discovered in the special experiments performed by Fineman and McBain.[12]

The above method of determining the degree of counterion binding requires data on the dependence of the chemical potential or, in particular, of the molal osmotic coefficient ϕ on concentration. We now briefly discuss the possibility of finding β from a single value of ϕ. By definition:

$$v\phi m = -N_{30}\ln a_3 \qquad (16)$$

where N_{30} is the number of moles of solvent in 1 kg of pure

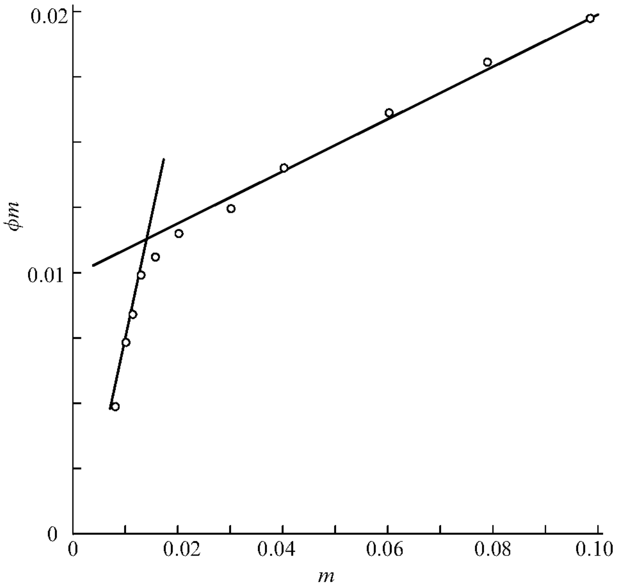

Figure 1 The dependence of ϕm on m for an aqueous solution of *N*-dodecylnicotinamide chloride at 25 °C according to the data of DeLisi *et al.*[5]

Table 1 The degree of counterion binding β calculated using equation (15) from the data on the vapour-pressure lowering at 25 °C by Fineman and McBain.[12]

Surfactant	$-d\ln p/dc$ kg mol^{-1}	β
Potassium laurate	0.0031	0.83
Potassium myristate	0.0034	0.81
Sodium laurate	0.0047	0.74
Cetylpyridinium chloride	0.0020	0.89
Cetyltrimethylammonium bromide	0.0023	0.87
Cetyldimethylbenzylammonium chloride	0.0037	0.79
Sodium oleate	0.0082	0.54

solvent ($N_{30} = 55.51$ for water) and a_3 is the activity of the solvent. For a sufficiently dilute micellar system:

$$\ln a_3 \approx -(N_{11} + N_{21} + N_M)/N_3 \qquad (17)$$

where N is the number of moles, the subscripts 11, 21, M and 3 refer to the monomeric surface active ion, monomeric counterion, micelles and solvent, respectively. Combining (16) and (17), we may write:

$$\nu\phi m \approx m_{11} + m_{21} + m_M \qquad (18)$$

Using $m_{11} = (1-\alpha)m\nu_1$, $m_{21} = (1-\alpha\beta)m\nu_2$ and $m_M = \alpha m\nu_1/n_1$, equation (18) becomes:

$$\nu\phi \approx \nu_1(1 - \alpha + \alpha/n_1) + \nu_2(1 - \alpha\beta) \qquad (19)$$

From here:

$$\beta \approx \nu(1 - \phi)/\nu_2\alpha - (\nu_1/\nu_2)(1 - 1/n_1) \qquad (20)$$

or, if $1 \gg 1/n_1$,

$$\beta \approx \nu(1 - \phi)/\nu_2\alpha - \nu_1/\nu_2 \qquad (21)$$

Equation (21) requires experimental values of ϕ and α in order to determine β. Similarly to the known approximation for non-ionics, one may write:

$$\alpha \approx (m - m_{cmc})/m \qquad (22)$$

where there are two uncertainties. The first uncertainty originates from the fact that α is assumed to be zero at the cmc. In reality, α_{cmc} is not zero and depends on the cmc definition. The analysis of 12 definitions based on quantities related to the surfactant chemical potential shows that α_{cmc} is really close to zero if the cmc is defined as the inflection point in the activity *versus* $\ln c$ dependence.[8] Otherwise, α_{cmc} can range from 0.01 to 0.1 and more.[8] [It is of note that for every cmc definition, α is uniquely related to the aggregation number[8] and may be calculated if the aggregation number is known. In this case the degree of counterion binding can be calculated from (21) exactly at the cmc.] The first uncertainty in (22) is smaller the larger the concentration as compared with the cmc. The second uncertainty in (22) is that the monomeric concentration m_{11} has been replaced by the cmc. In reality, m_{11} is slightly larger than m_{cmc}, the difference becoming greater the larger the concentration as compared with the cmc.

