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THE ENERGETICS OF HIGHLY CHARGED SPHERICAL MICELLES AS APPLIED TO SODIUM LAURYL SULPHATE

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The electrical free energy of micelle formation is treated for spherical micelles with a Gouy type double layer, allowing for high surface charge. Use is made of double layer computations carried out by *Hoskin* for spherical particles with high surface potential. A procedure is developed for inter-polating between *Hoskin*'s results. A correction is applied for the difference between the smeared out surface charge as in the model calculations and the actual assembly of discrete charges.

From the equilibrium equation for micellization in which this electrical free energy occurs together with terms depending on the concentrations of free ions and of micelles the non-electrical part of the standard free energy of micelle formation ($W-T\Delta S_o$) can be calculated.

The method is applied to micelles of sodium lauryl sulphate in aqueous sodium chloride solutions. In this system $W-T\Delta S_o$ is found to be 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 water to non-polar surroundings shows excellent agreement.

1. Introduction.

In a previous paper [1]) an equation has been derived for the equi-librium between micelles and single soap ions:

$$\frac{kT}{n} \ln \frac{f_n x_n}{n} - kT \ln f_1 x_1 + F_{el} + W - T\Delta S_o = O \quad \dots \quad (1)$$

n is the number of soap ions per micelle; x_n and x_1 are the concentrations

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[1]) *D. Stigter*, Rec. trav. chim. **73**, 593 (1954).

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 with its atmosphere of counterions is formed from single ions. ΔS_0 is the change of the standard state entropy of a soap ion upon micellization.

Several attempts have been made to evaluate the electrical effects which accompany micelle formation. Such calculations have been carried out for spherical [1]), disc-shaped [2]) [3]) and rod-shaped [4]) micelles. The influence of the counterions has been neglected [2]) or treated in the Debye-Hückel approximation [1]) [3]) [4]).

In this paper a general method is given for deriving F_{el} for spherical micelles, using the unapproximated Poisson-Boltzmann distribution of the counterions.

The theory is applied to micelles of sodium lauryl sulphate in aqueous sodium chloride solutions. For this case the non-electrical part of the standard free energy of micelle formation $W-T\Delta S_0$ is found to be nearly independent of micellar weight.

When preparing this paper we received the thesis of *Prins* [5]) in which the energetics of micelle formation has also been treated and which includes an extensive critical survey of the literature.

2. The charging process.

The equilibrium equation (1) has been obtained [1]) with the aid of an imaginary process in which one micelle with its double layer is formed from single ions, the total work in such a process being equal to zero.

The process was carried ous as follows:

In a solution containing micelles and single ions all species are discharged reversibly. The work connected with the mutual interaction per pair of single ions is

$$-kT \ln f_1 - kT \ln f_1' \quad . \quad . \quad . \quad . \quad . \quad (2)$$

f_1 and f_1' are the activity coefficients of the soap ions and the counterions respectively.

In the uncharged state n single soap ions associate to one micelle.

Finally all micelles and single ions are charged again. Assuming that

[2]) *P. Debije*, Ann. N.Y. Acad. Sci. **51**, 575 (1949).

[3]) *M. E. Hobbs*, J. Phys. & Colloid Chem. **55**, 675 (1951).

[4]) *K. Shinoda* and *K. Kinoshita*, Bull. Chem. Soc. Japan **27**, 73 (1954).

[5]) *W. Prins*, Studies on some long-chain sodium alkyl-1 sulfates, Thesis, Leyden, 1955.

the charge of the micelle is smeared out over its surface the work necessary to charge one micelle and its double layer is found to be [1])

$$nF'_{el} = \int_0^1 \psi'_0 \, \text{ned} \, \lambda + \int_0^1 d \, \lambda \int_{\substack{\text{double} \\ \text{layer}}} \psi' \frac{\varrho'}{\lambda} \, dV . \quad . \quad . \quad . \quad (3)$$

e is the charge of a soap ion; ψ_0' is the surface potential of the micelle; ϱ' is the charge density and ψ' is the electrical potential in the double layer.

When the charging parameter λ increases from 0 to 1, the primed quantities increase from 0 to their final values which will be indicated by unprimed symbols.

The last integral in (3) represents the work required to charge the double layer. In this term one should also account for the Debye-Hückel interaction between the ions in the double layer. This gives rise to a work term similar to $-kT \ln f_1'$ in the discharge step, (see eq. (2)) and of opposite sign. As the ionic concentrations in the double layer are higher than in the bulk of the aqueous solution the interionic effects will be different for the discharge step (in the bulk) and the recharge step (in the double layer). However, it is assumed that this difference is small and may be neglected in the present treatment. Thus only the term $-kT \ln f_1$ relating to the activity correction for the soap ions appears in the equilibrium eq. (1).

A more serious difficulty occurs in the first integral of eq. (3). This term represents the work to charge the micellized soap ions. Obviously one should consider only the interaction effects between the ions. However, in the present model of a micelle with a uniform surface charge the ionic heads of the soap ions are considered to be smeared out and it is impossible to distinguish separate ionic charges. For this reason the first integral in (3) contains also the work connected with the repulsion between various parts of the single ionic charges. Stated otherwise, F_{el}' includes the work to assemble the electronic charge on a smeared-out soap ion. This amount of work, Δ per micellized soap ion, should be subtracted from F_{el}' to give the interaction term F_{el} which figures in the equilibrium equation (1).

There are several ways to approximate this correction. In our micelle model Δ is the work required to charge the 1/nth part of the micelle surface in a reversible manner, the remaining part of the surface being uncharged.

In the trivial case $n = 1$ the ionic charge is smeared out over the whole surface of the sphere, and straightforward calculation gives:

$$\varDelta_1 = \frac{e^2}{2\varepsilon_w a_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where ε_w is the dielectric constant of the surrounding medium, i.e. water, and a_1 is the radius of the sphere.

With this correction $\varDelta_1$ the equilibrium equation (1) is satisfied for $n = 1$, i.e. for the charging cycle of a single soap ion. In this case W and $\varDelta S_0$ vanish since no micelles are formed. Furthermore, $\ln f_n$ vanishes as f_n is related to the effective volume of the micelles and their double layers [1]) which becomes negligibly small for $n = 1$. With $x_n = x_1$, eq. (1) thus reduces to

$$-kT \ln f_1 + F_{e1}' - \varDelta_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The Debye-Hückel expression for the activity coefficient of a single monovalent ion with radius a_1 is [6])

$$\ln f_1 = -\frac{e^2}{2\,\varepsilon_w kT}\,\frac{\varkappa}{1 + \varkappa a_1}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Expression (3) for F_{e1}' has been worked out with the Debye-Hückel approximation [1]). The result reads for $n = 1$

$$F_{e1}' = \frac{e^2}{2\,\varepsilon_w a_1\,(1 + \varkappa a_1)}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

With (6), (7) and (4), equation (5) is satisfied.

