

# Time-Resolved Fluorescence Quenching and Electron Paramagnetic Resonance Studies of the Hydration of Lithium Dodecyl Sulfate Micelles

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A spin-probe method to study the surface hydration of sodium dodecyl sulfate (SDS) micelles (Bales, B. L.; Messina, L.; Vidal, A.; Peric, M.; Nascimento, O. R. *J. Phys. Chem.* **1998**, *102*, 10347; referred to as **I**) is applied to lithium dodecyl sulfate (LiDS) micelles in order to test both the method and a model of micelle hydration. The method is based on the fact that the hyperfine spacing between the low- and center-field resonance lines,  $A_+$ , varies linearly with a polarity index,  $H(25\text{ }^\circ\text{C})$ , which is the volume fraction occupied by water in a solvent mixture that contains only water as a source of OH dipoles. The model successfully employed in **I** predicts that  $H(25\text{ }^\circ\text{C})$  is determined only by the geometry of the micelle; the amount of water associated with the micelle is determined by the volume available to house the water. Thus, SDS and LiDS micelles of the same aggregation number,  $N_A$ , ought to yield the same value of  $H(25\text{ }^\circ\text{C})$  (and, therefore  $A_+$ ) because, apart from their waters of hydration which are already taken into account by the geometrical model, neither  $\text{Li}^+$  nor  $\text{Na}^+$  occupies significant volume. Over the range of aggregation numbers  $N_A = 50\text{--}110$ , values of  $H(25\text{ }^\circ\text{C})$  determined from measurements of  $A_+$  in LiDS micelles were found to be within  $\pm 2\%$  of those in SDS micelles. These data support the geometric model and show that specific interactions due to  $\text{Li}^+$  or  $\text{Na}^+$  which might affect  $A_+$  are unimportant. The aggregation numbers of LiDS micelles are measured by time-resolved fluorescence quenching and are well described by  $N_A = \kappa_2([\text{Li}^+]_{\text{aq}})^\gamma$  with  $\kappa_2 = 112 \pm 2$  and  $\gamma = 0.180 \pm 0.005$ , where  $[\text{Li}^+]_{\text{aq}}$  is the concentration of lithium ions in the aqueous phase whether supplied by LiDS or by both LiDS and LiCl. Thus, LiDS micelles grow according to an empirical formula identical in form to that for SDS micelles, but at a slower rate. The aggregation numbers at the critical micelle concentration in the absence of added salt ( $\text{cmc}_0$ ) are the same for SDS and LiDS micelles, but above this concentration, LiDS micelles are significantly smaller than SDS micelles for a given ionic strength. By applying a simple model of a spherical hydrocarbon core surrounded by a polar shell and assuming that the spin-probe samples all portions of the shell, values of the polarity index  $H(25\text{ }^\circ\text{C})$  may be converted into values of  $N(\text{H}_2\text{O})$ , the number of water molecules per surfactant molecule residing in the polar shell. This conversion involves no adjustable parameters because the geometrical parameters are fixed from small-angle neutron scattering measurements. As the micelles grow in the range  $N_A = 50\text{--}110$ ,  $N(\text{H}_2\text{O})$  decreases from 9.6 to 5.4 water molecules per surfactant molecule because the volume per surfactant molecule in the polar shell decreases allowing less water to reside within the shell. The sphere–rod transition previously observed in **I** for SDS at  $N_A = 130$  cannot be reproduced in LiDS, because LiCl is not sufficiently soluble to achieve an aggregation number of 130; however, interesting small, unidentified transitions appear to occur near  $N_A = 112$  and 121. A byproduct of this work is that relative aggregation numbers for LiDS micelles may be determined from measured values of  $A_+$  with a precision of about one molecule from the following:  $A_+(N_A) = (15.468 \pm 0.004) - N_A(3.45 \pm 0.06) \times 10^{-3}$  where  $A_+(N_A)$  is in gauss. Since a given value of  $N_A$  may be prepared by choosing different combinations of SDS, LiDS, NaCl, and LiCl concentrations, neither interactions between the micelles nor the ionic strength influence the value of  $A_+$ .

## Introduction

It was previously shown<sup>1</sup> that sodium dodecyl sulfate (SDS) micelles grow as a power law of the concentration of sodium ion in the aqueous phase. One purpose of the present work is to show that lithium dodecyl sulfate (LiDS) micelles also obey a power law as follows:

$$N_A = \kappa_2([\text{Li}^+]_{\text{aq}})^\gamma \quad (1)$$

where  $[\text{Li}^+]_{\text{aq}}$  is the molar concentration of lithium ion in the

aqueous phase whether it is provided by LiDS, or by both LiDS and added LiCl and to determine the constants  $\kappa_2$  and  $\gamma$ . The contributions to  $[\text{Li}^+]_{\text{aq}}$  from the surfactant and added salt may be found from the conventional pseudophase ion exchange mass balance relationship,<sup>1</sup>

$$\begin{aligned} [\text{Li}^+]_{\text{aq}} &= \alpha([\text{LiDS}] - [\text{LiDS}]_{\text{free}}) + [\text{LiDS}]_{\text{free}} + [\text{Li}^+]_{\text{add}} \\ &= \alpha[\text{LiDS}] + \beta[\text{LiDS}]_{\text{free}} + [\text{LiCl}] \end{aligned} \quad (2)$$

where the brackets indicate molar concentrations,  $\alpha$  is the apparent degree of counterion dissociation,  $\beta = 1 - \alpha$ ,  $[\text{LiDS}]_{\text{free}}$

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is the concentration of monomeric LiDS, and  $[\text{Li}^+]_{\text{add}} = [\text{LiCl}]$  is the concentration of added common counterion.

Combining eqs 1 and 2 yields

$$N_A = \kappa_2(\alpha[\text{LiDS}] + \beta[\text{LiDS}]_{\text{free}} + [\text{LiCl}])^\gamma \quad (3)$$

Defining  $N_A^0 = \kappa_2(\text{cmc}_0)^\gamma$ , where  $\text{cmc}_0$  is the cmc in the absence of added salt, we may rewrite eq 3 as follows:

$$N_A = N_A^0 \left\{ \frac{\alpha[\text{LiDS}] + \beta[\text{LiDS}]_{\text{free}} + [\text{LiCl}]}{\text{cmc}_0} \right\}^\gamma \quad (4)$$

When  $[\text{LiDS}] = \text{cmc}_0 = [\text{LiDS}]_{\text{free}}$  and  $[\text{LiCl}] = 0$ , the fraction in the brackets becomes unity and  $N_A^0$  is seen to be the aggregation number at the cmc in the absence of added LiCl.

