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perature, and  $V_a$  the average volume calculated from the XRD data. Using their results for the "135-Å" particle size determined from the Scherrer formula, Kündig et al. obtained  $K = 4.7(10)^4$  erg/cm<sup>3</sup>. If, however, it is assumed that these particle sizes were in error, a true particle size may be estimated by multiplying by the ratio 100/180 or (80/135) found in the present study of two examples of this same material. It is then found that the calculated anisotropy constant is  $K \approx 3.5(10)^5$  erg/cm<sup>3</sup>. This result agrees with the values of  $5.5(10)^5$  and  $6(10)^5$  erg/cm<sup>3</sup> subsequently found by other workers using somewhat different procedures.<sup>8,9</sup> Thus the particle size inferred from the extent of superparamagnetic collapse in a

Mössbauer spectrum of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is equivalent to that obtained by XRD, i.e., interparticle effects in mosaic crystals are not important in determining the MES spectrum. Consequently, the same caution must be invoked in the use of MES data alone to estimate exposed surface area as in the use of XRD alone.

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(9) van der Kraan, A. M., Thesis, 1972 (unpublished), cited in ref 8.

## Quasi-Elastic Light Scattering Study of Intermicellar Interactions in Aqueous Sodium Dodecyl Sulfate Solutions

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Quasi-elastic light scattering measurements have been performed on aqueous sodium dodecyl sulfate solutions in the 0.1–0.6 M NaCl concentration range at 25 and 40 °C. The aggregation number  $m$ , the hydrodynamic radius  $R_H$ , and the amphiphile concentration dependence of static and transport coefficients of micellar solutions are obtained from the experimental data. The micellar parameters  $m$  and  $R_H$  increase with salt concentration and slightly decrease with temperature. The concentration dependence of the apparent molecular weight and of the mass diffusion coefficient is interpreted on the basis of DLVO theory of colloid stability. The fit to the experimental data, performed with the assumption that the Hamaker constant for micellar attraction  $A$  and the micellar electric charge  $q$  do not depend on the salt concentration, is satisfactory and gives  $A = 4.5 \times 10^{-20}$  J and  $q = 37$  electronic charges. The electric potential at the shear surface of the micelle goes from 70 mV at 0.1 M NaCl to  $\sim 30$  mV at 0.5–0.6 M NaCl.

### Introduction

We report in this paper quasi-elastic light scattering measurements performed on dilute aqueous solutions of an ionic amphiphile at various ionic strengths and temperatures. We derive from the experimental data both individual micellar parameters and the intermicellar pair interaction potential.<sup>1</sup>

The study of ionic micelles in the presence of an electrolyte is useful to understand the process of micelle formation, since the electrostatic repulsion among the charged heads is one of the factors which determine the size and shape of the micelle.<sup>2,3</sup> Furthermore the knowledge of the intermicellar interaction potential  $V$  is important for several reasons: (i) some micellar parameters can be directly derived from  $V$ ; for instance, the electrostatic part of  $V$  depends on the electric charge of the micelle; (ii) nonideality effects can be taken into account, and therefore micellar properties can be obtained without extrapolating the experimental data to the critical micelle concentration (cmc); (iii) the phase transitions occurring in micellar solutions may be better understood.

Many authors have performed static<sup>4–6</sup> and dynamic<sup>7–10</sup> light scattering experiments on solutions of ionic micelles at various ionic strengths, but a systematic investigation

of the electrolyte effect is still lacking. Although a large body of literature has been developed by colloid physical chemists about the problem of interactions among polyelectrolytes in aqueous solutions, very incomplete models have been used so far to describe intermicellar interactions.

Micellar solutions present some peculiarity with respect to typical colloid solutions, particularly because micelles may change size and shape by changing either the amphiphile or the electrolyte concentration.<sup>2,4–10</sup> Equilibrium and transport properties of micellar solutions are measured as functions of the amphiphile concentration  $c$ . Individual

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(8) M. Corti and V. Degiorgio in "Photon Correlation Spectroscopy and Velocimetry", H. Z. Cummins and E. R. Pike, Eds., Plenum Press, New York, 1977, p 450.

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micelle parameters are obtained by extrapolating the experimental data at the critical micelle concentration  $c_0$ . The concentration dependence of the apparent molecular weight  $M$  and of the diffusion coefficient  $D$  above  $c_0$  is generally due to the combination of two effects: intermicellar interactions and change of micelle size with  $c$ . The first problem in the interpretation of the experimental results is how to separate these two effects. At moderate ionic strength the first effect is predominant, whereas at large ionic strength the second effect may become more important.<sup>7</sup> We have worked with sodium dodecyl sulfate (SDS) solutions at NaCl concentrations in the range 0.1–0.6 M and at temperatures of 25 and 40 °C, so that the effect of interactions is larger than the change of micelle size in most of the situations that we have investigated.

The possibility offered by the quasi-elastic light scattering technique of accurately measuring the mass diffusion coefficient  $D$  of macromolecular and colloid solutions as a function of the solute concentration has stimulated many theoretical investigations<sup>11</sup> about the general relation connecting the pair interaction potential  $V$  to the concentration dependence of  $D$ . Only recently was this point satisfactorily clarified by Batchelor<sup>12</sup> and Felderhof.<sup>13</sup> The literature concerning the concentration dependence of  $D$  is confusing also because several authors do not compare their work with previous authors' works. We thought it useful to summarize the main results and to compare some of the published approaches.