In the case of arbitrary n the correction $\varDelta$ is more difficult to evaluate. Only a part of the surface of the sphere is to be charged. Consequently, the electric potential field and hence the work $\varDelta$ depend also on the dielectric properties of the sphere.

For purposes of calculation we consider the area over which the ionic charge e is smeared out as a circular plate with radius r_0 and a charge density σ identical to that of the micelle, i.e. $\sigma = ne/4\pi a^2$ in which a is the micelle radius. Consequently,

$$r_0 = \frac{2a}{\sqrt{n}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

A low estimate of $\varDelta$ is obtained by considering this plate to be completely surrounded by water. Calculation, details of which are given in appendix I, shows the work required to charge this plate reversibly to be

$$\varDelta_{low} = \frac{8}{3\pi}\,\frac{e^2}{\varepsilon_w r_0} = 0.85\,\frac{e^2}{\varepsilon_w r_0} \quad . \quad . \quad . \quad . \quad (9)$$

[6]) See e.g. *H. S. Harned* and *B. B. Owen,* The Physical Chemistry of Electrolytic Solutions, Reinhold, New York, 2nd ed., 1950, p. 38.

A high estimate is obtained by assuming the plate to be situated at the flat interface between water and a medium with a low dielectric constant ε_m. This leads to (see appendix I)

$$\Delta_{\text{high}} = \frac{16}{3\pi} \frac{e^2}{(\varepsilon_w + \varepsilon_m)r_o} = 1.70 \frac{e^2}{(\varepsilon_w + \varepsilon_m)r_o} \quad . \quad . \quad . \quad (10)$$

Considering the facts that the ionic heads of the soap ions project somewhat into the water phase, and that the micelle surface is curved, which both tend to lower the correction term, we consider the following to be a fair estimate of Δ (see appendix I for details)

$$\Delta = 1.1 \frac{e^2}{\varepsilon_w r_o}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

At room temperature this correction is about 1.8 kT.

3. The evaluation of F'_{el}.

As a first step the right hand side of eq. (3) is integrated with respect to the charge parameter λ. This integration may be carried out in a way similar to that used by *Verwey* and *Overbeek* for the flat double layer [7]). The detailed derivation is given in appendix II. The result is

$$\frac{nF_{el}'}{kT} = n\,\Phi_o - \frac{p}{\varkappa^3} \int_{\varkappa a}^{\infty} \left\{ \left(\frac{d\Phi}{dx}\right)^2 + 2\cosh\Phi - 2 \right\} 4\pi x^2 dx \ . \quad . \quad . \quad (12)$$

$$\Phi_o = \frac{e\psi_o}{kT} ; \ \Phi = \frac{e\psi}{kT}$$

a is the radius of the micelle: $\varkappa$ is the reciprocal thickness of the double layer, which for uni-univalent electrolytes is defined with $\varkappa^2 = \dfrac{8\pi pe^2}{\varepsilon\,kT}$. p is the number of ions of either sign per cm³ far from the micelles.

It may be remarked that an equivalent expression for F_{el}' is given by

$$nF_{el}' = \int_{0}^{n} \psi_o'\, edm, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where ψ_o' is the surface potential for a charge me on the surface.

In contradistinction to the charging process considered in eq. (3) where all the ions in the system are charged simultaneously, the integral in eq. (13) has to be calculated as if a single micelle with its gegenions is charged while all the other ions have conserved their normal charge.

[7]) *E. J. W. Verwey* and *J. Th. G. Overbeek*, Theory of the Stability of Lyophobic Colloids, Elsevier Pub. Cy., Amsterdam, 1948, p. 78.

Expression (13) may be transformed by integration by parts into:

$$\mathfrak{n} \, F_{el}' = \mathfrak{n} e \, \Psi_o - \int_o^{\Psi_o} emd \, \Psi_o' \cdot \quad \ldots \ldots \ldots \quad (14)$$

The integral in (14) which is equal to $pkT/\varkappa^3$ times the integral in (12) can be considered as the total free energy (electrical + chemical parts) of a double layer system of the conventional, potential determining ion type and as such has been tabulated by *Hoskin* [8]).

The free energy in eq. (12) is given in terms of n, Φ_0, $\varkappa$ and a. The data available for micelles are n, $\varkappa$ and a (see sec. 4) but not the surface potential ψ_0. The double layer theory leads, however, to a relation between n, Φ_0, $\varkappa$ and a. For a Gouy-Chapman type double layer around a sphere this relation has been tabulated by *Hoskin* [8]), who used an electronic computer to solve the Poisson-Boltzmann equation for the high charge densities and potentials with which we are concerned. As mentioned above, *Hoskin* [8]) also has given values for the total free energy of a spherical double layer, which allows us to calculate the integral in (12).

Hoskin has cast his results in the form of correction factors to the Debye-Hückel approximation. For the surface charge density, which is proportional to the normal derivative of the potential at the surface, he writes

$$\text{Debye-Hückel approximation} \left(\frac{d\Phi}{dx} \right)_{x=\varkappa a}^{D.H.} = - \frac{1 + \varkappa a}{\varkappa a} \varphi_o$$

$$\text{exact expression} \left(\frac{d\Phi}{dx} \right)_{x=\varkappa a}^{exact} = - \frac{1 + \varkappa a}{\varkappa a} \Phi_o \beta \, . \quad (15)$$

The coordinate x is $\varkappa$ times the distance r from the centre of the sphere. Similarly, the total free energy in the Debye-Hückel approximation is

$$F_{tot}^{D.H.} = - \frac{4\pi pkT}{\varkappa^3} \varkappa a \, (1 + \varkappa a) \, \Phi_o^2$$

The exact expression becomes $F_{tot}^{exact} = - \dfrac{4\pi pkT}{\varkappa^3} \varkappa a \, (1 + \varkappa a) \, \Phi_o^2 \alpha$ (16)

The factors α and β have been tabulated [8]) for a number of values of Φ_0 and $\varkappa a$.

It follows from Gauss' theorem that

$$ne = - \varepsilon a^2 \left(\frac{d\psi}{dr} \right)_{r=a} = - \frac{\varepsilon \, a^2 kT \varkappa}{e} \left(\frac{d\Phi}{dx} \right)_{x=\varkappa a} \quad \ldots \quad (17)$$

ε is the dielectric constant of the solution.

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[8]) *N. E. Hoskin*, Trans. Faraday Soc. **49**, 1471 (1953).

Elimination of $d\Phi/dx$ between (15) and (17) leads to

$$\Phi_0\beta = \frac{ne^2}{\varepsilon\, akT(1 + xa)} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (18)$$

Rewriting eq. (12) in terms of α and β, we find, remembering that $-pkT/x^3$ times the integral in (12) is equal to F as defined in (16):

$$\frac{n\, F_{el}'}{kT} = \frac{n^2 e^2}{2\,\varepsilon\, akT(1 + xa)}\frac{2\beta - \alpha}{\beta^2} = \frac{n^2 e^2}{2\,\varepsilon\, akT(1 + xa)}\frac{1}{\delta} \cdot \quad \cdot \quad (19)$$

Table I shows the values of $\delta = \beta^2/(2\beta - \alpha)$ calculated from *Hoskin's* data for α and β.