A second purpose of the work is to begin to test the spin-probe method of studying the surface hydration of micelles applied previously to SDS.<sup>2</sup> The method is based on the fact that the hyperfine coupling constants of nitroxide spin probes vary linearly with a nonempirical polarity index,<sup>3</sup>  $H(25^\circ\text{C})$ , defined to be the ratio of molar concentration of OH dipoles in a solvent or solvent mixture to that in water.  $H(25^\circ\text{C})$  shows good linear correlation with other measures of polarity,<sup>3</sup> such as the dielectric constant, with the obvious advantage that it is a straightforward matter to calculate the index from molecular structures and densities. Provided that the solvent mixture of interest is water and molecules possessing no OH bonds,  $H(25^\circ\text{C})$  is simply the volume fraction occupied by water. One untested aspect of the previous work was the neglect of a possible role of specific effects of the cation  $\text{Na}^+$  on the measured values of the hyperfine coupling constants. Here, we show that such effects are indeed negligible or that  $\text{Li}^+$  and  $\text{Na}^+$  behave in the same way.

A third purpose of the work is to begin to test a simple model of micelle surface hydration advanced previously.<sup>2</sup> The model is based on a polar shell surrounding a spherical hydrocarbon core. The polar shell is filled with water to the extent allowed by the shell's volume after subtracting the volume inaccessible to water due to the presence of other molecules or molecular moieties. The model did not distinguish between the waters of hydration and "free"<sup>4</sup> water in the calculation of  $H(25^\circ\text{C})$ . If this is valid, one expects neither  $\text{Li}^+$  nor  $\text{Na}^+$  to affect the value of  $H(25^\circ\text{C})$  very much since neither bare cation would occupy a significant fraction of the volume in the polar shell. This work provides a test of this assumption. In the companion paper<sup>5</sup> immediately following this one, we present a different type of test of the method and the model.

A motivation for pursuing these types of studies is that, using modern equipment and data fitting techniques, the hyperfine coupling constant may be measured with a relative precision of at least 2 orders of magnitude better than measurements of  $N_A$  itself permitting high-precision investigations of some of the subtle changes in micelles as a function of size and/or additives.

## Methods and Materials

In addition to materials described before,<sup>2,6</sup> the following reagents were used as received: LiDS, Sigma (Lot 13H06511) >99% (GC); 3,4-dimethylbenzophenone (DMBP), Aldrich 99%; and LiCl, Sigma ACS reagent >99.0%. The solutions were prepared with 18 M $\Omega$  Milli-Q water. Sample preparation was as described previously,<sup>2,6</sup> except that DMBP was used as the

quencher of the pyrene fluorescence. The experimental details of the TRFQ<sup>6</sup> and the EPR<sup>2</sup> measurements have been described previously.

## Results

**Fluorescence Quenching (TRFQ).** Decay curves, typical of pyrene fluorescence in the presence of varying concentrations of the quencher 3,4-dimethylbenzophenone (DMBP), were fit to the Infelta-Tachiya equation.<sup>7,8</sup> Allowing the quencher exit rate,  $k_-$ , to vary as an adjustable parameter yielded ratios of  $\phi = k_-/k_q$ , where  $k_q$  is the quenching rate constant, of the order  $\phi = 0.002$  or less, showing that DMBP does not migrate appreciably, as expected. Thus, the simpler form of the Infelta-Tachiya equation describing the fluorescence signal,  $f(t)$ , was used as follows:

$$f(t) = f(0) \exp\{-k_0 t + \langle N \rangle [\exp(-k_q t) - 1]\} \quad (5)$$

where  $k_0$  and  $k_q$  are the rate constants of decay for pyrene in the absence and presence of one quencher, respectively, and  $\langle N \rangle$  is the average number of quenchers per micelle given by

$$\langle N \rangle = \frac{[\text{DMBP}]}{[\text{micelles}]} \quad (6)$$

See, for example, ref 9 and references therein for details on the assumptions involved in eq 5, together with historical perspectives. Briefly, the main assumptions are that probe (pyrene) is immobile, the quenchers are distributed randomly according to the Poisson distribution, and the micelles have a small size dispersion. Implicit in eq 6 is the fact that a negligible fraction of the DMBP partitions into the aqueous phase.<sup>10</sup>

In eq 6, the square brackets denote molar concentrations. The concentration of micelles is

$$[\text{micelles}] = \frac{[\text{LiDS}] - [\text{LiDS}]_{\text{free}}}{N_A} \quad (7)$$

where  $[\text{LiDS}]$  and  $[\text{LiDS}]_{\text{free}}$  are the molar concentrations of total surfactant and monomeric surfactant, respectively, and  $N_A$  is the aggregation number. It follows from eqs 6 and 7 that

$$N_A = \langle N \rangle \frac{[\text{LiDS}] - [\text{LiDS}]_{\text{free}}}{[\text{DMBP}]} \quad (8)$$

The values of  $[\text{LiDS}]$  and  $[\text{DMBP}]$  are known;  $\langle N \rangle$  is the result of nonlinear least-squares fitting of the data to eq 5.