The choice of a realistic parameterized expression for the potential  $V$  still represents an open problem actively investigated in many theoretical and experimental groups. We have chosen the interaction potential of the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory of colloid stability.<sup>14</sup> This potential consists of a hard-sphere repulsive part, an electrostatic long-range repulsion, and a London–van der Waals attraction and contains only two unknown parameters, the electric potential at the shear surface of the micelle and the Hamaker constant. The idea of adding an attractive contribution to the interaction potential, although usual in colloid theory, is rather recent for micellar solutions. It was proposed by us 2 yr ago<sup>10</sup> and, independently, by Lips.<sup>15</sup> A similar approach has also been used in the interpretation of experiments concerning fusion of phospholipid vesicles.<sup>16</sup>

It should be stressed that, although the experimental results reported here refer only to micellar solutions, the technique may be equally well applied to any macromolecular or colloidal solution.

### Brownian Diffusion of Interacting Particles

The average intensity of light scattered by a solution of small, monodisperse and noninteracting particles is<sup>17</sup>

$$I = AcM_0 \quad (1)$$

where  $A$  is a calibration constant,  $c$  (g/cm<sup>3</sup>) is the macromolecular concentration, and  $M_0$  is the molecular weight of the macromolecules. The intensity correlation function is<sup>17</sup>

(11) W. Hess in "Light Scattering in Liquids and Macromolecular Solutions", V. Degiorgio, M. Corti, and M. Giglio, Eds., Plenum Press, New York, 1980, p. 31.

(12) G. K. Batchelor, *J. Fluid. Mech.*, **74**, 1 (1976).

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(17) H. Z. Cummins in "Photon Correlation and Light Beating Spectroscopy", H. Z. Cummins and E. R. Pike, Eds., Plenum Press, New York, 1975, p. 285.

$$G(\tau) = \langle I(t) I(t + \tau) \rangle = \langle I \rangle^2 (1 + B e^{-k^2 D_0 \tau}) \quad (2)$$

where  $B$  is an instrumental constant,  $D_0$  is the translational diffusion coefficient of the macromolecule, and  $k = (4\pi n/\lambda) \sin \theta/2$  is the modulus of the scattering vector,  $\lambda$  being the wavelength of the incident light and  $\theta$  the scattering angle.

For interacting particles, eq 1 and 2 can still be used to yield an apparent molecular weight  $M$  and a collective diffusion coefficient  $D$  which are concentration dependent. We review in this section the theoretical results which allow one to connect the concentration dependence of  $M$  and  $D$  in dilute solutions to the pair interaction potential  $V$ , and we discuss the available analytical expression for  $V$ .

To the first order in the concentration  $c$ ,  $M^{-1}$  and  $D$  can be written in the form

$$M^{-1} = M_0^{-1}(1 + k_I c) \quad (3a)$$

$$D = D_0(1 + k_D c) \quad (3b)$$

Theoretical results are usually expressed in terms of the volume fraction  $\phi$  of the particles; that is

$$M^{-1} = M_0^{-1}(1 + k'_I \phi) \quad (3c)$$

$$D = D_0(1 + k'_D \phi) \quad (3d)$$

where  $k'_I = k_I/\bar{v}$  and  $k'_D = k_D/\bar{v}$ , and  $\bar{v}$  is the specific volume of the solute particles.

The static coefficient  $k'_I$  is proportional to the second virial coefficient. If one considers the case of rigid spherical particles of radius  $a$  with a pair interaction potential  $V(x)$ , where  $x = (R - 2a)/(2a)$  and  $R$  is the distance between the centers of the two particles,  $k'_I$  is expressed by eq 4,<sup>18</sup> where

$$k'_I = 8 + 24 \int_0^\infty dx (1 + x)^2 [1 - e^{-V(x)/(k_B T)}] \quad (4)$$

8 is the hard-sphere contribution. The calculation of  $k'_D$  considers two types of interactions, the first due to interparticle forces and the second resulting from the fact that movement of one particle through the fluid generates a velocity field which affects the motion of neighboring particles. From the generalized Einstein relation<sup>12</sup>

$$D(\phi) = \frac{\phi}{1 - \phi} \frac{(\partial \mu / \partial \phi)_{p,T}}{f(\phi)} \quad (5)$$

where  $\mu$  is the chemical potential and  $f$  is the friction coefficient, the following expression for  $k'_D$  can be derived

$$k'_D = k'_I - k'_f \quad (6)$$

where  $k'_f$  takes into account the volume-fraction dependence of the friction coefficient. Whereas the expression for  $k'_I$  is well established, there are still discrepancies among the calculations of  $k'_f$  presented by different authors. It is possible to write down a relation for  $k'_f$  which has the same structure as eq 4, that is

$$k'_f = k'_{f0} + \int_0^\infty dx F(x) [1 - e^{-V(x)/(k_B T)}] \quad (7)$$

where  $k'_{f0}$  is the hard-sphere contribution.

The most complete treatments appear to be those by Batchelor,<sup>12</sup> who obtains

$$k'_{f0} = 6.55$$

$$F(x) = 11.89(1 + x) + 0.706 - 1.69(1 + x)^{-1} \quad (8)$$

(18) P. N. Pusey in "Photon Correlation and Light Beating Spectroscopy", H. Z. Cummins and E. R. Pike, Eds., Plenum Press, New York, 1975, p. 387.

and by Felderhof,<sup>13</sup> who finds

$$k'_{f0} = 6.44$$

$$F(x) =$$

$$12(1+x) - \frac{15}{8}(1+x)^{-2} + \frac{27}{64}(1+x)^{-4} + \frac{75}{64}(1+x)^{-5} \quad (9)$$

An earlier treatment by Pyun and Fixman,<sup>19</sup> reformulated by Goldstein and Zimm,<sup>20</sup> gives

$$k'_{f0} = 7.16$$

$$F(x) =$$

$$12(1+x) + \frac{15}{8}(1+x)^{-2} - \frac{3}{4}(1+x)^{-4} + \frac{15}{128}(1+x)^{-6} \quad (10)$$

A critical comparison of most of the published approaches can be found in ref 11 and 13.