<center>Table I.</center>

<center>Values of the correction factor for the free energy of micelle formation F_{el}'.</center>

$$\delta = \frac{1}{F_{el}'}\frac{ne^2}{2\,\varepsilon\, a(1 + xa)}$$

$a x$ \ Φ_0	1	2	4	6	8
0	1	1	1	1	1
1	1.007	1.032	1.163	1.553	2.555
3	1.014	1.059	1.302	1.970	3.568
5	1.016	1.070	1.357	2.114	3.905
15	1.019	1.084	1.425	2.298	4.551
∞	1.0214	1.0924	1.4643	2.3911	4.4944

The right hand side of eq. (18) can be calculated directly from the available data on micellar size, assuming that the number of elementary charges is equal to that of detergent ions in the micelle. $\Phi_0\beta$ is hence known. *Hoskin's* data on β as a function of Φ_0 and xa are used to estimate the values of β and Φ_0 separately. For the value of Φ_0 found in this way δ is estimated from table I, thus giving us all the data necessary to calculate F_{el}'/kT.

In practice this method presents the difficulty that *Hoskin's* data are not numerous enough (only 4 values of xa and 5 values of Φ_0) to allow easy interpolation and for values of $xa < 1$ extrapolation is even necessary.

So long as more extended data are not available, the following procedure gives acceptable results (Cf. [9]).

First calculate values of β and δ for $xa = \infty$. The theory for the flat Gouy double layer shows that

$$\beta_{xa=\infty} = \frac{2}{\Phi_0}\sinh(\Phi_0/2) = \beta_f \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (20)$$

$$\alpha_{\varkappa a = \infty} = \frac{2\cosh(\Phi_o/2) - 2}{(\Phi_o/2)^2} = \alpha_f \cdot \quad . \quad . \quad . \quad . \quad (21)$$

Consequently, as $\delta = \dfrac{\beta^2}{2\,\beta - \alpha}$,

$$\delta_{\varkappa a = \infty} = \frac{\sinh^2(\Phi_o/2)}{\Phi_o \sinh(\Phi_o/2) + 2 - 2\cosh(\Phi_o/2)} = \delta_f \quad . \quad . \quad (22)$$

The values for δ_f have also been inserted in table I.

Now $(\beta - 1)/(\beta_f - 1) = D_Q$ and $(\delta - 1)/(\delta_f - 1) = D_F$ have been plotted against log $\varkappa a$ in figs. 1 and 2.

The interpolation functions, D, vary only slightly with Φ_o, which facilitates interpolation. To extrapolate the functions D_Q and D_F below $\varkappa a = 1$, use is made of an analytical expression for the limiting value of D_Q for small Φ_o derived in an earlier paper [9]), to which the curves for higher Φ_o are nearly parallel in the region around $\varkappa a = 1$.

Moreover *Hoskin* [8]) has shown that good approximations for β can be calculated from a series expansion proposed by *Levine* [10]). This series leads to values for β which are very good for $\Phi_o = 1$ and $\Phi_o = 2$ and which are about 1 %, about 6 % and about 16.5 % too low for $\Phi_o = 4$, 6 and 8 respectively. We have also used this expansion with the correction factors found for $\varkappa a = 1$ to extend the β values to about $\varkappa a = 0.5$. The results agree with those obtained by graphical extrapolation of the D_Q – log $\varkappa a$ curves.

As the D_F curves are nearly coincident with those for D_Q extrapolation of D_F below $\varkappa a = 1$ has been based on the corresponding D_Q curves.

It is noted that in figs. 1 and 2 the points for $\Phi_o = 8$, $\varkappa a = 15$ are definitely too high. This must be due to errors in *Hoskin's* values for α and β which both seem to be too high.

The procedure for evaluation of F_{el}' can now be summarized as follows:

Calculate $\Phi_o\beta$ according to eq. (18) from the available data. Read off D_Q and D_F for round values of Φ_o and the relevant values of $\varkappa a$ from figs. 1 and 2. Make linear plots of D_Q against Φ_o for these values of $\varkappa a$ and determine, by trial and error in these plots, sets of values of Φ_0 and D_Q, such that

$$\Phi_o\beta = \Phi_o D_Q(\beta_f - 1) + 1 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

is equal to the experimental value of $\Phi_0\beta$. Use the value of Φ_0 so found to interpolate the value of D_F in a linear plot of D_F against Φ_0 (at

[9]) *D. Stigter* and *K. J. Mysels*, J. Phys. Chem. **59**, 45 (1955).
[10]) *S. Levine*, J. Chem. Phys. **7**, 831 (1939).
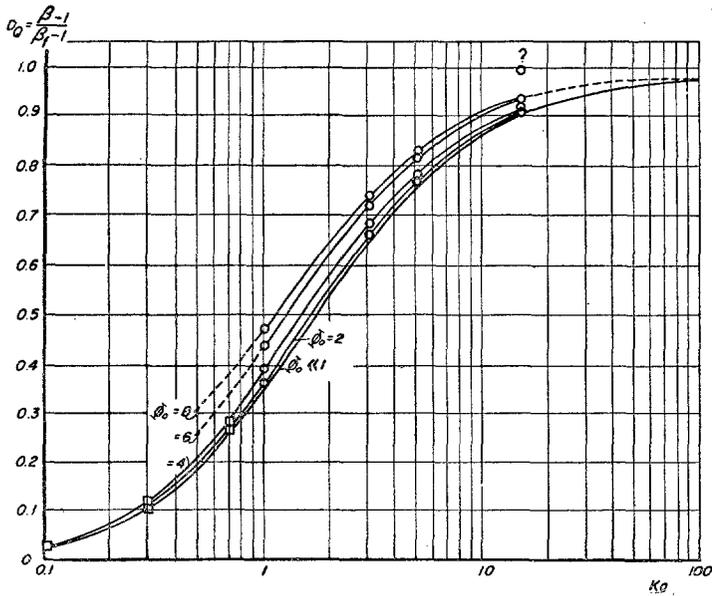
Fig. 1. Interpolation function for the charge-potential relation. Circles based on *Hoskin's* computation, squares on an expansion [9].
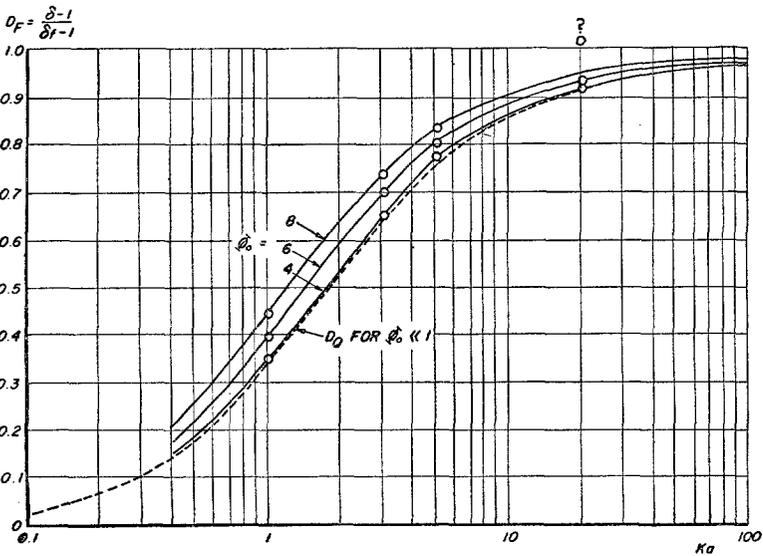
Fig. 2. Interpolation function for the electric free energy of micelle formation F_{el}'. Circles based on *Hoskin's* computations. Broken line is D_Q for $\Phi_0 \langle\langle 1$.