**Values of  $\beta$  and  $[\text{LiDS}]_{\text{free}}$ .** Previously, in the case of SDS, we chose to adopt the value of  $\beta$  derived from activity measurements;<sup>11</sup> however, such data are not available for LiDS. An alternate approach is available from the well-known result<sup>12</sup>

$$\log(\text{cmc}) = -K_3 - K_4 \log(\text{cmc} + [\text{M}^+]) \quad (9)$$

where  $[\text{M}^+]$  is the molar concentration of added common counterion and  $K_3$  and  $K_4$  are constants. Mass action theory<sup>11,12</sup> predicts  $\beta \approx K_4$  in the limit of large  $N_A$ . Generally, the excellent linearity in plots of eq 9 is taken to be evidence that  $\beta$  is constant; however, small variations might not be detected.<sup>13</sup> To appreciate the level of approximation in using a value of  $\beta$  for LiDS derived from eq 9, we note that, for SDS, the value of  $\beta$  from activity measurements is  $\beta = 0.73$ , while  $\beta \approx K_4 = 0.678$ <sup>1</sup> derived from a fit to eq 9. This 7% difference is small compared with the divergence in values for  $\beta$  estimated from various experimental techniques. Using the data of Mukerjee et al.,<sup>14</sup> a

**TABLE 1: TRFQ Sample Compositions and Values<sup>a</sup> of [LiDS]<sub>free</sub>**

[LiDS], mM	[LiCl], mM	[NaCl], mM	[LiDS] <sub>free</sub> , mM	[Li <sup>+</sup> ] <sub>aq</sub> , mM
25	0	0	6.0	12.1
50	0	0	4.5	19.2
100	0	0	3.0	34.3
200	0	0	1.9	65.9
50	15.4	0	2.9	33.5
50	72.3	0	1.4	89.4
50	258	0	0.6	275
50	690	0	0.3	706
50	0	250	0.6	

<sup>a</sup> Computed from eq 10 with  $\beta = 0.68$  and  $\text{cmc}_0 = 8$  mM.

linear least-squares fit to eq 9 yields  $\beta \approx K_4 = 0.677$ , i.e., identical to the value for SDS. Setting  $[\text{LiCl}] = 0$  in eq 9 yields  $K_3 = -(1 + \beta) \log(\text{cmc}_0)$ .

Values of  $[\text{LiDS}]_{\text{free}}$  are calculated from eq 5 of ref 1 as follows:

$$\log([\text{LiDS}]_{\text{free}}) = (1 + \beta) \log(\text{cmc}_0) - \beta \log([\text{Li}^+]_{\text{aq}}) \quad (10)$$

Values of the  $\text{cmc}_0$  depend on the experimental technique employed as follows:  $\text{cmc}_0 = 0.00893$  M (specific conductivity),  $0.0079$  M (surface tension), and  $0.00877$  M (equivalent conductivity).<sup>15</sup> For this work, we adopt  $\beta = 0.68$  and  $\text{cmc}_0 = 0.008$  M.

Table 1 details the composition of the samples used in the TRFQ measurements together with values of  $[\text{Li}^+]_{\text{aq}}$  and  $[\text{LiDS}]_{\text{free}}$ . One sample was prepared using 50 mM LiDS and 250 mM NaCl. For this sample, the value of  $[\text{LiDS}]_{\text{free}}$  was computed from eq 5 of ref 1 ignoring the effect of the small concentration of  $\text{Li}^+$ .

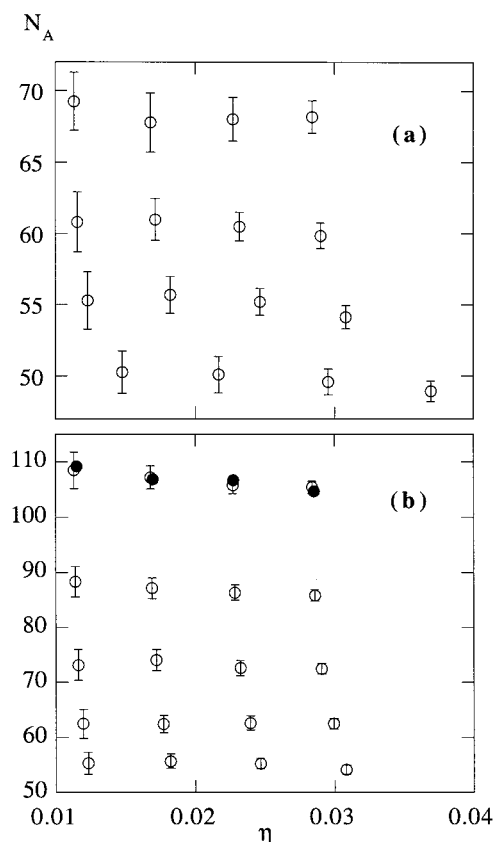
**Aggregation Numbers  $N_A$ .** Figure 1 shows values of  $N_A$  for LiDS micelles computed from eq 8 as a function of the quencher concentration scaled as follows:

$$\eta = \frac{[\text{DMBP}]}{[\text{LiDS}] - [\text{LiDS}]_{\text{free}}} \quad (11)$$

Parts a and b of Figure 1 give results without and with added LiCl, respectively, employing values of  $[\text{LiDS}]_{\text{free}}$  given in Table 1. Uncertainties in the values of  $[\text{LiDS}]_{\text{free}}$  lead to systematic errors in the values of  $N_A$ . These uncertainties are dominated by the uncertainties in the value of  $\text{cmc}_0$  which we estimate to be  $\pm 10\%$  judging from the differences using different techniques. This propagates to uncertainties in  $N_A$  of about  $\pm 1.5$  and  $\pm 0.8$  molecules for the  $[\text{LiDS}] = 25$  and  $50$  mM salt-free samples, respectively, and to negligible uncertainties for all other samples. Using values of  $\text{cmc}_0$  rather than  $[\text{LiDS}]_{\text{free}}$  in eq 8 introduces severe errors in  $N_A$  that amount to increases of 3–16 molecules in these samples.

If the assumptions of a Poisson distribution of DMBP and small size dispersity, are correct, Figure 1 ought to yield horizontal curves. In all cases, a horizontal line passes through the data within the error bars. Since the data do form horizontal lines, we average the values of  $N_A$  over all values of  $\eta$ . After this is done, the systematic errors due to uncertainties in  $[\text{LiDS}]_{\text{free}}$  are added and these are used as the uncertainties in the rest of this paper.