The interaction potential  $V(x)$ , as it is usually written in DLVO theory,<sup>14</sup> is the sum of a repulsive interaction  $V_R$  and an attractive London-van der Waals interaction  $V_A$ . The expression of  $V_A$  derived by Hamaker<sup>21</sup> for the case of two spheres is eq 11, where  $A$  is the Hamaker constant.

$$V_A = -(A/12)[(x^2 + 2x)^{-1} + (x^2 + 2x + 1)^{-1} + 2 \ln(x^2 + 2x)/(x^2 + 2x + 1)] \quad (11)$$

Eq 11 does not take into account retardation effects and therefore is not valid for large values of  $x$ .<sup>20</sup> The range of ionic strengths considered in this paper is such, however, that the region of large separations between the particles is not relevant for the fit to the experimental results.

The repulsive interaction is due to the electric charge of the spheres. The layer of ions surrounding the sphere is divided into two regions, a thin inner region called the Stern layer and a diffuse outer region called the Gouy layer, where the ions are treated as point charges obeying the Poisson-Boltzmann equation. In this picture the long-range repulsion is determined by the potential of the diffuse layer  $\psi_0$ . Unfortunately no exact analytical solution of the Poisson-Boltzmann equation is available. Approximate solutions may be derived by assuming that  $\psi_0 \ll k_B T/e$ , where  $e$  is the electronic charge. Under this assumption, the Poisson-Boltzmann equation reduces to

$$\nabla^2 \psi = \kappa^2 \psi \quad (12)$$

where  $\kappa$  is the Debye-Hückel reciprocal length parameter given by

$$\kappa^2 = 8\pi c_s e^2 z^2 / (\epsilon k_B T) \quad (13)$$

where  $\epsilon$  is the dielectric constant of the suspending medium,  $z$  is the valence of the ionic species in solution, and  $c_s$  is the concentration (ions/cm<sup>3</sup>) of the same species. Approximate expressions for the interaction potential  $V_R$  have been derived from eq 12 in the two limit cases of  $\kappa a \ll 1$  and  $\kappa a \gg 1$ . In the former case, the expression of  $V_R$  is<sup>22</sup>

$$V_R = \frac{q^2 e^2}{2\epsilon a(1 + \kappa a)^2} \frac{e^{-2\kappa a x}}{(1+x)} \quad (14)$$

where  $qe$  is the electric charge of the particle. The latter case gives<sup>23,24</sup>

$$V_R = (\epsilon a \psi_0^2 / 2) \ln [1 + \exp(-2\kappa a x)] \quad (15)$$

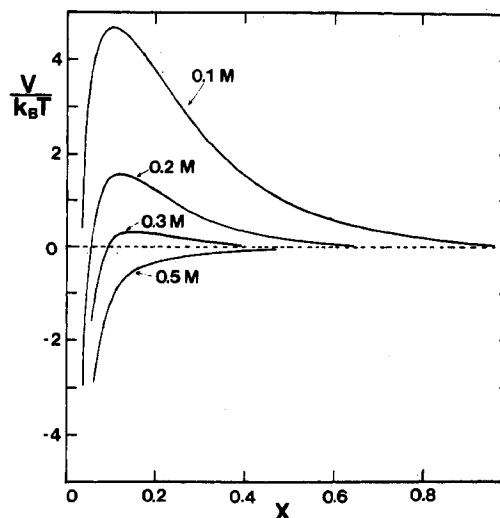


Figure 1. Plots of the pair interaction potential  $V(x)$  as a function of the reduced and normalized distance  $x$  at four distinct salt concentrations. Values of the parameters are given in the text.

where the surface potential  $\psi_0$  is related to the charge  $qe$  through the expression<sup>25</sup>

$$\psi_0 = (2k_B T/e) \sinh^{-1} [2\pi\epsilon\kappa^{-1}qe/(4\pi a^2\epsilon k_B T)] \quad (16)$$

Equation 16 is not restricted to the condition  $\psi_0 \ll k_B T/e$ .

We show in Figure 1 the behavior of  $V(x)/(k_B T)$  for a set of salt concentration. The plots have been computed by using eq 11 and 15 with the following values for the parameters:  $a = 25$  Å,  $T = 298$  K,  $A = 11.3k_B T$ , and  $q = 37$ .

The expression of  $k'_I$  becomes particularly simple if  $\kappa a \ll 1$ ,  $V_R/(k_B T) \ll 1$ , and the contribution of  $V_A$  can be neglected. Indeed, by putting  $1 - \exp[-V(x)/(k_B T)] \simeq V(x)/(k_B T)$  into eq 4 and using for  $V(x)$  the expression given in eq 14, it is easy to derive eq 17, where  $M$  is the

$$k'_I = 8 + q^2/(20Mm_s) \quad (17)$$

molecular weight of the particle and  $m_s$  (mol/cm<sup>3</sup>) is the electrolyte concentration. Equation 17 has been known for a long time;<sup>26</sup> we believe, however, that the present derivation is useful because it shows clearly the limits of validity of the formula.

It is important to realize that the Hamaker expression for  $V_A$  makes the integrals which appear in eq 4 and 7 divergent. To eliminate the divergence, one has to impose a lower cutoff  $x_L > 0$ . The physical origin of  $x_L$  is that the two particles cannot approach closer than the Stern layer thickness.<sup>20</sup>

It is easy to see from the structure of eq 4 that a purely repulsive interaction potential produces a positive  $k'_I$  and that  $k'_I$  is larger when the amplitude and (or) the range of the repulsive potential are larger. The attractive part of the potential tends to reduce  $k'_I$  and may lead, if large enough, to negative values of  $k'_I$ . When  $k'_I < 0$ , attraction is more effective than repulsion, and consequently the particles in solution may aggregate. Of course, a thorough discussion of the particle aggregation process cannot be made by considering only  $k'_I$ , which contains integral information on  $V(x)$ , but the shape of the interaction potential should also be taken into account. Indeed the critical concentration of electrolyte required to flocculate

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(26) C. Tanford, "Physical Chemistry of Macromolecules", Wiley, New York, 1961, p 229.

