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364

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SOLUBILIZATION AND MICELLES

THE ENERGETICS OF HIGHLY CHARGED SPHERICAL MICELLES AND THEIR SIZE DISTRIBUTION AS APPLIED TO SODIUM LAURYL SULPHATE

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The thermodynamics of micellar solutions is treated. The contribution of the electrical double layer to the free energy of micellization is derived for spherical micelles. By comparison with experimental data on sodium lauryl sulphate it is shown that the Debye-Hückel theory leads to erroneous results. An improved calculation, allowing for high surface potentials, gives better results. Micelle size distributions calculated on this basis are rather narrow. The non-electrical part of the free energy of micellization is nearly independent of micelle size and slightly above 1 kT per carbon atom in the chain. Comparison with other data on the free energy change in the transfer of aliphatic chains from aqueous to non-polar surroundings shows good agreement.

It has been shown in various ways that in aqueous soap solutions single ions may associate to micelles. The tendency of the hydrocarbon tails to be squeezed out of the water medium may be considered as the driving force for micelle formation. It is opposed by the mutual repulsion between the ionic heads, which form an electrical double layer at the micelle surface with the surrounding free ions. The decrease of entropy connected with the decrease of the number of free kinetic units is also a factor unfavourable to micelle formation.

This paper deals with the thermodynamics of micelle formation. The free energy changes (electrical and non-electrical) which accompany micelle formation in detergent solutions with or without the addition of simple electrolytes are evaluated and the size distribution of the micelles is derived. Experimental data are taken from the system sodium lauryl sulphate (NaLS) in aqueous salt (NaCl) solutions.

OUTLINE OF THEORY

In thermodynamic equilibrium no work is required to form one micelle with its double layer from single ions. For micelles containing n soap ions this condition gives the relation¹

$$\frac{kT}{n} \ln \frac{f_n x_n}{n} - kT \ln f_1 x_1 + F_{el} + W - TS_0 = 0 \quad \dots (1)$$

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x_n and x_1 are the concentrations in mole fractions of the micellar soap and of the unassociated soap, respectively (based on the formula weight of the soap); f_n and f_1 are the respective activity coefficients; nF_{el} is the change of the electrical free energy and nW is the change of the van der Waals energy of the system when one micelle is formed; S_0 is the change of the standard state entropy of a soap ion upon micellization.

The electrical free energy F_{el} can be evaluated on the basis of a suitable model. As it is difficult to account for interaction between micelles, we restrict ourselves to soap solutions near the critical micellar concentration (c.m.c.) (i.e. the soap concentration at which micelles begin to appear).

In general, a range of micelle sizes is to be expected and one equation (1) for each n value is required to describe the system. In such a set of equations all terms, except f_1x_1 , change with n . It is evident that always $dF_{el}/dn > 0$, since the electrical work per micellized ion increases with the micelle size. The change of $W - TS_0$ can be discussed with equation (2) which is obtained from (1) by differentiation with respect to n

$$\frac{d}{dn} (W - TS_0) = -\frac{dF_{el}}{dn} + \frac{kT}{n^2} \left(1 + \ln \frac{f_n x_n}{n} \right) - \frac{kT}{n} \frac{d}{dn} (\ln f_n x_n) \quad \dots (2)$$

At the maximum of the micelle (weight) distribution the last term in equation (2) cancels say at $n = n_0$, if f_n changes only slowly with n . Furthermore, $f_n x_n/n \ll 1$ so that $1 + \ln(f_n x_n/n) < 0$. Hence it follows from equation (2) that $(W - TS_0)$ always decreases with increasing n , at least in the range $n < n_0$.

In the following we apply equations (1) and (2) to NaLS micelles for which experimental data on the c.m.c. and on the average size are available as a function of NaCl concentration. If the weight distribution of micelles is not too asymmetrical the last term of equation (2) vanishes for the average size determined by light scattering. Furthermore, f_1x_1 is known from c.m.c. data and suitable estimates of $f_n x_n$ can be made. These data are combined in equations (1) and (2) with values of F_{el} and dF_{el}/dn derived on the basis of a model for the micelle. In this way, $W - TS_0$ and $d(W - TS_0)/dn$ are obtained for a range of NaCl concentrations, i.e. for a range of n values. The comparison of these data provides a sensitive test on the model employed for the calculation of F_{el} and dF_{el}/dn . Actually, we shall use two different models.