Using equations (21) and (22) and the experimental data of DeLisi *et al.*[5] (Figure 1), we have calculated the degree of counterion binding for an aqueous solution of *N*-dodecylnicotinamide chloride ($m_{\text{cmc}} = 0.0124$, $\nu = 2$, $\nu_1 = \nu_2 = 1$) as a function of concentration (Table 2). It is seen that only the first point, which is too close to the cmc, produces the wrong result. All others oscillate near the value $\beta \approx 0.8$ which was obtained above by comparing the slopes of ϕm *versus* m.

All the above equations for ionics may be converted into relationships for a single non-ionic by setting $\nu = \nu_1 = 1$ and $\nu_2 = \beta = 0$. The resulting relationships contain only the aggregation number as an unknown and may be used for finding this quantity. Equation (6) becomes:

$$d\mu/d\ln c = kT/[1 + \alpha(n - 1)] \qquad (23)$$

from which it follows that:

$$1/n = (d\mu/d\ln c)_{\alpha=1}/(d\mu/d\ln c)_{\alpha=0} = [d(\phi m)/dm]_{\alpha=1} \qquad (24)$$

Correspondingly, equation (19) becomes:

$$\phi \approx 1 - \alpha + \alpha/n \qquad (25)$$

Since $1/n$ is usually small, the procedure for finding $1/n$ should be very precise, and the question arises of whether a small term related to n can be compared with a correction for non-ideality which is absent in the above equations. The first attempt of accounting for non-ideality was undertaken by Desnoyers *et al.*[4] by combining some relationships for ideal and non-ideal systems, but the theory needs further development along these lines.

Table 2 The degree of micellization α and the degree of counterion binding β calculated using equations (21) and (22) from data on the osmotic coefficient ϕ for an aqueous solution of *N*-dodecylnicotinamide chloride at 25 °C by DeLisi *et al.*[5]

m	ϕ	α	β
0.01551	0.8040	0.201	0.955
0.02001	0.6586	0.380	0.795
0.02971	0.4683	0.583	0.825
0.03996	0.3790	0.690	0.801
0.06004	0.2824	0.793	0.809
0.07909	0.2325	0.843	0.820
0.09884	0.1990	0.875	0.832
0.1474	0.1686	0.916	0.816
0.1986	0.1537	0.938	0.805
0.2955	0.1448	0.958	0.785
0.3956	0.1413	0.969	0.773

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References

1 G. Douheret and A. Viallard, *J. Chim. Phys. Phys.-Chim. Biol.*, 1981, **78**, 85.
2 J. B. Rosenholm, *Colloid Polym. Sci.*, 1981, **259**, 1116.
3 R. DeLisi, G. Perron, J. Paquette and J. E. Desnoyers, *Can. J. Chem.*, 1981, **59**, 1865.
4 J. E. Desnoyers, G. Caron, R. DeLisi, D. Roberts, A. Roux and G. Perron, *J. Phys. Chem.*, 1983, **87**, 1397.
5 R. DeLisi, E. Fisicaro, S. Milioto, E. Pilizzetti and P. Savarino, *J. Solution Chem.*, 1990, **19**, 247.
6 A. I. Rusanov and V. B. Fainerman, *Dokl. Akad. Nauk SSSR*, 1989, **308**, 651 [*Dokl. Phys. Chem.* (*Engl. Transl.*), 1989, **308**, 777].
7 A. I. Rusanov, *Adv. Colloid Interface Sci.*, 1992, **38**, 271.
8 A. I. Rusanov, *Mitselloobrazovanie v rastvorakh poverkhnostno-aktivnykh veshchestv* (*Micellization in Surfactant Solutions*), Khimiya, St. Petersburg, 1992 (in Russian).
9 V. A. Prokhorov and A. I. Rusanov, *Kolloidn. Zh.*, 1990, **52**, 1109 [*Colloid J. USSR* (*Engl. Transl.*), 1990, **52**, 955].
10 R. Wüstneck, P. Enders and H. Fiedler, *Langmuir*, 1994, **10**, 3955.
11 V. G. Babak, A. N. Pavlov, T. F. Svitova, A. N. Danilenko, V. V. Egorov and E. A. Varlamova, *Kolloidn. Zh.*, 1996, **58**, 5 (in Russian).
12 M. N. Fineman and J. W. McBain, *J. Phys. Colloid Chem.*, 1948, **52**, 881.

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