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(20) B. Goldstein and B. H. Zimm, *J. Chem. Phys.*, **54**, 4408 (1971).

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(22) D. Stigter and T. L. Hill, *J. Phys. Chem.*, **63**, 551 (1959).

(23) B. Derjaguin, *Kolloid-Z.*, **69**, 155 (1934); *Acta Physicochim. URSS*, **10**, 333 (1939).

(24) R. Hogg, T. W. Healy, and D. W. Fuerstenau, *Trans. Faraday Soc.*, **62**, 1638 (1966).

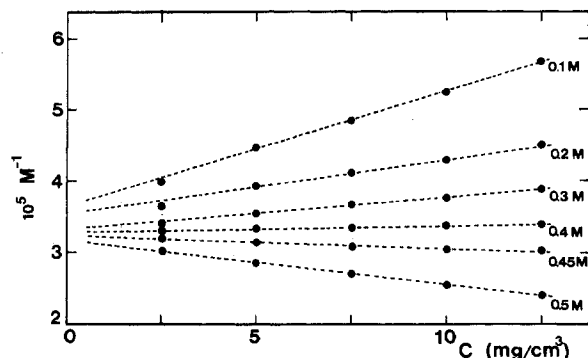


Figure 2. Reciprocal of the apparent molecular weight of the micelle  $M$  plotted as a function of the amphiphile concentration  $c$  at six distinct salt concentrations and at 25 °C.

the colloid is usually calculated by the condition that the maximum in the potential-energy curve (see Figure 1) occurs at zero potential.<sup>27</sup>

The discussion above about the sign of  $k_I$  can be equally well applied to  $k_D$ . This statement may be easily justified by considering that the leading term in  $F(x)$  (see eq 4) is the first one,  $12(1+x)$ , which is positive. Note, incidentally, that the leading term coincides in the formulations by Felderhof<sup>13</sup> and by Pyun and Fixman<sup>19</sup> and is only slightly different from that by Batchelor.<sup>12</sup> However, since the factor  $1 - \exp[-V(x)/(k_B T)]$  is weighted in the expression for  $k_D$  by a weight distinct from that appearing in eq 4, the condition  $k_I = 0$  may not coincide with the condition  $k_D = 0$ .

### Experimental Results

The optical source on the light scattering apparatus is an argon laser operating at 5145 Å with an output power of ~50 mW. The average scattered intensity and the time-dependent correlation function of the scattered intensity are measured at a scattering angle  $\theta = 90^\circ$ . Sodium dodecyl sulfate is prepared according to the standard method and purified by three recrystallizations from 95% ethanol. The alkyl chain composition of SDS was checked by gas-liquid chromatography on fatty alcohol recovered after acid hydrolytic cleavage and resulted as 99.7% C<sub>12</sub> pure fraction. Further details about the apparatus and the sample-preparation procedure can be found in our previous papers.<sup>28,29</sup>

The measurements have been performed at 25 and 40 °C on aqueous NaCl solutions in the NaCl concentration range 0.1–0.55 M and in the SDS concentration range 2–30 mg/cm<sup>3</sup>. In order to improve the signal-to-noise ratio in the correlation-function measurements, we have taken the dynamic light scattering data at higher amphiphile concentrations as compared with the average intensity data. Following the procedure originally developed for macromolecular solutions and successively adapted to micellar solutions, we have calculated from the intensity data the quantity  $M^{-1} = A(c - c_0)/(I_r - 1)$  as a function of the reduced amphiphile concentration  $c - c_0$ , where  $c_0$  is the critical micelle concentration and  $I_r$  is the ratio of the light intensity scattered from the solution to that scattered from the solvent. The quantity  $M^{-1}$  is proportional to the reciprocal of the osmotic compressibility of the micellar solution, and the calibration constant  $A$  is defined in such a way as to make  $M$  coincident, in the limit  $c \rightarrow c_0$ , with the molecular weight of the micelle  $M_0$ . The quantity  $M$

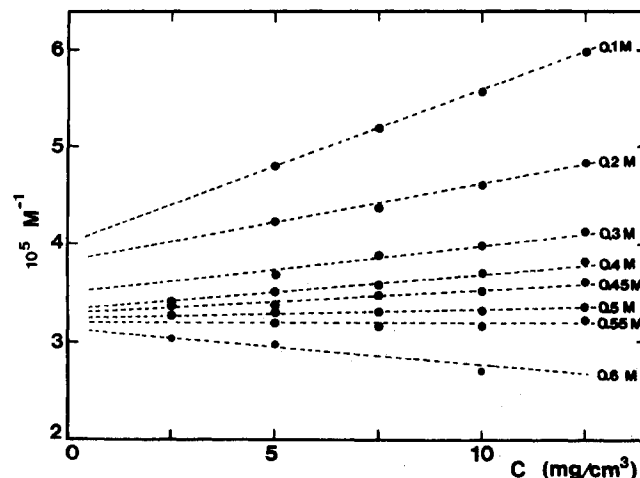


Figure 3. The same as Figure 2 at 40 °C. The 0.6 M curve is drawn by using the data given in ref 39.

TABLE I: Scattered Intensity Data at 25 °C<sup>a</sup>

$m_s$ , M	$c_0$ , mg/cm <sup>3</sup>	$10^{-4} \times M_0$	$m$	$k_I$ , cm <sup>3</sup> /g	
				exptl	theor
0.10	0.43	2.7	94	40.2 ± 4.5	29.3
0.20	0.27	2.8	97	21.1 ± 2.1	14.3
0.30	0.24	3.0	104	13.7 ± 1.4	8.2
0.40	0.17	3.05	106	3.0 ± 1.0	3.9
0.45	0.16	3.1	108	-5.1 ± 1.0	2.5
0.50	0.15	3.15	110	-19.5 ± 2.0	0.7

<sup>a</sup> The critical micelle concentration  $c_0$ , the extrapolated molecular weight of the micelle  $M_0$ , the corresponding aggregation number  $m = M_0/M_1$  (where  $M_1 = 288$  is the molecular weight of the SDS monomer), and the experimental and theoretical slopes  $k_I$  reported as functions of NaCl molar concentration  $m_s$ . The values of  $c_0$  are taken from ref 5 and 6. The theoretical  $k_I$  is calculated by using the best-fit parameters of eq 19. Relative errors in the determination of  $M_0$  are small. The absolute error in the calibration can be ~10%.