In Figure 1b, the filled circles nearly overlaying the data corresponding to  $[\text{LiDS}] = 50$  mM and  $[\text{LiCl}] = 690$  mM are data derived from the sample with  $[\text{LiDS}] = 50$  mM and  $[\text{NaCl}]$



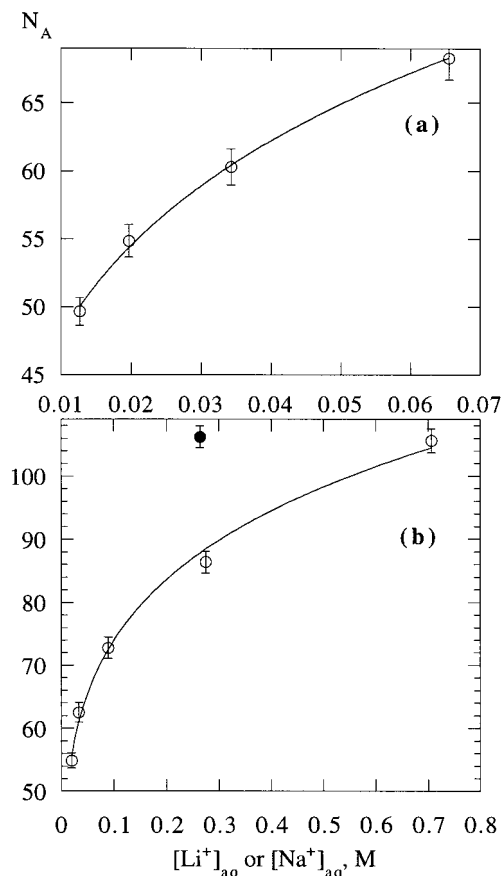
**Figure 1.** Aggregation numbers of LiDS micelles versus quencher concentration for  $[\text{LiDS}]/[\text{LiCl}]$ , in units of millimolar, as follows: (a) 25/0, 50/0, 100/0, and 200/0 for the sets of points from the bottom to the top, respectively, and (b) 50/0, 50/15.4, 50/72.3, 50/258, and 50/690. The filled circles in (b) nearly coincident with the data for  $[\text{LiDS}]/[\text{LiCl}] = 50/690$  mM/mM are measurements on a sample  $[\text{LiDS}]/[\text{NaCl}] = 50/250$  mM/mM.

$= 250$  mM. Thus, LiCl concentrations much higher than NaCl concentrations are required to produce a micelle of the same size.

Figure 2 shows the variation of  $N_A$  with  $[\text{Li}^+]_{\text{aq}}$  for samples (a) varying  $[\text{LiDS}]$  with no added salt and (b) varying added  $[\text{LiCl}]$  with  $[\text{LiDS}] = 0.05$  M. The solid lines are linear least-squares fits of the data to eq 1 yielding (a)  $\kappa_2 = 115 \pm 2$  and  $\gamma = 0.19 \pm 0.01$  (no added LiCl) and (b)  $\kappa_2 = 111 \pm 2$  and  $\gamma = 0.18 \pm 0.01$  (added LiCl). Fitting all of the data to eq 1 yields  $\kappa_2 = 112 \pm 1$  and  $\gamma = 0.18 \pm 0.005$  (both with and also without added LiCl) the uncertainties being calculated from the fits in the usual way.<sup>16</sup> Also included in Figure 2b is the data point (solid circle) for NaCl added to LiDS illustrating the fact that  $\text{Na}^+$  induces faster growth in dodecyl sulfate micelles. The solid circle is predominantly an “SDS micelle” data point lying far from the data corresponding to LiDS micelles, as expected. Clearly, here as in the case of SDS,<sup>1</sup> eq 1 is an excellent description of the growth of LiDS micelles with increasing surfactant or added salt.

Table 2 gives the values of  $N_A$  measured in this work together with the values predicted by eq 1 with  $\kappa_2 = 112$  and  $\gamma = 0.18$ . From the definition preceding eq 4,  $N_A^0 = \kappa_2(\text{cmc}_0)^\gamma = 47.0$  which, within the uncertainties involved, is equal to  $N_A^0 = 49.5$  for SDS.<sup>2</sup> Thus, SDS and LiDS micelles are the same size at the  $\text{cmc}_0$ , both grow according to the power law eq 1; however, SDS micelles grow faster.

Figure 3 shows a comparison between the values of  $N_A$  measured in this work, shown as filled circles, and literature



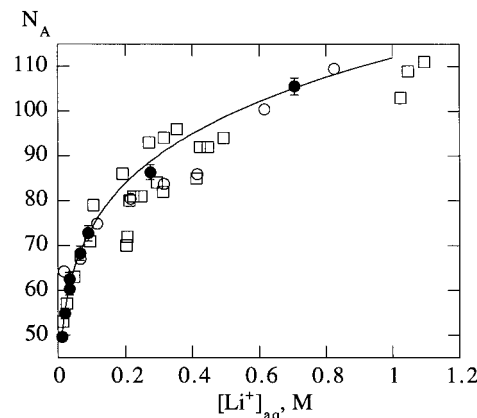
**Figure 2.** Aggregation numbers of LiDS micelles versus  $[\text{Li}^+]_{\text{aq}}$  for samples in which (a) the concentration of LiDS is varied in the absence of LiCl and (b)  $[\text{LiDS}] = 50$  mM and the concentration of LiCl is varied. The data point plotted as the solid circle is due to the sample in which  $[\text{LiDS}] = 50$  mM and  $[\text{NaCl}] = 250$  mM. The solid circle is predominantly an “SDS micelle” data point lying far from the data corresponding to LiDS micelles, as expected. The solid lines are linear least-squares fits of the data to eq 1.