When the model calculation is successful up to this stage the theory can be taken one step further. The $W - TS_0$ curve obtained above (which is the same for all salt concentrations) is now combined with an F_{el} v. n curve computed for a particular salt concentration. Introducing these data, along with the relevant value of f_1x_1 , into equation (1) the size distribution of the micelles at this salt concentration can be obtained. In this way the initial assumption of symmetrical distributions can be checked.

MODELS FOR CALCULATION OF ELECTRICAL FREE ENERGY, F_{el}

We have used:

(1) A spherical micelle with a uniform surface charge and surrounded by an electrical double layer in which the ionic concentrations obey the Debye-Hückel approximation of the Maxwell-Boltzmann distribution.

(2) A refined model in which the Debye-Hückel approximation is replaced by the complete exponential function as used in the Gouy-Chapman theory, thus allowing for high surface potentials.

All models with a uniform surface charge involve a difficulty. In addition to contributions from the interaction between different ions, the free energy calculated for such a model contains also contributions deriving from the mutual interaction of different parts of individual ions. Stated otherwise, F_{el} includes the work to assemble the elementary charge on a single smeared out ion in the micelle surface. This amount of work², Δ per micellized soap ion, must be subtracted from the calculated work in order to get the correct value of F_{el} which appears in equation (1). An exact estimation of Δ is difficult. Fortunately, in the application of the theory discussed in the preceding section, only the salt-dependent part of F_{el} enters and the correction Δ may be considered as a part of $W - TS_0$.

THE DEBYE-HÜCKEL MODEL

We consider micelles with radius a , total surface charge ne and surrounded by a double layer of thickness $1/\kappa$ in a medium of dielectric constant ϵ . The Debye-Hückel approximation for the surface potential of the micelles is³

$$\psi_0 = \frac{ne}{\epsilon a(1 + \kappa a)} \quad \dots (3)$$

and the expression for the electrical free energy of the double layer is²

$$nF_{el} = \int_{n=0}^{n=n} \psi_0 e dn = \frac{n^2 e^2}{2\epsilon a(1 + \kappa a)} \quad \dots (4)$$

Remembering the correction Δ , we have

$$F_{el} = \frac{ne^2}{2\epsilon a(1 + \kappa a)} - \Delta \quad \dots (5)$$

Assuming that the micelle radius a varies as $n^{1/3}$, equation (5) gives

$$\frac{d}{dn} (F_{el} + \Delta) = \frac{F_{el} + \Delta}{3n} \cdot \frac{2 + \kappa a}{1 + \kappa a} \quad \dots (6)$$

In *Table I* some experimental results on NaLS micelles in NaCl solutions are recorded as well as data computed with the present model.

We have assumed, quite arbitrarily, that at the c.m.c. $x_n = x_1/50$. For a wide micelle distribution x_n might be considerably lower. However, the results are very insensitive to the value of x_n . Even a 50-fold decrease of x_n would change $W - TS_0 - \Delta$ and $n d(W - TS_0 - \Delta)/dn$ only by

$$kT/n \ln 1/50 \approx -0.04 kT$$

which is insignificant. Furthermore, the term $kT/n \ln f_n$ which is of the order of $10^{-5}kT$ is neglected¹.

The values of $W - TS_0 - \Delta$ in *Table I* increase with n . The values of the slope, however, predict a decrease of $W - TS_0 - \Delta$ with n . In order to make the comparison more quantitative, we have plotted the values of

$$n d\{(W - TS_0 - \Delta)/kT\}/dn \text{ versus } n$$

The function $-12.5 + 0.0889n$ was found to give a good approximation of these values, and leads on integration to

$$(W - TS_0 - \Delta)/kT = -12.5 \ln n + 0.0889n + \text{constant} \quad \dots (7)$$