TABLE II: Scattered Intensity Data at 40 °C<sup>a</sup>

$m_s$ , M	$10^{-4} M_0$	$m$	$k_I$ , cm <sup>3</sup> /g	
			exptl	theor
0.10	2.44	85	38.0 ± 4.0	30.7
0.20	2.62	91	20.3 ± 2.0	15.6
0.30	2.81	98	13.4 ± 1.5	9.7
0.40	2.99	104	10.7 ± 1.5	6.4
0.45	3.03	105	7.1 ± 1.0	4.8
0.50	3.09	107	2.9 ± 1.0	3.2
0.55	3.13	109	0.0 ± 0.5	1.0
0.60	3.21	112	-3.7 ± 1.0	-0.5

<sup>a</sup> The symbols are the same as for Table I.

may be therefore called the apparent molecular weight of the micelle. The numerical value of the constant  $A$  depends on many parameters.<sup>29</sup> We have only performed relative measurements. The absolute values of  $M_0$  are derived by assigning to the calibration constant  $A$  the value that gives  $M = 27000$  for 0.1 M NaCl solutions at 25 °C.<sup>10,28</sup>

The plots of  $M^{-1}$  derived from the experimental data are shown in Figures 2 and 3. The data points have been fitted with the linear expression  $M(c)^{-1} = [1 + k_I(c - c_0)]/M_0$ . The obtained values of  $M_0$  and  $k_I$  are reported in Tables I and II. The values of  $c_0$  at 25 °C are derived from ref 5 and 6. The values of  $c_0$  at 40 °C are taken to coincide with those at 25 °C. This assumption can be partially justified by the temperature dependence of  $c_0$  for SDS solutions without electrolyte reported in Figure 2.5 of ref 30.

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TABLE III: Intensity Correlation Data at 25 °C<sup>a</sup>

$m_s$ , M	$10^6 D_0$ , cm <sup>2</sup> /s	$R_H$ , Å	$\alpha$	$\nu$	$k_D$ , cm <sup>3</sup> /g	
					exptl	theor
0.10	0.96 ± 0.02	25.3	5.19	0.05 ± 0.03	16.1 ± 2.0	16.2
0.20	0.95 ± 0.02	25.5	7.48	0.04 ± 0.03	8.3 ± 1.5	6.0
0.30	0.92 ± 0.02	26.0	9.35	0.03 ± 0.03	4.4 ± 1.0	2.2
0.40	0.88 ± 0.02	26.9	11.21	0.05 ± 0.03	-0.5 ± 0.5	-0.6
0.45	0.88 ± 0.02	26.9	11.89	0.09 ± 0.03	-7.2 ± 1.5	-1.4
0.50	0.84 ± 0.02	27.9	12.98	0.17 ± 0.03	-13.9 ± 1.5	-2.4

<sup>a</sup> The extrapolated diffusion coefficient  $D_0$ , the hydrodynamic radius  $R_H$ , the parameter  $\alpha = 2\kappa R_H$ , the fractional variance  $\nu$ , and the experimental and theoretical slopes  $k_D$  reported as functions of NaCl molar concentration  $m_s$ . The parameter  $\alpha$  is the reciprocal Debye-Hückel length normalized to the micellar diameter. The theoretical  $k_D$  is calculated by using the best-fit parameters of eq 19.

TABLE IV: Intensity Correlation Data at 40 °C<sup>a</sup>

$m_s$ , M	$10^6 D_0$ , cm <sup>2</sup> /s	$R_H$ , Å	$\alpha$	$k_D$ , cm <sup>3</sup> /g	
				exptl	theor
0.10	1.37 ± 0.03	25.4	5.07	18.6 ± 2.0	17.2
0.20	1.35 ± 0.03	25.5	7.24	10.6 ± 1.5	7.0
0.30	1.33 ± 0.03	25.6	8.96	7.3 ± 1.5	3.1
0.40	1.32 ± 0.03	25.6	10.34	3.6 ± 1.0	1.1
0.50	1.30 ± 0.03	25.8	11.93	-0.8 ± 0.5	-1.0
0.55	1.23 ± 0.03	27.1	13.22	-3.8 ± 1.0	-2.3
0.60	1.17 ± 0.03	28.4	14.47	-10.6 ± 1.5	-3.2

<sup>a</sup> The symbols are the same as for Table III.

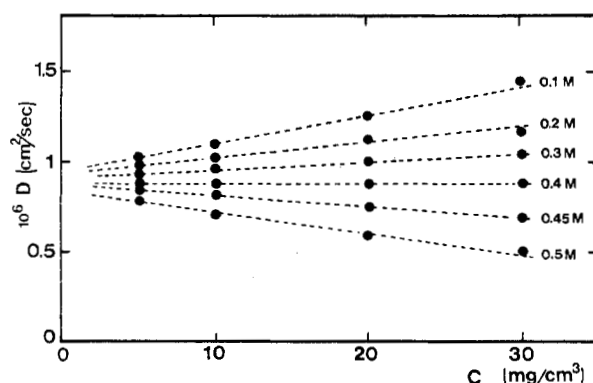


Figure 4. Mass diffusion coefficient  $D$  plotted as a function of the amphiphile concentration  $c$  at various salt concentrations and at 25 °C.