**TABLE 2: Aggregation Numbers of LiDS Micelles ( $T = 25$  °C)**

[LiDS], mM	[LiCl], mM	[NaCl], mM	$N_A$	eq 1
25	0	0	$49.6 \pm 1.0$	51.0 <sup>a</sup>
50	0	0	$54.9 \pm 1.2$	55.2 <sup>a</sup>
100	0	0	$60.3 \pm 1.3$	61.0 <sup>a</sup>
200	0	0	$68.3 \pm 1.6$	68.6 <sup>a</sup>
50	15.4	0	$62.5 \pm 1.6$	60.9 <sup>a</sup>
50	72.3	0	$72.8 \pm 1.7$	72.6 <sup>a</sup>
50	258	0	$86.4 \pm 1.7$	88.8 <sup>a</sup>
50	690	0	$105.6 \pm 1.9$	105.2 <sup>a</sup>
50	0	250	$106.2 \pm 1.7$	117.5 <sup>b</sup>

<sup>a</sup>  $\kappa_2 = 112$ ,  $\gamma = 0.18$ ; this work. <sup>b</sup>  $\kappa_2 = 164$ ,  $\gamma = 0.25$ ; ref 1.

values derived from two sets of small-angle neutron scattering (SANS) measurements. The square symbols, data due to Chen<sup>17</sup> taken at 37 °C, are plotted directly from Table 1 of ref 17. A few measurements by Chen<sup>17</sup> at lower temperatures show that a correction to 25 °C would involve adding 3–4 molecules to the values of  $N_A$ ; however, these corrections would not be significant on the scale of Figure 3. The open circles are data due to Berr and Jones<sup>18</sup> multiplied by a factor of 1.2. These authors<sup>18</sup> were not concerned with absolute values; rather, they were concentrating on the differences in the effect of  $\text{Na}^+$  and  $\text{Li}^+$  on the dodecyl sulfate micelle. For this reason and those discussed in ref 1, the absolute values of  $N_A$  are not reliable.



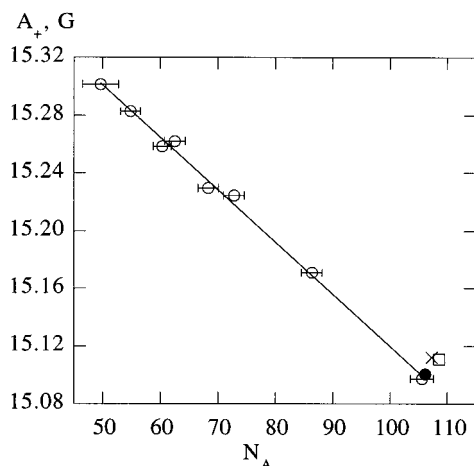
**Figure 3.** Aggregation numbers of LiDS micelles versus  $[\text{Li}^+]_{\text{aq}}$  from TRFQ measurements (●) varying either surfactant or salt, this work; from SANS<sup>17</sup> measurements (□) varying either surfactant or salt, and SANS<sup>18</sup> measurements multiplied by 1.2 (○) varying salt. The solid line is eq 1 with  $\kappa_2 = 112$  and  $\gamma = 0.180$ .

We arrived at the factor 1.2 in the following way: since Berr and Jones<sup>18</sup> measured the values of  $N_A$  for both SDS and LiDS in the same experiment, we fit their SDS data to eq 1 yielding  $\kappa_2 = 136$  and  $\gamma = 0.25$  ( $r = 0.968$ ). Comparing these results with  $\kappa_2 = 164$  and  $\gamma = 0.25$  previously found to fit a wide variety of experiments,<sup>1</sup> we may bring the results of Berr and Jones<sup>18</sup> into agreement with other experiments by multiplying by a factor of  $164/136 = 1.2$ . We make the assumption that this scaling factor appropriate for SDS would also be appropriate for LiDS. At any rate, the purpose of the scaling is to be able to compare the functional dependence of  $N_A$  on  $[\text{Li}^+]_{\text{aq}}$  between the three sets of data in Figure 3. The agreement between the present TRFQ data and SANS data is rather good taking into account the difficulties in both methods.

**EPR.** The same nitroxide spin probe used previously,<sup>2</sup> 5-doxylstearic acid methyl ester (5DSE) was purchased from Sigma and used as received. Three-line narrow EPR spectra of 5DSE in LiDS micelles typical of nitroxide free radicals undergoing approximately isotropic motion in the motional narrowing region were observed under all conditions in this work. See Figure 1a of ref 2. The nitrogen hyperfine coupling constant,  $A_0$ , in magnetic field units, is approximately equal to one-half the difference in the resonance fields of the high- and low-field lines. There begin to be small departures of  $A_0$  from the true hyperfine coupling constants as the rotational correlation times increase due to increasing viscosity in larger micelles. These departures are due to second-order shifts in the line positions discussed previously.<sup>2</sup> Therefore, for purposes of measuring the polarity of the micelle surface, the difference in resonance fields between the center and low-field lines,  $A_+$ , is preferred because it is less affected by second-order shifts. Under the conditions of this experiment, the second-order shifts in  $A_+$  are negligible.<sup>2</sup>

Figure 4 shows the variation of  $A_+$  with  $N_A$  on the same set of samples in Table 1, except using the probe 5DSE rather than pyrene. The solid line is a linear least-squares fit to the data yielding  $A_+ = 15.482 - 0.00362N_A$ , with  $A_+$  in gauss. The linearity of these data is an accident, a departure from the theory; however, this linearity could be used to measure relative aggregation numbers in LiDS micelles. The filled circle is the data point from the 50 mM LiDS 250 mM NaCl sample; i.e., the sample producing the filled circles in Figures 1b and 2b. Were the data in Figure 4 plotted as a function of ionic strength, the NaCl data point would lie distant from the locus of the other





**Figure 4.** Hyperfine spacing between the center- and low-field lines of the spin probe 5DSE,  $A_+$ , versus the aggregation number measured by TRFQ: (○) [LiDS]/[LiCl]; (●) [LiDS]/[NaCl] samples detailed in Table 1. Data from ref 2 for (×) the [SDS]/[NaCl] = 100/156 mM/mM and (□) [SDS]/[NaCl] = 50/178 mM/mM plotted against  $N_A$  calculated from eq 1 using parameters appropriate for SDS,  $\kappa_2 = 164$  and  $\gamma = 0.25$ .