Table I. Data on Micelles of NaLS in Aqueous NaCl Solutions at 25°C; Debye-Hückel Mode

c_{NaCl} mole/l	c.m.c. (a) m mole/l	n (b)	a (c) Å	κa	$\frac{F_{el} + \Delta}{kT}$ D.H.	$n \frac{d}{dn} \left(\frac{F_{el} + \Delta}{kT} \right)$ (e) D.H.	$\ln x_1$	$\ln f_1$ (f)	$\frac{1}{n} \ln \frac{x_n}{n}$	$\frac{W - TS_0 - \Delta}{kT}$ (g)	$n \frac{d}{dn} \left(\frac{W - TS_0 - \Delta}{kT} \right)$ (h)
0	8.12	80	20	0.570	9.08	4.95	-8.85	-0.09	-0.21	-17.81	-5.16
0.01	5.29	89	20.7	0.808	8.48	4.39	-9.28	-0.12	-0.20	-17.68	-4.58
0.03	3.13	99.5	21.5	1.235	7.38	3.56	-9.80	-0.16	-0.18	-17.16	-3.74
0.05	2.27	104.5	21.9	1.59	6.58	3.04	-10.13	-0.20	-0.18	-16.73	-3.21
0.1	1.46	112	22.4	2.26	5.47	2.38	-10.57	-0.25	-0.17	-16.12	-2.55
0.2	0.924	118.5	22.8	3.22	4.39	1.81	-11.04	-0.30	-0.17	-15.56	-1.97
0.4	0.576	124	23.1	4.63	3.35	1.32	-11.50	-0.35	-0.16	-15.04	-1.47

(a) determined in various ways⁴.(b) from light-scattering data⁶.(c) computed from n using 1.14 gr/cm³ for the micelle density⁶.

(d) from equation (5).

(e) from equation (6).

(f) interpolated from NaCl activity coefficients⁷.

(g) from equation (1).

(h) from equation (2).

In *Figure 1* this function is compared with the data of *Table I*, using 32.11 for the integration constant in (7).

Figure 1 shows clearly that for the present model equations (1) and (2) give results which differ far beyond any experimental errors in the c.m.c. or in the

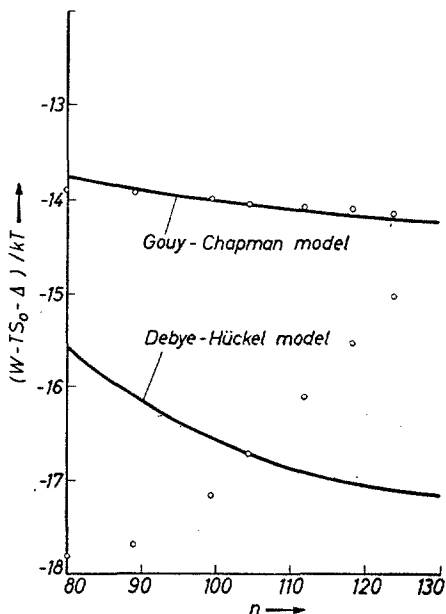


Figure 1. Test of micelle models with equations (1) and (2). Circles: equation (1); solid lines: equation (2)

micelle size. Therefore it must be concluded that the Debye-Hückel model is inadequate to describe the electrical effects in micelle formation.

THE GOUY-CHAPMAN MODEL

No analytical expressions for ψ_0 and F_{el} exist which are valid for high potentials in the electrical double layer around spherical particles. However, Hoskin⁸ has treated this problem for a number of values of ψ_0 and κa with the help of an electronic computer. His results can be used in terms of correction factors to the Debye-Hückel expressions (3) and (4). Since his data are not very numerous, direct interpolation would introduce large errors and therefore we have developed an interpolation procedure, based on transformed correction functions, which ensures an accuracy of 1 or 2 per cent for arbitrary values of ψ_0 and κa . Details are given elsewhere². An extension of this method gives correction factors to equation (5) which are also accurate to a few per cent.

With the above procedure we have obtained corrected values of $F_{el} + \Delta$ and of $n d(F_{el} + \Delta)/dn$ for NaLS micelles based on the experimental data of *Table I*. Further data required in equations (1) and (2) were also taken from *Table I* and the final results are collected in *Table II*.