The intensity correlation results are analyzed by performing a cubic polynomial fit to the logarithm of the time-dependent part of the measured correlation function.<sup>10</sup> Such a fit allows one to derive the average diffusion coefficient  $D$  and the fractional variance  $\nu = \langle \delta D^2 \rangle / \langle D \rangle^2$ . The obtained diffusion coefficients are plotted in Figures 4 and 5. The experimental data have been fitted with the linear function  $D = D_0[1 + k_D(c - c_0)]$ . The values of  $D_0$  and  $k_D$  are reported in Tables III and IV, together with the hydrodynamic radius  $R_H$  derived from the Einstein-Stokes relation,  $R_H = k_B T / (6\pi\eta D_0)$ , where  $\eta$  is the viscosity of the solvent.

We see from Tables I and II that the aggregation number  $m$  at the cmc increases with the salt concentration and decreases with the temperature. A similar trend is followed by  $R_H$ .

The observed dependence of  $m$  on  $m_s$  and  $T$  is in agreement with the results of many investigations of SDS solutions, as shown by the exhaustive lists of experimental data reported in a recent review paper by Kratochvil.<sup>31</sup> As far as the absolute value of  $m$  is concerned, it should be kept in mind that the uncertainty in the calibration con-

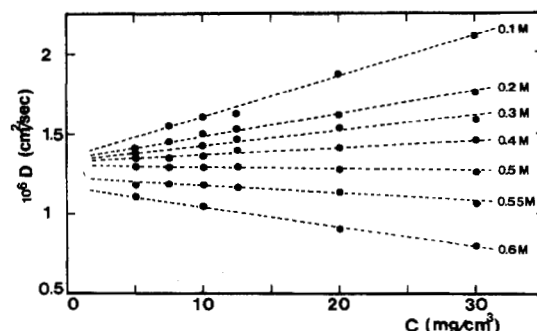


Figure 5. The same as Figure 4 at 40 °C. The 0.6 M curve is drawn by using the data given in ref 39.

stant is estimated to be ~10% in our case, and, presumably, it is similar for the data of other authors.

The slopes  $k_I$  and  $k_D$  are decreasing functions of  $m_s$ , going from large positive values at low ionic strength to negative values of high ionic strength. Although no systematic investigation of this type was previously reported in the literature, such a trend could be expected from the results of ref 5–10. It is interesting to correlate the behavior of  $k_I$  and  $k_D$  with the shape of the interaction potential shown in Figure 1. The slopes decrease, following closely the reduction of the height of the potential barrier due to the decrease of the Debye-Hückel length  $\kappa^{-1}$ .

The salt concentrations corresponding to zero slope, as calculated by interpolation of the results of Tables I–IV, are the following:

$$\begin{aligned}
 k_I = 0 & \quad \text{at } m_s = 0.42 \text{ M and } 25^\circ\text{C} \\
 k_D = 0 & \quad \text{at } m_s = 0.39 \text{ M and } 25^\circ\text{C} \\
 k_I = 0 & \quad \text{at } m_s = 0.55 \text{ M and } 40^\circ\text{C} \\
 k_D = 0 & \quad \text{at } m_s = 0.49 \text{ M and } 40^\circ\text{C}
 \end{aligned} \quad (18)$$

The fact that the salt concentration giving  $k_I = 0$  does not coincide with the concentration giving  $k_D = 0$  is well explained by the considerations reported at the end of the previous section. The increase of the zero-slope salt concentrations going from 25 to 40 °C can be mainly attributed to the increase of the Debye-Hückel length with temperature.

The fractional variance  $\nu$  obtained through the cumulant fit from the experimental correlation function measured at  $c = 20 \text{ mg/cm}^3$  is reported in Table III. At low ionic strength  $\nu$  is zero within the experimental errors, whereas at large ionic strength, when  $k_D$  becomes negative,  $\nu$  markedly increases.

## Data Interpretation

Micelle formation is a stepwise self-association process characterized by the fact that the transition from the predominantly unassociated state to the micellar state does

(30) B. Lindman and H. Wennerström, *Top. Curr. Chem.*, 87 (1979).

(31) J. P. Kratochvil, *Adv. Colloid Interface Sci.*, submitted.

occur usually over a narrow critical range of concentration.<sup>2</sup> For the sake of simplicity, this narrow critical range is characterized by a single concentration  $c_0$ . Solutions with  $c$  larger than  $c_0$  are assumed to contain a concentration  $c - c_0$  of micellar amphiphile and a concentration  $c_0$  of monomeric amphiphile, the latter giving a negligible contribution to the excess scattered light. The description of micelle formation in terms of a stepwise association implies that the average aggregation number is an increasing function of concentration. The concentration dependence of  $D$  and  $M$  is due therefore to the combination of two effects, intermicellar interactions and change of micelle size with  $c$ . In order to interpret our experimental results, we have made the simplifying assumption that the second effect is negligible. A more thorough discussion of this point was given by us in a previous paper.<sup>1</sup>

We have calculated the theoretical values of the slopes  $k_I$  and  $k_D$  by using eq 4, 6, and 7. We have inserted into eq 7 the expressions of  $k'_0$  and  $F(x)$  obtained by Felderhof<sup>13</sup> and reported by eq 9. A numerical test of the effect produced on  $k_D$  by using eq 8 and 10 instead of eq 9 was also performed. These effects are negligible in all practical cases. The interaction potential  $V = V_R + V_A$  is given, according to DLVO theory, by eq 11 and 15, where the particle radius  $a$  is taken to coincide with  $R_H$ . The unknown parameters are the electric potential  $\psi_0$  (or, equivalently, the electric charge  $q$ ), the Hamaker constant  $A$ , and the lower cutoff  $x_L$  of the particle separation  $x$ .