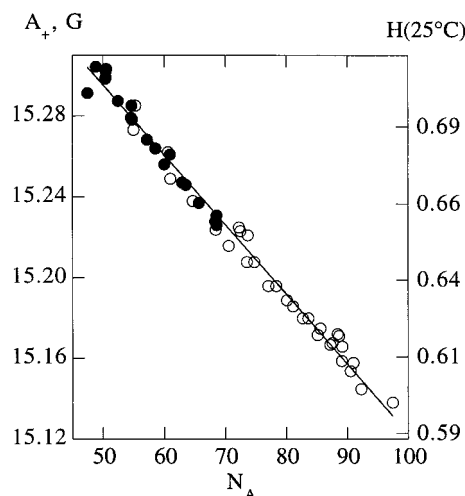
data, similar to Figure 2b. Figure 4 emphasizes the point that the polarity of the micelle surface is determined to an excellent approximation by the aggregation number of the micelle and not by the ionic strength which differs by a factor of 2.8 for the open versus the filled circle near  $N_A = 106$ . Two further points are plotted in Figure 4 taken from ref 2; the cross is a data point for a sample with 100 mM SDS and 156 mM NaCl, while the open square corresponds to 50 mM SDS and 178 mM NaCl. The abscissa for these latter two points is eq 1 appropriate for SDS; i.e.,  $\kappa_2 = 164$  and  $\gamma = 0.25$ . For a given value of  $N_A$ , the value of  $A_+$  is almost the same for LiDS  $\pm$  LiCl, LiDS  $\pm$  NaCl, and SDS  $\pm$  NaCl; however, it appears that, near  $N_A = 110$ , the points derived from LiDS are slightly below those derived from SDS.

Since the aggregation numbers for LiDS are well predicted by eq 1, we may use eq 1 to conveniently carry out more extensive EPR measurements. Typical measurements are given in Figure 5 varying [LiDS] without adding LiCl (solid circles) or varying [LiCl] at constant [LiDS] (open circles). The solid line is a fit:  $A_+ = (15.468 \pm 0.004) - (0.00345 \pm 0.00006)N_A$ . The separate data points are derived from measurements of different sample preparations. The reproducibility from a given sample is better than the size of the plotting symbols. For some reason, for LiDS, the data are slightly less reproducible from one sample preparation to the next than in the case of SDS as judged by spread of the data points in Figure 5 compared with Figures 2 and 3 of ref 2. For either SDS or LiDS, the limiting factor in determining  $N_A$  is the accuracy of the TRFQ (or other) measurements.

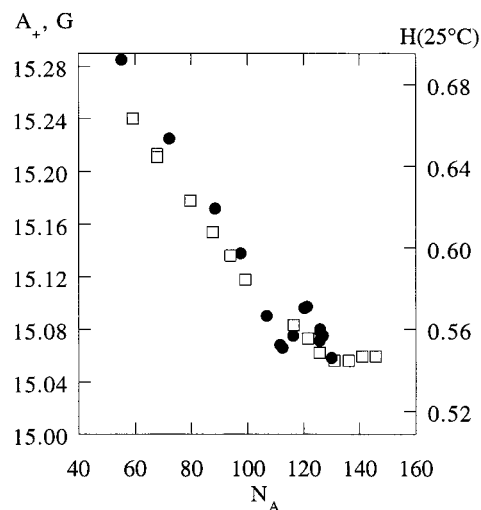
**Dependence of  $A_+$  on the Polarity Index  $H(25^\circ\text{C})$ .** Mukerjee and co-workers<sup>3</sup> introduced a polarity index denoted by  $H(25^\circ\text{C})$  defined to be the ratio of molar concentration of OH dipoles in a solvent or solvent mixture to that in water. Previously,<sup>2</sup> we showed that  $A_+$  is a linear function of  $H(25^\circ\text{C})$  as follows:

$$A_+(H) = 14.210 + 1.552H(25^\circ\text{C}) \quad (12)$$

for values of  $H(25^\circ\text{C}) = 0.446\text{--}0.828$ . Thus, measurements of  $A_+$  yield values of  $H(25^\circ\text{C})$ . These values are given as the right-hand ordinates of Figures 5 and 6.



**Figure 5.** Hyperfine spacing  $A_+$  for 5DSE versus the aggregation number calculated from eq 1 using parameters appropriate for LiDS,  $\kappa_2 = 112$  and  $\gamma = 0.18$ : (●) varying [LiDS] in the absence of LiCl and (○) varying [LiCl] with [LiDS] fixed at either 50 or 100 mM. The line is a linear least-squares fit yielding  $A_+ = (15.468 \pm 0.004) - (0.00345 \pm 0.00006)N_A$ . The right-hand ordinate is the polarity index  $H(25^\circ\text{C})$ , computed from eq 12.



**Figure 6.** Hyperfine spacing for 5DSE versus aggregation number of (●) LiDS micelles by varying LiCl to a maximum of [LiCl] = 2.27 M and of SDS micelles (□) taken from ref 2 varying NaCl to a maximum of [NaCl] = 0.59 M. The abscissa is computed from eq 1 using the values appropriate to LiDS,  $\kappa_2 = 112$  and  $\gamma = 0.18$ , or to SDS,  $\kappa_2 = 164$  and  $\gamma = 0.25$ , respectively. Above  $N_A = 106$  and 130, for LiDS and SDS, respectively, eq 1 no longer applies, so the true aggregation numbers are larger than those read from the abscissa. The solubility limit of LiCl in LiDS solutions did not permit extending the measurements above  $N_A = 130$  where the sphere-rod transition takes place in SDS micelles. The "transitions" in the LiDS data near  $N_A = 112$  and 117 are reproducible. The nearly coincident data points in the range  $N_A = 110\text{--}130$  are derived from measurements of the two sample preparations. The reproducibility of the data points from a single sample is smaller than the symbol size. The right-hand ordinate is the polarity index  $H(25^\circ\text{C})$ , computed from eq 12.