It appears that the electrical terms are much smaller than found previously. Furthermore, the values of $W - TS_0 - \Delta$ decrease with n as expected. For a quantitative test we approximate

$$n \frac{d}{dn} \left(\frac{W - TS_0 - \Delta}{kT} \right) = -2.323 + 0.0126n \quad \dots (8)$$

Table II. Data on Micelles of NaLS in Aqueous NaCl Solutions at 25°C; Gouy-Chapman Model

c_{NaCl} mole/l	n	$\frac{F_{el} + \Delta}{kT}$	$n \frac{d}{dn} \left(\frac{F_{el} + \Delta}{kT} \right)$	$\frac{W - TS_0 - \Delta}{kT}$	$n \frac{d}{dn} \left(\frac{W - TS_0 - \Delta}{kT} \right)$
0	80	5.17	1.143	-13.90	-1.345
0.01	89	4.73	1.012	-13.93	-1.199
0.03	99.5	4.24	0.891	-14.02	-1.065
0.05	104.5	3.91	0.833	-14.06	-1.002
0.1	112	3.44	0.748	-14.09	-0.911
0.2	118.5	2.95	0.669	-14.12	-0.827
0.4	124	2.48	0.602	-14.17	-0.757

This leads to

$$(W - TS_0 - \Delta)/kT = -2.323 \ln n + 0.0126n + \text{constant} \quad \dots (9)$$

Using -4.58 for the integration constant in (9), the results are compared in *Figure 1* with those of the fifth column of *Table II*. The results are remarkably superior to those of the Debye-Hückel approximation. In fact, the differences between the curves based on equations (1) and (2) are now of the order of the computational errors. The slight difference in slope of the curves might be due to the model, but also to systematic errors in $\ln f_1 x_1$ or in the n values from light scattering. At this stage further improvement of the model seems irrelevant.

THE MICELLE DISTRIBUTION

The results so far obtained with the Gouy-Chapman model are now used to estimate micelle distributions. The essential difficulty here is the extreme sensitivity of the micelle distribution to small variations in $F_{el} + W - TS_0$. According to equation (1) a change of only $0.001kT$ in this term corresponds already to a change of 10 per cent in $f_n x_n$ when $n \sim 100$. The desired accuracy is achieved in the following way.

For $W - TS_0 - \Delta$ the analytical expression (9) is used, which is assumed to be independent of the ionic strength. Analytical expressions for $F_{el} + \Delta$ have been derived from Hoskin's data³ by using interpolation procedures as mentioned in the preceding section. These expressions are:

$$(F_{el} + \Delta)/kT = 1.334 \ln n - 0.00238n - 0.485 \quad \dots (10)$$

in 0.05 M NaCl

$$(F_{el} + \Delta)/kT = 0.906 \ln n - 0.0007n - 0.221$$

These analytical expressions are valid only between $n = 50$ and $n = 130$. Inserting now the expressions (9) and (10) with suitable values for $f_1 x_1$ in equation (1) allows us to determine $f_n x_n$ as a function of n . In the absence of salt we take $\ln f_1 x_1 = -8.791$; for 0.05 M NaCl, $\ln f_1 x_1 = -10.309$. These figures do not correspond exactly to the data of *Table I*, because the smoothed values of $W - TS_0 - \Delta$ (equation (9)) are slightly different from the values in *Table II*.

Figure 2 shows the course of individual terms over a large range of micelle sizes. The dotted lines are estimated extrapolations for small values of n . The

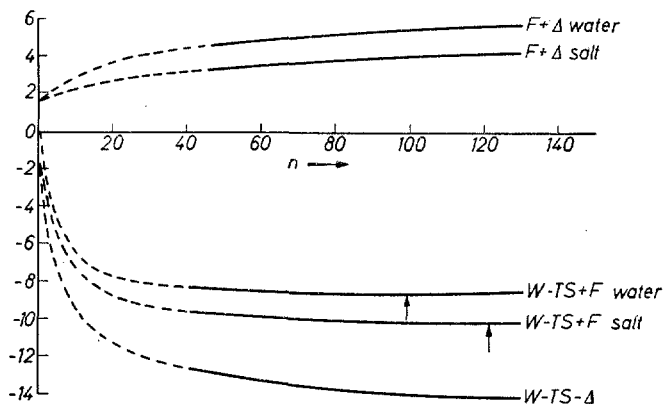


Figure 2. Free energy functions of micelle formation versus micelle size in aqueous NaLS solutions. Arrows indicate minima of total standard free energy.