We note, incidentally, that eq 11 and 15 apply only to spherical particles. SDS micelles are probably not spherical,<sup>10</sup> but their axial ratio is smaller than 2, so that it is still reasonable to use eq 11 and 15.

The best-fit computations have been performed with a lower cutoff  $x_L = 8 \times 10^{-2}$  which corresponds to a distance of closest approach between two micelles of 2 Å. The best fit parameters are not considerably modified if  $x_L$  is chosen between  $4 \times 10^{-2}$  and  $8 \times 10^{-2}$ .

In order to obtain an evaluation of the unknown parameters appearing in the expression for the interaction potential  $V$ , we have made the simplifying assumption that  $A$  and  $q$  are both independent of the salt concentration. With regard to  $A$ , there is a recent measurement of forces between two surfaces in aqueous electrolyte solutions<sup>32</sup> which shows indeed that the attractive London-van der Waals forces are largely independent of the type and concentration of the aqueous electrolyte solution. With regard to the assumption of constant  $q$ , there are recent experimental results on SDS micelles<sup>30</sup> which indicate that  $q$  does not depend appreciably on the salt concentration.

The values

$$q = 37 \quad A = 11.3k_B T \approx 4.5 \times 10^{-20} \text{ J} \quad (19)$$

have been obtained through the graphical procedure shown in Figure 6. The two curves in the plane  $(q, A)$  are computed from eq 6, 7, and 9 by imposing respectively the two experimental conditions  $k_D = 16$  at 0.1 M NaCl and 25 °C and  $k_D = -0.5$  at 0.4 M NaCl and 25 °C. The intersection of the two curves gives the best-fit parameters of eq 19. The same values of  $q$  and  $A$  were used to compute all of the theoretical slopes reported in Tables I-IV.

The best-fit procedure can be qualitatively understood in the following way. The value of  $k_D$  at small ionic strength (0.1 M NaCl) is weakly sensitive to  $A$ , and therefore the best-fit value of  $q$  can be fixed almost exactly by using only the data at 0.1 M NaCl. The condition  $k_D \approx 0$  (0.4 M NaCl) imposes a complete balance between

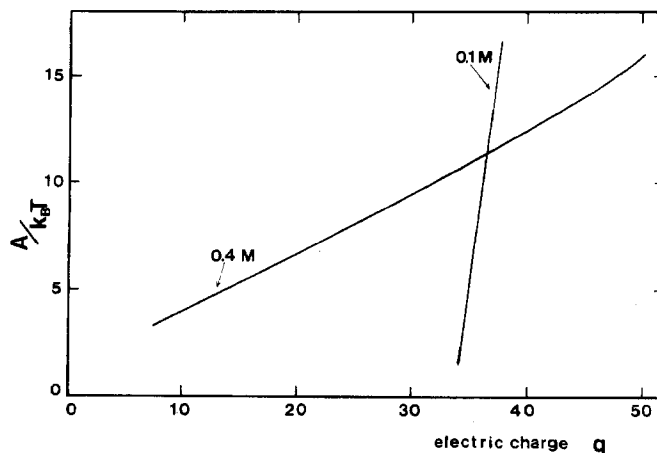


Figure 6. Best fit of the parameterized potential  $V(x)$  to the experimental data at 25 °C. The two curves are the locus of points in the  $(q, A)$  plane for which  $k_D = -0.5$  at 0.4 M NaCl and  $k_D = 16.1$  at 0.1 M NaCl, respectively. The intersection of the two curves gives the best-fit parameters  $q$  and  $A$  (see eq 19 in the text).

TABLE V: Electric Potential at the Shear Surface of the Micelle,  $\psi_0$ , as a Function of the Salt Concentration  $m_s$  and of the Temperature, Derived from Eq 16 by Using the Best-Fit Value  $q = 37$

$m_s$ , M	0.1	0.2	0.3	0.4	0.45	0.5	0.55	0.6
$e\psi_0/(k_B T)$ , 25 °C	2.93	2.30	1.92	1.63	1.54	1.38		
$e\psi_0/(k_B T)$ , 40 °C	2.88	2.27	1.93	1.70		1.51	1.32	1.18

attraction and repulsion, and consequently it is mainly sensitive to the ratio  $q/A$ .

We have calculated from eq 16, with  $q$  given by eq 19, the ratio  $e\psi_0/(k_B T)$  as a function of salt concentration. The results are shown in Table V. As one can see from eq 16, the assumption that  $q$  does not depend on  $m_s$  implies that  $\psi_0$  decreases almost proportionally to the Debye-Hückel length  $k^{-1}$ .

## Discussion

We have put on a quantitative basis the picture, already proposed in ref 10, which describes intermicellar interactions in terms of a balance between a repulsive and an attractive potential. At low ionic strength the excluded volume and electrostatic repulsion effects are predominant. At increasing ionic strength the Coulomb potential is screened more and more effectively; the London-van der Waals attraction becomes important and may lead, above a critical electrolyte concentration, to coagulation of micelles.

Taking into account the many approximations inserted into the theoretical model, one can consider the agreement to be satisfactory for the data taken both at 25 and 40 °C. The largest deviations concern the slope  $k_I$  at 25 °C and all negative values of the slopes  $k_I$  and  $k_D$ . About the first point, we recall that in a previous measurement<sup>10</sup> at 25 °C we found  $k_I \approx 29$ , which is very close to the theoretical value reported in Table I. We do not know the reason of the discrepancy between the two measurements. With regard to the second point, it should be considered that, in the region of negative slopes, the predominant contribution to  $k_I$  and  $k_D$  comes from the short-range part of  $V(x)$ . The observed deviations indicate that our description of  $V(x)$  is not adequate for small values of  $x$ .