**Search for a Sphere-Rod Transition in LiDS Micelles.** In SDS, at values of  $N_A$  above 130 ( $[\text{Na}^+]_{\text{aq}} \approx 0.4\text{ M}$ ), the values of  $A_+$  no longer increased with micelle size.<sup>2</sup> This was interpreted<sup>2</sup> as being the sphere-rod transition, the leveling of  $A_+$  being due to the fact that the surface hydration per surfactant molecule no longer decreased with micelle size. After the TRFQ measurements were finished, it became clear that those mea-

measurements were not carried out at sufficiently high salt concentrations to reach the critical size of  $N_A = 130$ . Therefore, the failure to observe<sup>17,18</sup> a sphere-rod transition in LiDS is because experiments had never been extended to large enough salt concentrations. If eq 1 were to hold up to  $N_A = 130$ , then we may predict that a salt concentration of 2.3 M would be required. Therefore, we made a few measurements of  $A_+$  on a sample of 53 mM LiDS with LiCl added to higher concentrations as shown by the filled circles in Figure 6. The abscissa is computed using eq 1; however, we must keep in mind that eq 1, is quantitative only up to about  $N_A = 106$ . The highest two LiCl concentrations (1.92 and 2.27 M, respectively) were prepared by heating the samples to 50 °C and stirring for a few minutes. The samples remained transparent during the measurements, but turned cloudy a few hours later at room temperature ( $22 \pm 2$  °C). A second experiment with freshly prepared samples showed that the data are reproducible; the nearly coincident data points in the range  $N_A = 110-130$  are derived from measurements of the two sample preparations. The reproducibility of the data points from a single sample is smaller than the symbol size. Selected SDS data from ref 2 are also plotted in Figure 6 for comparison. The highest salt concentration used in the SDS work<sup>2</sup> was 0.59 M.

We did not pursue the high-salt region further because it would take us afield from our purposes; however, it might prove to be interesting to study in the future.

**Hydration Model.** In solvent systems in which water is the only source of OH dipoles,  $H(25$  °C) is just the volume fraction of the solvent system occupied by water,

$$H(25\text{ °C}) = \frac{30N(\text{H}_2\text{O})}{V} \quad (13)$$

where  $N(\text{H}_2\text{O})$  is the number of water molecules within the volume  $V$  ( $\text{\AA}^3$ ), taking the volume of a water molecule to be  $30 \text{ \AA}^3$ . Given a model to compute the volume  $V$ , measured values of  $H(25$  °C) may be converted into values of  $N(\text{H}_2\text{O})$ .

Previously,<sup>2</sup> we constructed a simple geometrical model to compute values of  $H(25$  °C) as a function of  $N_A$ . The model is based upon a classical picture of the micelle as having a hydrocarbon core with very little water penetration<sup>19</sup> surrounded by a polar shell. The nitroxide moiety of the spin probe 5DSE executes rapid, almost isotropic motion<sup>20</sup> which is assumed to sample all portions of the polar layer. Thus, the volume sampled by the spin probe is the volume of the polar shell. Writing eq 13 in terms of the volume in the polar shell per surfactant molecule,  $V_p$ ,

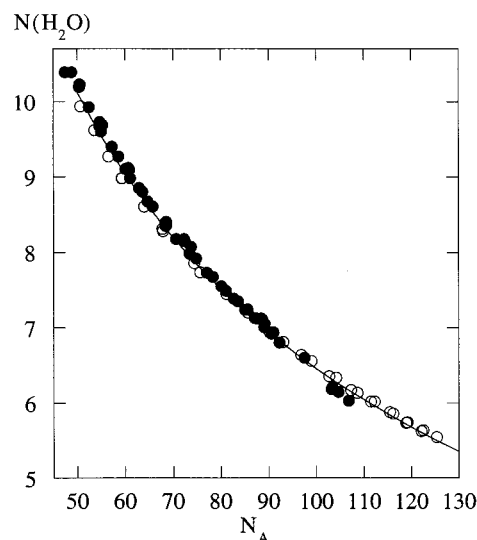
$$H(25\text{ °C}) = \frac{30N(\text{H}_2\text{O})}{V_p} \quad (14)$$

where  $N(\text{H}_2\text{O})$  is the number of water molecules housed in this shell per surfactant molecule.

In this model the inner spherical hydrocarbon core has a radius,  $R_c$ , that is determined by the volume of the surfactant alkyl chains. The thickness of the polar shell,  $R_m - R_c$ , where  $R_m$  is the radius of the micelle, is taken to be constant. The volume of the core is taken to be  $N_A V_{\text{tail}}$ , where  $N_A$  is the aggregation number and  $V_{\text{tail}}$  is the volume occupied by the saturated hydrocarbon chain, calculated according to Tanford (p 52 of ref 21) as

$$V_{\text{tail}} = 27.4 + 26.9N_c \quad (15)$$

where  $V_{\text{tail}}$  is in cubic angstroms and  $N_c$  is the number of carbon



**Figure 7.** The number of water molecules per surfactant molecule residing in the polar shell of LiDS micelles (●) (this work) and of SDS (○) (ref 2) computed from eqs 12, 14, 16, and 17 using a constant polar shell thickness of  $5 \text{ \AA}$ <sup>22</sup> for both types of micelles. The solid line is the theoretical prediction of the geometric model, eq 18, with the volume inaccessible to water fixed at  $V_{\text{dry}} = 134 \text{ \AA}^3$ .

atoms per chain that are embedded in the micelle core. Thus, the core radius is found from

$$N_A V_{\text{tail}} = \frac{4\pi}{3} R_c^3 \quad (16)$$

The volume per surfactant molecule in the polar shell,  $V_p$ , is given by

$$V_p = \frac{4\pi}{3N_A} (R_m^3 - R_c^3) \quad (17)$$

We take  $N_c = N$ , the total number of carbons in the alkyl chain in keeping with adopting the simplest approach, yielding  $V_{\text{tail}} = 350 \text{ \AA}^3$ . See the details of the assumptions and the calculations in ref 2.

Figure 7 gives the values of  $N(\text{H}_2\text{O})$  for LiDS micelles derived from measured values of  $A_+$  employing eqs 12, 14, 16, and 17. The polar shell thickness was taken to be  $5 \text{ \AA}$  (constant) to conform to SANS measurements.<sup>22</sup> For comparison, some representative data for SDS micelles are included.<sup>2</sup> Note that while the absolute value of the ordinate depends on the model, the values of  $N(\text{H}_2\text{O})$  in LiDS relative to those in SDS are model independent.