$$\begin{aligned}
 F + \Delta \text{ water: } (F_{e1} + \Delta)/kT \text{ in water} &= 1.334 \ln n - 0.00238 n - 0.485 \\
 F + \Delta \text{ salt: } (F_{e1} + \Delta)/kT \text{ in } 0.05 \text{ M NaCl} &= 0.906 \ln n - 0.0007 n - 0.221 \\
 W - TS + F \text{ water: } (W - TS_0 + F_{e1})/kT \text{ in water} &= -0.989 \ln n + 0.01022 n - 5.065 \\
 W - TS + F \text{ salt: } (W - TS_0 + F_{e1})/kT \text{ in } 0.05 \text{ M NaCl} &= -1.417 \ln n + 0.0119 n - 4.801 \\
 W - TS - \Delta: (W - TS_0 - \Delta)/kT &= -2.323 \ln n + 0.0126 n - 4.58
 \end{aligned}$$

lower half of Figure 3 shows the relevant part of the $1/n \ln (f_n x_n/n)$ curve on a larger scale. In the top half of Figure 3 micelle distributions are given.

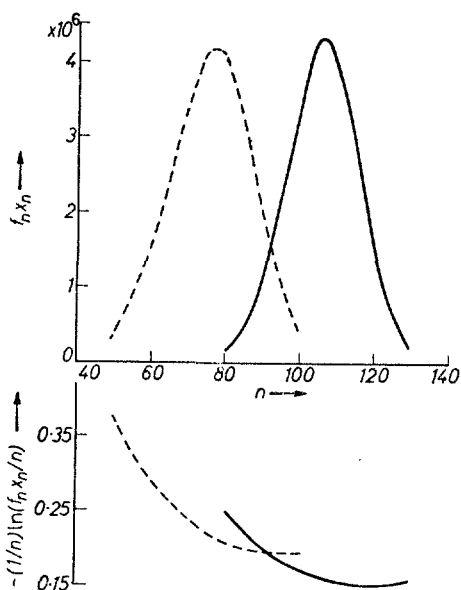


Figure 3. Distributions of NaLS micelles and the corresponding functions $(W - TS_0 + F_{e1})/kT - \ln f_1 x_1 = -1/n \ln (f_n x_n/n)$
 ---: in water;
 —: in 0.05 M NaCl

In both cases the micelle distributions are nearly symmetrical with a half-width of $n \sim 25$.

Further calculations show that an increase of only 0.02 in $\ln f_1 x_1$ increases $f_n x_n$ by a factor of about 10; the shape of the distribution remains virtually the same, while the peak shifts about 2 units toward larger micelle sizes.

It is pointed out that the activity coefficient f_n is nearly independent of micelle size and close to unity for small micelle concentrations¹. Hence the above conclusions hold for the weight distributions of micelles (x_n versus n).

REVIEW

(1) At first sight it seems surprising that the very flat free energy curves of *Figure 2* give rise to the rather sharp micelle distributions of *Figure 3*. This is due, however, to the smallness of the contribution of the micelles to the configurational entropy (the factor $1/n$ in $(kT/n(\ln(f_n x_n/n)))$ which exaggerates the influence of small changes in the standard free energy terms.

It is not easy to estimate the influence of possible errors in the model or in the experimental data on the micelle distribution. However, the slope of the electrical free energy is certainly positive and its order of magnitude correct. The small negative slope of $W - TS_0$ is qualitatively expected and has been quantitatively adjusted so as to lead to average micelle sizes in agreement with the experiments cited in *Table 1*. It follows unequivocally from these assumptions that the micelle distributions are rather narrow and not greatly dependent on detergent concentration.

(2) The correction Δ for the charging of a single ion in the micelle is not known with precision. Still it has been shown² that a reasonable estimate in the present case is $\Delta = 1.7kT$ and that Δ is insensitive to the micelle size. As $W - TS_0 - \Delta \approx -14kT$, this leads to $W - TS_0 \approx -12.3kT$, i.e. an average of $-1.02kT$ per methylene group in the chain. This result compares favourably with estimates from various sources.

(a) Shinoda⁸ finds $-1.07kT$ per methylene group from the change of the c.m.c. with the chain length in a homologous series of soaps under conditions of constant ionic strength.

(b) The solubility of homologous aliphatic compounds into water diminishes to about one third with the addition of each methylene radical. This gives $W - TS_0 \approx -1.08kT$ per methylene group transferred from the aqueous to the oil phase⁸.

The agreement between these data and ours is as good as may be expected.

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