constant $\varkappa a$) and calculate δ from D_F. With δ calculate F_{el}' according to eq. (19).

An alternative procedure for finding Φ_0 is to plot log $\Phi_0\beta$ against Φ_0 (for the relevant values of $\varkappa a$) and read off Φ_0 from this plot at the experimental value for $\Phi_0\beta$.

The estimated accuracy of the whole procedure is better than 1 % both in Φ_0 and in F_{el}'.

4. Application to micelles of sodium lauryl sulphate.

The behaviour of micelles of sodium lauryl sulphate (NaLS) in aqueous sodium chloride solutions has been studied extensively by *Mysels* et al. Some of their results are presented in columns 1–3 of table II. The c.m.c. has been determined in various ways [11]) and n has been obtained from data on light-scattering [12]). The micelle radii a have been computed from n, using 1.14 for the micelle density [13]). For the evaluation of $\varkappa$ the ionic strength has been assumed equal to $c_{NaCl} +$ c.m.c.

From the data on n, a and $\varkappa a$ the quantities Φ_0 and F_{el}'/kT are computed as outlined in the preceding section. For comparison table II also presents the data obtained with the relevant Debye-Hückel expressions. The results show clearly that the corrections to the Debye-Hückel approximation are important.

The correction to the smeared-out Gouy model calculated with eq.

Table II.

Data on micelles of NaLS in aqueous NaCl solutions at 25° C.

c_{NaCl} mol/l	c.m.c. mmol/l	n	a $\overset{o}{A}$	$\varkappa a$	Φ_0		F_{el}'/kT		$\frac{1}{kT}(F_{el}' - F_{el}) = \frac{1.1 \, e^2}{\varepsilon_w r_0 \, kT}$
					Gouy	D.H.	*Gouy*	D.H.	
0	8.1_2	80	20	0.57_0	7.4_2	18.1_7	5.1_7	9.0_8	1.76
0.01	5.2_9	89	20_7	0.80_8	6.9_7	16.9_6	4.7_3	8.4_8	1.79
0.03	3.1_3	99_5	21_5	1.23_5	6.3_0	$14\,7_6$	4.2_4	7.3_8	1.82
0.05	2.2_7	104_5	21_9	1.59	5.8_8	13.1_7	3.9_1	6.5_7	1.83
0.1	1.4_6	112	22_4	2.26	5.3_0	10.9_4	3.4_4	5.4_7	1.86
0.2	0.92_4	118_5	22_8	3.22	4.7_2	8.7_7	2.9_5	4.3_9	1.87
0.4	0.57_6	124	23_1	4.63	4.0_9	6.7_9	2.4_8	3.3_5	1.89

[11]) R. J. *Williams*, J. N. *Phillips* and K. J. *Mysels,* Trans. Faraday Soc. **51,** 728 (1955).

[12]) J. N. *Phillips* and K. J. *Mysels,* J. Phys. Chem. **59,** 325 (1955).

[13]) D. *Stigter,* R. J. *Williams* and K. J. *Mysels,* J. Phys. Chem. **59,** 330 (1955).

(11), sec. 2, is given in the last column of table II. This correction, though quite large, is fairly insensitive to the micelle size as it varies only proportional to the sixth root of n.

The information on F_{el} enables us to evaluate the non-electrical part of the standard free energy of micelle formation, $W-T\Delta S_0$, by means of the equilibrium equation.

To this end it is assumed that at the c.m.c. 2 % of the soap is micellized. This corresponds roughly with the operational definition of the c.m.c. by *Mysels* et al.[11]). Furthermore, values of ln f_1 are interpolated from tables of NaCl activities[14]) and the term $1/n$ ln f_n, which is of the order of 10^{-5} [1]), is neglected.

The criticism of *Prins*[5]) against our calculation of f_n [1]) does not affect its order of magnitude and need, therefore, not be considered here.

Using the Gouy values for F_{el}' from table II, with the relevant correction, F_{el} is obtained and $W-T\Delta S_0$ is found with the equilibrium eq. (1). The results are collected in table III as a function of NaCl concentration.

Table III.

The terms of the equilibrium equation (1) for NaLS micelles.

c_{NaCl} mol/l	$\dfrac{1}{n}\ln\dfrac{x_n}{n}$	$\ln x_1$	$\ln f_1$	F_{el}/kT	$(W-T\Delta S)/kT$
0	—0.21	—8.85	—0.09	3.4_1	$—12._{14}$
0.01	—0.20	—9.28	—0.12	2.9_4	$—12._{14}$
0.03	—0.18	—9.80	—0.16	2.4_2	$—12._{20}$
0.05	—0.18	—10.13	—0.20	2.0_8	$—12._{23}$
0.1	—0.17	—10.57	—0.25	1.5_8	$—12._{23}$
0.2	—0.17	—11.04	—0.30	1.0_8	$—12._{25}$
0.4	—0.16	—11.50	—0.35	0.5_9	$—12._{28}$

5. Discussion.

1. In the analysis of NaLS micelles we have used micellar weights derived from data on light-scattering and we have assumed uniformity of micelles.

However, it is anticipated that one always deals with a distribution of micelle sizes. In fact, light-scattering determines only the average by weight of this distribution.

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[14]) *H. S. Harned* and *B. B. Owen*, The Psysical Chemistry of Electrolytic Solutions, Reinhold, New York, 2nd ed., 1950, p. 360, 362.

The analysis of conductivity data [15]) suggests that the average size of NaLS micelles in water does not change appreciably with the concentration of NaLS. It was concluded previously [15]) that this indicates a narrow distribution of micelle sizes. However, *Lamm* [16]) has derived how, in the case of a Gaussian size distribution, the change of the average size with concentration depends on the width of the distribution and on the average size. It follows from *Lamm*'s formula that, for large micelles such as found in NaLS solutions, the size distribution may be wide even though the change of average size with concentration is very small.