We report, for comparison with eq 18, the theoretical values of  $m_s$  corresponding to zero slopes:

(32) J. N. Israelachvili and G. E. Adams, *J. Chem. Soc., Faraday Trans. 1*, 74, 975 (1978).



$$\begin{aligned}
 k_I &= 0 & \text{at } m_s &= 0.51 \text{ M and } 25^\circ\text{C} \\
 k_D &= 0 & \text{at } m_s &= 0.39 \text{ M and } 25^\circ\text{C} \\
 k_I &= 0 & \text{at } m_s &= 0.57 \text{ M and } 40^\circ\text{C} \\
 k_D &= 0 & \text{at } m_s &= 0.46 \text{ M and } 40^\circ\text{C}
 \end{aligned} \quad (20)$$

We note again that the agreement is very good for all data, except for  $k_I$  at  $25^\circ\text{C}$ .

The obtained values of  $\psi_0$  are close to those expected from theoretical calculations<sup>33</sup> on SDS micelles. It should be noted that our result contradicts the assumption  $e\psi_0 \ll k_B T$  introduced to linearize the Poisson–Boltzmann equation. Numerical studies of this equation indicate, however, that the linear approximation is not too bad even when  $e\psi_0 \simeq 2k_B T$ .<sup>24</sup>

The obtained Hamaker constant is not in contrast with the values reported for hydrocarbons and derivatives by Visser<sup>34</sup> and by Derjaguin et al.<sup>35</sup>

The increase of the temperature has two effects: (i) the ratio between the interaction energy  $V(x)$  and the thermal energy  $k_B T$  becomes smaller and (ii) the Debye–Hückel length, at constant  $m_s$ , becomes larger. Both effects tend to increase the critical coagulation concentration, as shown by the comparison between the data at  $25$  and  $40^\circ\text{C}$ . The fact that the data obtained at  $40^\circ\text{C}$  are well described by the same parameters derived from the fit to the  $25^\circ\text{C}$  data constitutes a good verification of the model.

The insertion of an attractive term in the interaction potential not only is necessary to explain the change in sign of the slopes  $k_I$  and  $k_D$  for the increasing  $m_s$  but also allows one to derive more realistic values for  $\psi_0$  and  $q$  than those obtained by considering only the electrostatic repulsion.

Our determination of micellar charge,  $q = 37$  (which corresponds to a counterion binding factor  $\simeq 0.4$ ), compares quite well indeed with the recent results on SDS and other ionic amphiphiles summarized in Table II of ref 4 but differs considerably from other light scattering (or sedimentation) determinations.<sup>6,9,36</sup> Classical light scattering<sup>4-6,36</sup> and sedimentation measurements<sup>36</sup> were analyzed with eq 14, which neglects the attractive part of the potential and uses for the Coulomb part an approximation valid only at very low ionic strength ( $<0.01 \text{ M}$ ), as explained in the second section. This is the reason that the values of  $q$  derived from classical light scattering and sedimentation data are much smaller than those reported here or obtained from other more direct techniques.<sup>4</sup>

Rohde and Sackmann<sup>9</sup> have very recently reported a quasi-elastic light scattering investigation of low-concentration SDS solutions in the salt concentration range  $0$ – $0.2 \text{ M NaCl}$ . They have interpreted the concentration dependence of the diffusion coefficient with the model proposed by Stephen.<sup>37</sup> Stephen's model has a very limited range of applicability because it assumes that  $k_I = k_D$ , that is, the concentration dependence of the friction coefficient

(see eq 6) is neglected, and also because only the electrostatic contribution to the interaction potential is considered. Furthermore, this contribution is calculated with an approximation essentially equivalent to that used to derive the second term in the right-hand side of eq 17 and implies therefore  $\kappa R_H \ll 1$  and  $V(x)/(k_B T) \ll 1$ . We believe that Stephen's model is not adequate for SDS solutions when  $m_s > 0.01 \text{ M NaCl}$ . Indeed the value of the micellar charge given in ref 9 is too small with respect to the values obtained by other techniques<sup>4</sup> or given in this paper.

At very high ionic strength the apparent molecular weight  $M$ , the hydrodynamic radius  $R_H$ , and the polydispersity index  $\nu$  increase considerably, as shown in several papers.<sup>38-41</sup> The picture proposed in this paper explains qualitatively this behavior by suggesting that the large aggregates formed at high salt concentration are due to coagulation of the small micelles formed at the cmc. The model as it is can only predict the limiting slope, for  $c \rightarrow c_0$ , of the plots  $M^{-1}$  vs.  $c - c_0$  and  $D$  vs.  $c - c_0$ . At high ionic strength such plots are nonlinear, as discussed in a previous paper,<sup>39</sup> so that the model may be only applied in a small region of amphiphile concentration very close to  $c_0$ . It should be recalled that Missel et al.<sup>40</sup> have developed a thermodynamic theory of micelle formation which describes very well the experimental results obtained on high ionic strength SDS solutions in a wide range of temperatures. We are presently investigating whether it is possible to establish a connection between the two approaches which are presently complementary as far as the range of applicability is concerned.

The application of the best-fit procedure illustrated in Figure 6 is not limited, obviously, to the case of  $A$  and  $q$  independent of  $m_s$ . The only requirement is that the dependence of the two parameters on the salt concentration is known. In a first attempt<sup>1</sup> to obtain a rough evaluation of  $V(x)$ , we have used, for instance, the assumption that  $A$  and  $\psi_0$  are independent of  $m_s$ .

We wish finally to mention three points which could lead to an improvement of the quantitative agreement between theory and experiment: (i) The DLVO theory can be refined or modified by including other terms in the potential  $V(x)$ . Indications about this point are given in two recent papers.<sup>32,35</sup> (ii) The electrostatic potential  $V_R$  can be evaluated more accurately by using the nonlinear Poisson–Boltzmann equation or by other models, as discussed by several authors.<sup>42</sup> (iii) The physical meaning of the cutoff distance  $x_L$  should be better clarified also in order to understand whether the assumption that  $x_L$  does not depend on the salt concentration is justified.

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