The theoretical prediction of the values of  $N(\text{H}_2\text{O})$  is

$$N(\text{H}_2\text{O}) = (V_p - V_{\text{dry}})/30 \quad (18)$$

where  $V_{\text{dry}}$  is the volume per surfactant molecule inaccessible to water. The solid line in Figure 7 is the theoretical prediction of the geometrical model by fixing  $V_{\text{dry}} = 134 \text{ \AA}^3$ . See ref 2 for a discussion of the comparison of theoretical and experimental values of  $N(\text{H}_2\text{O})$ . Briefly, values of  $N(\text{H}_2\text{O})$  are dependent upon the model employed for the micelle as well as the numerical values of the parameters, notably  $N_c$  and the thickness of the polar shell. Therefore, Figure 7 ought not be taken to prove that a hydration number near  $N_A = 100$  of about  $N(\text{H}_2\text{O}) = 6$  is better than, say,  $N(\text{H}_2\text{O}) = 7$ . The important point is that a simple model with reasonable assumptions after fixing one

parameter gives the rate of decrease of polarity with micelle size consistent with experiment in both SDS and LiDS.

## Discussion

**The Method.** Two potential problems<sup>2</sup> in applying the method turned out to be unimportant. First, specific cation effects on the value of  $A_+$  are small. This was a concern; in aqueous and methanolic solutions, dissolved salts had been found to produce small changes in the values of  $A_+$  for small, neutral, water-soluble spin probes.<sup>23,24</sup> Depending upon the salt and the solution, values of  $A_+$  could increase or decrease.<sup>23</sup> Neglecting such effects appears to be sound. Second, treating waters of hydration and "free" water together in the calculation of  $H(25\text{ }^\circ\text{C})$  might have been worrisome; however, at least for these two cations, it seems not to be a problem. Provided that these two problems did not interfere, it was predicted that the hydration of LiDS and SDS micelles would be the same.

We repeat here an observation made previously:<sup>2</sup> in the model, it was supposed that the nitroxide moiety sampled all of the polar shell and only the polar shell. The fact that the model gives reasonable results for  $N(\text{H}_2\text{O})$  supports this view. The spin probe 5DSE is quite hydrophobic except for the NO group. It seems reasonable that the hydrophilic NO group of 5DSE resides in the polar shell because, in order for the group to range very far outside the polar shell, either the hydrophobic moieties attached to the NO group would have to be dragged out into the hydrophilic region or the hydrophilic NO group would have to reside in hydrophobic region contrary to the findings of Mukerjee and co-workers.<sup>25</sup> Nevertheless, any rapid motion involving excursions of the NO group into the hydrocarbon core and into the aqueous region would involve averaging values of  $H(25\text{ }^\circ\text{C})$  near unity and zero, respectively, and would be difficult to detect. For example, excursions of equal probability into these regions would yield  $H(25\text{ }^\circ\text{C}) = 0.5$  which would have to be averaged, with the appropriate statistical weight, with the values of  $H(25\text{ }^\circ\text{C})$  appropriate to the polar shell. It is clear from Figure 5 that such excursions would affect the reported polarity minimally since  $H(25\text{ }^\circ\text{C}) = 0.5$  is similar to the values reported.

The remarks in the previous paragraph would apply to any spin probe composed only of hydrophobic moieties except for the NO group. In particular, the entire series of doxylstearic acid esters with the doxyl attached at various carbon atoms ought to report about the same polarity in an LiDS micelle. In contrast, the doxylstearic acids, particularly those labeled near the charged carboxyl group, would possess an additional hydrophilic moiety which would be expected to alter the average location of the NO group, possibly leading to different results.

**Relative Aggregation Numbers.** The micropolarity sensed by the 5DSE probe depends directly on the aggregation number of the LiDS micelle and not on the ionic strength of the solution. This is demonstrated by the fact that for a given value of  $N_A$  attained using different combinations of  $[\text{LiCl}]$  and  $[\text{LiDS}]$ , the method yields the same value of  $A_+$ . This means that the polarity of the surface of the micelle is independent of  $[\text{LiCl}]$  except through the salt's role in determining  $N_A$ . The micropolarity for a given value of  $N_A$  is also independent of the number of micelles in solution, within the limits of these experiments; that is, interactions between micelles do not affect the surface polarity.

A linear least-squares fit of all of the data over the range  $N_A = 50\text{--}100$  yields

$$A_+ = 15.468 - 0.00345 N_A \quad (19)$$

See ref 2 for a discussion of the factors that control the precision in the determinations of relative aggregation numbers. For LiDS micelles, as was the case for SDS micelles, it is relatively easy to attain a relative precision of  $\pm$ one molecule.

**Growth of Dodecyl Sulfate Micelles.** The fact that all of the normal sodium alkyl sulfates from 8 to 12 carbons follow a growth law<sup>1</sup> of the form of eq 1 is interesting. This work shows that LiDS may also be added to the family of micelles exhibiting such growth. Is this type of growth an accident, or does it have theoretical significance? Given the dependence of  $\kappa_2$  and  $\gamma$  on the cation, it would seem to be worthwhile to study other cations to provide an experimental guide to understanding the dependence theoretically.

There appear to be "transitions" of some kind near values of  $N_A \approx 112$  and 121 in LiDS micelles that are qualitatively different than in SDS. In SDS micelles, the sphere-rod transition occurred at  $N_A = 130$  ( $[\text{Na}^+]_{\text{aq}} \approx 0.4\text{ M}$ ); above this value of  $N_A$ ,  $H(25\text{ }^\circ\text{C})$  became constant. Here in LiDS micelles, LiCl is not sufficiently soluble to reach values of  $N_A$  above 130.

## Conclusions

The aggregation numbers of LiDS micelles as determined by TRFQ are well described by the power law, eq 1, with  $\kappa_2 = 112 \pm 2$  and  $\gamma = 0.180 \pm 0.005$  whether the concentration of  $\text{Li}^+$  in the aqueous phase is provided by LiDS or both LiDS and LiCl. The maximum deviation of the measured values of  $N_A$  from those predicted by eq 1 is two molecules; however, the absolute accuracy of the aggregation numbers is limited by the uncertainties in the method which we estimate to be  $\pm 5\%$ . The polarity of LiDS micelles as reported by values of  $A_+$  for the spin probe 5DSE depends on the micelle aggregation number only; not on the combination of surfactant and salt concentrations. Over the range  $N_A = 50\text{--}100$  molecules, a measurement of  $A_+$  and the use of eq 18 lead to relative values of  $N_A$  precise to within about one molecule. The same model describing the dehydration of the SDS micelle surface provides an excellent description of the hydration of the LiDS micelle without introducing any adjustable parameters.

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