Since the size distribution of micelles in NaLS solutions is virtually unknown, the question arises what error might result from the approximation of uniform micelles.

Eq. (1) is valid for any micelle size in the mixture provided we insert for x_n the mole fraction of soap micellized in the micelle size under consideration, instead of the total mole fraction of micellized soap. The assumption that the size distribution is extremely wide and flat and that only 1/50 of the micellized soap occurs in the micelles of the size given by light-scattering, would imply a change of only $\dfrac{kT}{n} \ln \dfrac{1}{50} \sim -0.04\ kT$ in the first term of eq. (1), which is clearly insignificant.

An erroneous value for n affects the final results only through its influence on F_{el} as the term $kT/n \ln n$ in eq. (1) is in any case small.
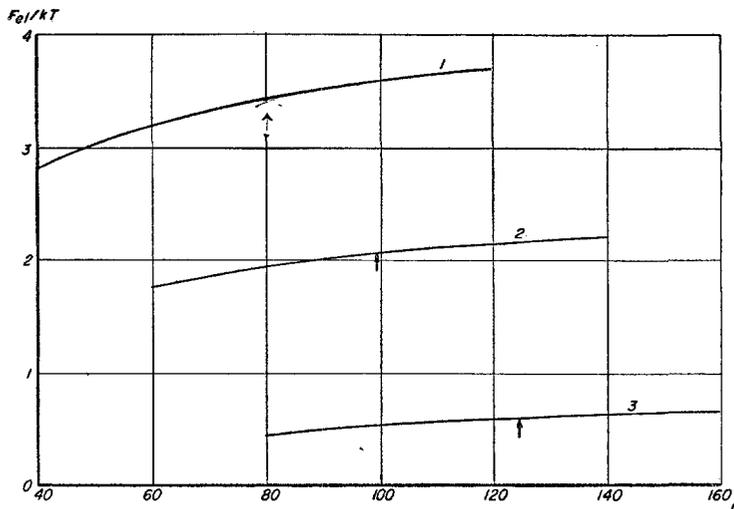
Fig. 3. The electrical free energy of formation of NaLS micelles as a function of association number in solutions of ionic strength 0.00812 (curve 1, $c_{NaCl} = 0$), 0.052 (curve 2, $c_{NaCl} = 0.05$ mol/l) and 0.4 (curve 3, $c_{NaCl} = 0.4$ mol/). Arrows indicate micelle size derived from light-scattering, table II.

15) *D. Stigter*, Rec. trav. chim. **73**, 611 (1954).

16) *O. Lamm*, Arkiv Kemi Mineral Geol. **18 A**, No. 9 (1944).

Fig. 3 shows F_{el}/kT as a function of micelle size for three solutions of different ionic strength. It appears that the variation of F_{el} with n is fairly small, in particular in the case of high ionic strength.

Consequently, even somewhat serious shortcomings in the inter-pretation of the light-scattering results would not introduce an error larger than, say, $1/2\ kT$ in the computed value of $W-T\Delta S_o$.

2. From a physical point of view the present micelle model has four obvious shortcomings:

a) For $n > 100$ the NaLS micelle cannot be spherical. It must be at least slightly ellipsoidal. Now it was shown above that the effect of micelle size on F_{el} is small. It is expected that F_{el} is even less sensitive to the micelle shape, in particular in solutions of high ionic strength where the large micelles are found.

b) The dimensions of the counterions are neglected. An inclusion of these effects would give rise to a more extended double layer, which leads to higher values of F_{el}.

c) The possible penetration of the counterions into the rough micelle surface [9]) is disregarded. By taking such a penetration into account lower values of F_{el} would be obtained.

Effects b) and c) are presumably relatively large and are not easy to estimate, but they may compensate for each other to a large extent. *Davies* and *Rideal* [17]), experimenting with soap films adsorbed at water/air and water/oil interfaces, concluded that even up to a relatively high compression of the film, where the packing density was of the same order as that in micelles, the simple Gouy treatment gives a satisfactory description of the experiments, so that effects b) and c) must largely cancel.

d) The fact that the surface charge is composed of individual ions has been taken into account in the correction term Δ discussed in sec. 2. Even with this correction the concept is unrealistic in so far as the surface charge is considered to be built up from disc-shaped ions, instead of from more or less spherical ones. By comparing the work necessary to assemble certain arrangements (e.g., a square lattice) of flat, smeared-out ions with a similar assembly of point charges, it was found that the form of the ion affects the final result only to an extent comparable with the uncertainty of 10 to 20 % that in any case exists in Δ. In view of our restricted knowledge of the actual topography of the interfacial area it was not thought worth while to pursue this matter further.

[17]) *J. T. Davies* and Sir *Eric Rideal*, J. Colloid Sci. suppl. **1**, 1 (1954).

3. a) According to table III, $W-T\Delta S_0$ is about -12.2 kT per NaLS molecule. This amounts to an average of -1.02 kT per methylene group. It is interesting to compare this value with results from different sources.

b) *Shinoda* [18]) points out that the solubilities of homologous aliphatic compounds into water diminish to about $1/3$ with the addition of each methylene radical. This gives $W-T\Delta S_0 = -1.08$ kT per methylene group transferred from the aqueous to the oil phase.

c) From the change of c.m.c. with the chain length of the soap ion, under condition of constant ionic strength, *Shinoda* [18]) finds $W-T\Delta S_0 = -1.07$ kT per methylene group.

The comparison of these values neglects the difference between a methyl and a methylene group (a), the activity coefficient of the un-associated soap (b) and the dependence of $W-T\Delta S_0$ on the micellar weight (c). However, these are all second order corrections (see also 1. above) and the agreement is as good as may be expected.

In particular, the fact that differential values $b)$ and $c)$ agree with the integral value $a)$ for $W-T\Delta S_0$ is noteworthy. In the evaluation of F_{el} we have neglected changes of hydration energy on an ion entering the micelle and of a counterion approaching the micelle surface. Hence, the possible changes of hydration energy are incorporated in our values of $W-T\Delta S_0$.

Shinoda's values, on the other hand, measure the change due to extension of the hydrocarbon chain in homologous series. Therefore, hydration effects cancel in his considerations. The mutual agreement between the results for $W-T\Delta S_0$ suggests forcibly that in micelle formation the changes of the free energy of hydration of the ions are small.

4. As discussed in point 1, one always deals with a distribution of micelle sizes. Such a distribution can be described with a set of equations (1) in which x_n, F_{el}, W and ΔS_0 are functions of n.

The activity coefficient of the micelles, f_n, is related to the volume fraction of the solution which is effectively occupied by the micelles and their double layers [1]). Thus, f_n is virtually the same for all micelles.

The change of $W-T\Delta S_0$ with n is obtained by differentiating both sides of eq. (1) with respect to n. After rearrangement, this gives

$$\frac{d}{dn}\left(\frac{W-T\Delta S}{kT}\right) = -\frac{d}{dn}\left(\frac{F_{el}}{kT}\right) + \frac{1}{n^2}\left(1 + \ln\frac{f_n x_n}{n}\right) - \frac{1}{n}\frac{d}{dn}(\ln f_n x_n) \quad (24)$$

The first and second term in the right-hand side of (24) are always negative. The sign of the last term depends on n and on the type of

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[18]) *K. Shinoda*, Bull. Chem. Soc. Japan 26, 101 (1953).

distribution. Suppose we deal with a weight distribution of micelles which has a maximum at, say, $n = n_0$. Then

$$- \frac{1}{n} \frac{d}{dn} (\ln f_n x_n) \leq 0 \text{ for } n \leq n_0. \text{ Consequently, } \frac{d}{dn} \left(\frac{W - T \Delta S_0}{kT} \right) < 0,$$

certainly for $n < n_0$.

There is sound evidence that the distribution of NaLS micelles in water and in NaCl solutions actually has a maximum. The average sizes found by light-scattering and by self diffusion are in fair agreement [13]. Moreover, only one fairly sharp peak is observed in the sedimentation diagram [19]. This suggests that the size spread is not too large and that the maximum in the distribution is near the average size obtained from light-scattering. Accepting these arguments, eq. (24) proves that $W - T \Delta S_0$ decreases steadily with n in the range under investigation. Actually this is in accordance with the calculated $W - T \Delta S_0$ values of table III.

Going one step further, eq. (24) can be used as a quantitative check on our set of $W - T \Delta S_0$ values. Let us suppose that $\frac{1}{n} \frac{d}{dn} (\ln f_n x_n)$ is negligibly small for the weight average size determined by light-scattering. It follows from fig. 3 that $- \frac{d}{dn} \left(\frac{F_{el}}{kT} \right)$ is, say, -0.01 (in water) to -0.002 (in 0.4 M NaCl). Furthermore, the figures of table III give a value of about -0.0025 (in water) to -0.0012 (in 0.4 M NaCl) for the term $\frac{1}{n^2} \left(1 + \ln \frac{x_n}{n} \right)$. Thus $\frac{d}{dn} \left(\frac{W - T \Delta S_0}{kT} \right)$ is found to vary from -0.012 at $n = 80$ (in water) to -0.004 at $n = 124$ (in 0.4 M NaCl).

Assuming a fairly wide micelle distribution, the activity $f_n x_n$ of the micelles may be, say, 50 times smaller than the x_n value used in the above estimate. This would add a term $1/n^2 \ln 1/50 \approx -4 \cdot 10^{-4}$ to the calculated slope.

It can be seen from table II and III that $W - T \Delta S_0$ decreases by 0.14 kT when n increases from 80 to 124. The experimental value of $\frac{d}{dn} \left(\frac{W - T \Delta S_0}{kT} \right)$ is, therefore, $-0.14/44 = -0.003_2$ in fair agreement with the calculated values given above. Of course it should be realized that the small difference in $W - T \Delta S_0$ taken from table III contain all kinds of errors. Nevertheless, the internal consistency of the results is a support for the present approach.

In principle it should be possible to calculate the size distribution of

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[19] *H. Reerink*, private communication.

micelles, using a smoother $W-T\Delta S_0$ vs. n curve derived from table III and F_{el} vs. n data as given in fig. 3. Unfortunately, the computation of F_{el} is not accurate enough for this rigorous application of the theory.

It is interesting to compare eq. (24) with the starting point of *Debye*'s micelle theory [2]), that has also been used by *Hobbs* [3]) and *Shinoda* [4]). *Debye* has omitted the term $\dfrac{1}{n^2}\left(1 + \ln\dfrac{f_n x_n}{n}\right)$ in the condition of optimum micelle size when supposedly the last term $\dfrac{1}{n}\dfrac{d}{dn}(\ln f_n x_n)$ vanishes. In view of the above figures for NaLS micelles it seems that all but the last term in eq. (24) are of the same order of magnitude and should be retained in any refined theory.

5. *Phillips* [20]) has evaluated $W-T\Delta S_0 = \Delta G^0$ from the c.m.c., the association number n and the effective charge of the micelle. He accounts for the interaction between micelles and counterions by assuming that n–p counterions are associated with the micelle, the remaining p counterions being completely free. With $p/n \approx 0.15$ as derived from the non-ideality of light-scattering, the law of mass action gives $\Delta G^0 = -15.9$ kT for NaLS micellles. This differs by about 3.7 kT from our values in table III. On the other hand, substitution of $p/n \approx 0.5$ into *Phillips'* equation gives ΔG^0 values which agree with our results. This may demonstrate that in *Phillips'* semi-empirical method the essential question is how to define the association between micelles and counterions. Obviously, widely different association factors have to be assumed to explain the non-ideality of light-scattering and the free energy of micellization. This fact removes much of the value of these factors. A similar criticism, more especially directed against the use of the law of mass action by *Phillips,* has been brought forward by *Prins* [5]).

6. It is interesting to compare the potential at the micelle surface, ψ_0, als calculated above with the ζ potential derived from micelle electrophoresis [9]). In fig. 4 these quantities are plotted for NaLS micelles. One finds the approximate relation $\zeta = 0.51\ \psi_0$ in solutions up to 0.1 molar NaCl.

Davies and *Rideal* [17]) obtain $\zeta \approx 0.55\ \psi_0$ for monolayers of cetyltrimethylammonium ions spread at a water/oil interface. The agreement with our result again points to the marked similarities between micelles and monolayers.

Amsterdam, April 1956.

[20]) *J. N. Phillips,* Trans. Faraday Soc. **51**, 561 (1955).
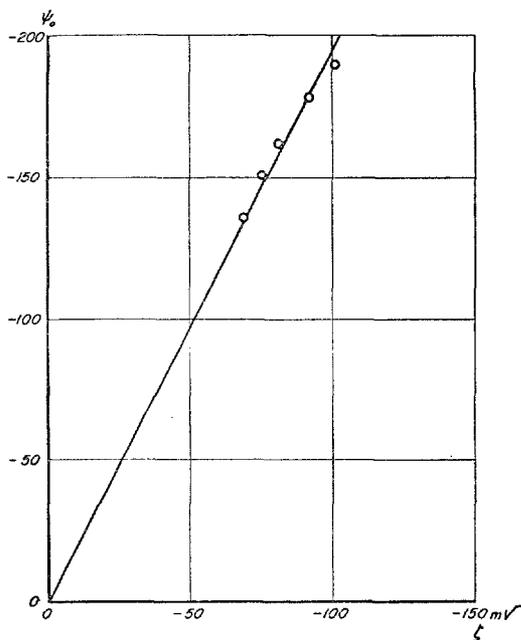
Fig. 4. Relation between $\psi_0 = \dfrac{kT}{e}\, \Phi_0$ and ζ for NaLS micelles. Φ_0 values according to data from table II. ζ from micelle mobilities determined with dye-tracer electrophoresis [9]). Straight line $\zeta = 0.51\ \psi_0$.

Appendix I.

The free energy of charging of individual ions constituting the surface charge

Let us consider two media with dielectric constants ε_w and ε_m separated by a flat interface. A point charge Q at a distance s from the interface leads to a potential field in medium I that can be described by the introduction of a virtual charge Q' in B, the mirror point of A, with

$$Q' = \frac{\varepsilon_w - \varepsilon_m}{\varepsilon_w + \varepsilon_m}\, Q. \text{ See fig. 5.}$$

The potential in medium I is given by

$$\psi_{\mathrm{I}} = \frac{Q}{\varepsilon_w r_A} + \frac{\varepsilon_w - \varepsilon_m}{\varepsilon_w + \varepsilon_m}\, \frac{Q}{\varepsilon_w r_B}$$

r_A and r_B are the distances from A and B respectively. The field in II is described with an imaginary charge $\dfrac{2\,\varepsilon_m}{\varepsilon_w + \varepsilon_m}\, Q$ in A:
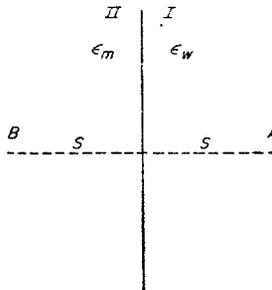
Fig. 5.

$$\psi_{II} = \frac{2Q}{(\varepsilon_w + \varepsilon_m)r_A}$$

It follows from these expressions for ψ_I and ψ_{II} that the potential at a distance r from a point charge Q *in* the interface between I and II is

$$\psi_I = \psi_{II} = \frac{2Q}{(\varepsilon_w + \varepsilon_m)r}$$

We shall now consider a circular plate with radius c, surface charge density $\sigma = e/\pi r_0^2$ and located in the interface between I and II, see figs. 5 and 6. The potential at the rim of the plate is
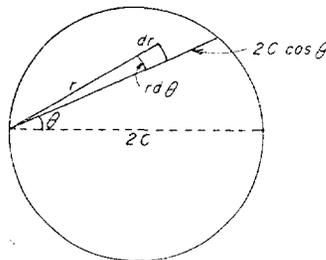
Fig. 6.

$$\psi_P = 2\int_0^{\pi/2} d\Theta \int_0^{2c \cos \Theta} \frac{2\sigma}{\varepsilon_w + \varepsilon_m} dr = \frac{8\sigma c}{\varepsilon_w + \varepsilon_m}.$$

The work necessary to add a ring of width dc and charge density σ to the plate is $\psi_P \sigma 2\pi c\, dc$. The total work Δ_{high} to charge a plate with radius r_0 is obtained by integrating with respect to c from 0 to r_0. The result is

$$\Delta_{high} = \frac{16}{3\pi} \frac{e^2}{(\varepsilon_w + \varepsilon_m)r_0} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (10)$$

Actually, the ionic charges at the micelle surface will not be situated exactly at the interface. It may be assumed that the ionic heads project into the water. Therefore, the influence of the hydrocarbon part of the micelle, with $\varepsilon_m = 4$, can be expected to be less than expressed by eq. (10). A low estimate of $\varDelta$ is obtained when this influence is neglected completely, i.e. when we put $\varepsilon_w = \varepsilon_m = 78$ in eq. (10):

$$\varDelta_{low} = \frac{8}{3\pi} \frac{e^2}{\varepsilon_w r_o} \qquad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (9)$$

This value is nearly 50 % smaller than $\varDelta_{high}$. The correct value must be expected to lie between $\varDelta_{low}$ and $\varDelta_{high}$. A fair estimate is obtained when the smeared-out soap ion is put in the water phase at a small distance s from the hydrocarbon/water interface.

By analogy with the case of fig. 5, the electric field is described with the aid of the real charge with density σ in plane A and an imaginary

charge with density $\sigma' = \dfrac{\varepsilon_w - \varepsilon_m}{\varepsilon_w + \varepsilon_m} \sigma$ in the mirror plane B at distance 2s

from A (see fig. 7). The calculation of the potential ψ_P at the rim of the
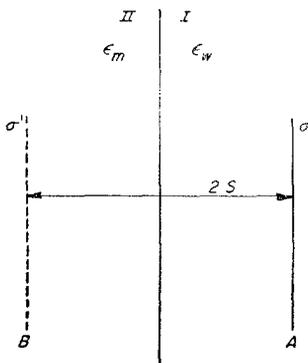
Fig. 7.

plate A with radius c is the same as in the case of fig. 6, provided that
$\dfrac{2\sigma}{(\varepsilon_w + \varepsilon_m)r}$ is replaced by

$$\frac{\sigma}{\varepsilon_w r} + \frac{\sigma'}{\varepsilon_w \sqrt{4s^2 + r^2}} \cdot$$

In this case we obtain

$$\psi_P = \frac{4\sigma c}{\varepsilon_w} + \frac{4\sigma'}{\varepsilon_w} \int_0^{\pi/2} \sqrt{s^2 + c^2 \cos^2 \Theta} \, d\,\Theta - \frac{2\pi s \sigma'}{\varepsilon_w}$$

The work required to charge plate A with radius r_0 is

$$\varDelta = \int\limits_0^{r_0} \psi_P\, \sigma\, 2\pi c\, dc = \frac{8\pi\sigma^2\, r_0^3}{3\varepsilon_w} - \frac{2\pi^2\sigma\sigma'\, s\, r_0^2}{\varepsilon_w} +$$

$$+ \frac{8\pi\sigma\sigma'\, s^3}{3\varepsilon_w} \int\limits_0^{\pi/2} \frac{1}{\cos^2\Theta} \left\{ \left(1 + \frac{r_0^2}{s^2}\cos^2\Theta\right)^{3/2} - 1 \right\} d\Theta$$

After partial integration $\varDelta$ can be expressed in terms of complete elliptic integrals which are tabulated [21]:

$$\varDelta = \frac{8e^2}{3\pi\,\varepsilon_w r_0} \left\{ 1 + \frac{\varepsilon_w - \varepsilon_m}{\varepsilon_w + \varepsilon_m}\, f\left(\frac{s}{r_0}\right) \right\}$$

with $f\left(\dfrac{s}{r_0}\right) = \dfrac{1-k^2}{k^3} \int\limits_0^{\pi/2} \dfrac{d\Theta}{\sqrt{1-k^2\sin^2\Theta}} + \dfrac{2k^2-1}{k^3} \int\limits_0^{\pi/2} \sqrt{1-k^2\sin^2\Theta}\, d\Theta -$

$$\frac{3}{4}\frac{\pi}{k}\sqrt{1-k^2}.$$

$$k^2 = \frac{r_0^2}{s^2 + r_0^2}\,.$$

Some values of $f(s/r_0)$ are given in the table below.

$\dfrac{s}{r_0}$	0	0.1	0.3	0.5	0.7	1	∞
$f\left(\dfrac{s}{r_0}\right)$	1	0.812	0.580	0.441	0.351	0.266	0

In practical cases we have $r_0 \approx 4.5$ Å and, say, $s = 2$ Å, which leads to $\varDelta = 1.20\, e^2/\varepsilon_w r_0$. Considering, furthermore, that the curvature of the micelle surface tends to lower $\varDelta$, a reasonable approximation of $\varDelta$ is assumed to be

$$\varDelta = 1.1\, \frac{e^2}{\varepsilon_w r_0}\,. \qquad \qquad \qquad (11)$$

Appendix II.
The integration of (3) for the Gouy-model.

For a spherical micelle with radius a eq. (3) becomes

$$F_{el}' = e\underbrace{\int\limits_0^1 \psi_0'\, d\lambda}_{I_1} + \frac{1}{n}\underbrace{\int\limits_{r=a}^{\infty}\int\limits_{\lambda=0}^1 \frac{\varrho'\psi'}{\lambda}\, d\lambda\, 4\pi r^2\, dr}_{I_2}$$

[21] P. F. Byrd and M. D. Friedman, Handbook of elliptic integrals for engineers and physicists, Springer, Berlin, 1954, p. 193.

With the substitutions $\varrho' = -\dfrac{\varepsilon}{4\pi}\dfrac{1}{r}\dfrac{d^2(r\,\psi')}{dr^2} = -2pe\,\lambda\sinh\left(\dfrac{\lambda e\,\psi'}{kT}\right)$

and $\psi' = \dfrac{\partial(\lambda\psi')}{\partial\lambda} - \lambda\dfrac{\partial\psi'}{\partial\lambda}$ the second integral is worked out as follows:

$$I_2 = -\frac{2\,pe}{n}\int\limits_{r=a}^{\infty}\int\limits_{\lambda=0}^{1}\sinh\left(\frac{\lambda e\,\psi'}{kT}\right)d(\lambda\psi')\,4\pi r^2 dr +$$

$$\frac{\varepsilon}{n}\int\limits_{r=a}^{\infty}\int\limits_{\lambda=0}^{1}\frac{\partial^2(r\,\psi')}{\partial r^2}\frac{\partial(r\,\psi')}{\partial\lambda}\,d\lambda\,dr = -\frac{2pkT}{n}\int\limits_{a}^{\infty}\left\{\cosh\left(\frac{e\psi}{kT}\right)-1\right\}4\pi r^2 dr +$$

$$+\frac{\varepsilon}{n}\int\limits_{r=a}^{\infty}\int\limits_{\lambda=0}^{1}\frac{\partial}{\partial r}\left\{\frac{\partial(r\psi')}{\partial r}\frac{\partial(r\psi')}{\partial\lambda}\right\}d\lambda\,dr - \frac{\varepsilon}{n}\int\limits_{r=a}^{\infty}\int\limits_{\lambda=0}^{1}\frac{\partial(r\psi')}{\partial r}\frac{\partial^2(r\psi')}{\partial r\,\partial\lambda}\,d\lambda\,dr$$

$$\qquad\qquad\qquad\qquad I_3 \qquad\qquad\qquad\qquad\qquad\qquad I_4$$

$$I_3 = -\frac{\varepsilon}{n}\int\limits_{o}^{1}\left\{\frac{\partial(r\psi')}{\partial r}\cdot\frac{\partial(r\psi')}{\partial\lambda}\right\}_{r=a}d\lambda = -\frac{\varepsilon a}{n}\int\limits_{O}^{\psi_o}\left\{\psi'_o + a\left(\frac{\partial\psi'}{\partial r}\right)_{r=a}\right\}d\,\psi'_o$$

Remembering that $\left(\dfrac{\partial\psi'}{\partial r}\right)_{r=a} = \lambda\left(\dfrac{d\psi}{dr}\right)_{r=a} = -\lambda\dfrac{ne}{\varepsilon a^2}$ we obtain

$$I_3 = -\frac{\varepsilon a}{2n}\psi_o^2 + e\int\limits_{O}^{\psi_o}\lambda d\,\psi'_o \text{ and combination with } I_1 \text{ gives}$$

$$I_1 + I_3 = -\frac{\varepsilon a}{2n}\psi_o^2 + e\,\psi_o.$$

It remains to evaluate I_4:

$$I_4 = -\frac{\varepsilon}{2n}\int\limits_{\lambda=0}^{1}\int\limits_{r=a}^{\infty}\frac{\partial}{\partial\lambda}\left\{\frac{\partial(r\psi')}{\partial r}\right\}^2 d\lambda\,dr = -\frac{\varepsilon}{2n}\int\limits_{r=a}^{\infty}\left\{\frac{\partial(r\psi)}{\partial r}\right\}^2 dr$$

$$= -\frac{\varepsilon}{2n}\int\limits_{a}^{\infty}\left(\frac{d\psi}{dr}\right)^2 r^2 dr + \frac{\varepsilon a}{2n}\psi_o^2$$

Addition of the results gives

$$F_{el}' = e\,\psi_o - \frac{2pkT}{n}\int\limits_{r=a}^{\infty}\left\{\cosh\left(\frac{e\psi}{kT}\right)-1\right\}4\pi r^2 dr - \frac{\varepsilon}{2n}\int\limits_{a}^{\infty}\left(\frac{d\psi}{dr}\right)^2 r^2 dr$$

This expression can be converted into (12) with the substitutions

$$\frac{e\psi}{kT} = \Phi, \varkappa r = x \text{ and } \varkappa^2 = \frac{8\pi p e^2}{\varepsilon kT}.$$

(Received May 25th 1956).

ERRATA

Page 996,   Table I, *au lieu de* ,,rétro-C_{20}-acid, $C_{22}H_{28}O_2$'', *lire:* rétro-C_{20}-acid, $C_{20}H_{28}O_2$.

,,   997,   Table II, *au lieu de* ''trans- et cis-β-C_{15}-alcohol anthraquinone-β-carboxylate, $C_{30}H_{34}O_4$'' *lire:* trans- et cis-β-C_{15}-alcohol anthraquinone-β-carboxylate, $C_{30}H_{30}O_4$.

,,   1002,   ligne 11 du bas, *au lieu de* ,,β-C_{20}-hydroyethylester'', *lire* β-C_{20}-hydroxyethylester.

,,   1018,   ligne 16, *au lieu de* ,,Methyl 1,3,5,6-tetrachloro-4-amino-cyclohexadiene-3,5-carboxylate-1'', *lire:* ,,Methyl 1,3,5,6-tetrachloro-4-amino-cyclohexadiene-3,5-one-
2-carboxylate-1.''