

# Articles

## Size, Hydration, and Shape of SDS/Heptane Micelles Investigated by Time-Resolved Fluorescence Quenching and Electron Spin Resonance

Radha Ranganathan,\* Miroslav Peric, Rosa Medina, Ulises Garcia, and Barney L. Bales

Department of Physics, California State University Northridge (CSUN), Northridge, California 91330

Mats Almgren

Department of Physical Chemistry, Uppsala University, Uppsala S-75121, Sweden

Received February 12, 2001. In Final Form: August 13, 2001

Time-resolved fluorescence quenching (TRFQ) and electron spin resonance (ESR) are used to investigate sodium dodecyl sulfate/heptane micelles in water in the presence of varying amounts of sodium chloride (NaCl). Aggregation numbers are obtained from TRFQ and the micelle hydration from ESR. At any zero or any fixed sodium chloride concentration  $\leq 375$  mM, micelles grow with heptane while maintaining the volume fraction of water in the polar shell of the micelle, referred to as hydration index, constant. Core-shell model calculations, using simple geometry, show that some hydrocarbon density extends into the polar shell. The shell comprises about 15–17% of the core hydrocarbon in addition to the headgroups and hydration water. The rate of micelle growth with sodium chloride is smaller in the presence of heptane, and at higher salt concentrations ( $>375$  mM), the micelles decrease in size with heptane. The rate of variation of hydration index with [NaCl] or aggregation number is indicative of micelle shape and shows that the sphere-to-rod transformation occurs at higher aggregation numbers and higher salt concentrations when heptane is present.

### Introduction

Solubilization of compounds otherwise sparingly soluble or insoluble in water is the phenomenon behind most technical applications of micelles,<sup>1,2</sup> and various aspects of solubilization have been studied extensively. Some examples are the extent of solubilization and its dependence on the chemical natures of surfactant and solubilize, localization of the solubilize within the micelle, changes of size of micelles, and phase changes that occur in micellar systems upon addition of solubilizes. This work is concerned with sodium dodecyl sulfate (SDS) micelles and changes of the micelle and its properties, in particular of the micelle–water interface, induced by the dissolution of a saturated hydrocarbon, heptane. The investigation is a follow-up of an old study, by static fluorescence quenching, of the effects of solubilizes on the size of SDS micelles.<sup>3</sup> It was then concluded that, upon solubilization of nonpolar hydrocarbons that increase the volume of the nonpolar core of the micelle, the micelle responded by growing so that the density of charged surfactants at the micelle–water interface remained approximately unchanged. The scope of the present study is wider, due to the complementary use of the tech-

niques of time-resolved fluorescence quenching (TRFQ), to determine the aggregation number and bimolecular collision rates of micellar additives, and electron spin resonance (ESR), to determine the micelle hydration and microviscosity of the micelle–water interface. This work is an extension of our program to use multiple tools to develop physical models for micelles and also characterize them as variable reaction media.<sup>4</sup> The ESR and TRFQ techniques are well established. The determination of aggregation numbers by TRFQ has been reviewed.<sup>5,6</sup> In the past few years, ESR measurements of spin probes incorporated in micelles have been shown to provide new information on micelles, based on a hydration model.<sup>7–10</sup> A line shape analysis of the ESR lines yields a measure of the polarity, to an unprecedented degree of sensitivity, of the environment of the spin probe. This is expressed by  $H$ , the volume fraction of water or, more precisely, of OH dipoles, in the vicinity of the spin probe. A spin probe incorporated in a micelle senses the amount of water dipoles in its environment. Because of their

\* Corresponding author. E-mail radha.ranganathan@csun.edu.  
(1) McBain, M. E. L.; Hutchinson, E. *Solubilization and Related Phenomena*; Academic Press: New York, 1955.  
(2) Mittal, K. L.; Mukerjee, P. *Micellization, Solubilization, and Microemulsions*; Plenum: New York, 1977.  
(3) Almgren, M.; Swarup, S. *J. Phys. Chem.* **1982**, *86*, 4212.

(4) Bales, B. L.; Ranganathan, R. *J. Phys. Chem. B* **2001**, *105*, 7465.  
(5) Gehlen, M. H.; De Schryver, F. C. *Chem. Rev.* **1993**, *93*, 199.  
(6) Almgren, M. *Adv. Colloid Interface Sci.* **1992**, *41*, 9.  
(7) Bales, B. L.; Shahin, A.; Lindblad, C.; Almgren, M. *J. Phys. Chem. B* **2000**, *104*, 256.  
(8) Bales, B. L.; Howe, A. M.; Pitt, A. R.; Roe, J. A.; Griffiths, P. C. *J. Phys. Chem. B* **2000**, *104*, 264.  
(9) Bales, B. L.; Stenland, C. *Chem. Phys. Lett.* **1992**, *200*, 475.  
(10) Bales, B. L.; Messina, L.; Vidal, A.; Peric, M.; Nascimento, O. R. *J. Phys. Chem.* **1998**, *102*, 10347.

polarity, spin probes are believed to be localized at the micelle/water interface and sense the water associated with the micelle surface. In other words,  $H$  gives a measure of the micelle hydration. In the core-shell model of a micelle, the interface is a shell of headgroups, water, and counterions that surrounds a core comprised of the hydrocarbon tails of the surfactant molecules. In the particular case of micelles therefore  $H$  is defined by the volume fraction of water in the polar shell of the micelle, that is

$$H = \frac{V_w}{V_{\text{shell}}} \quad (1)$$

where  $V_{\text{shell}}$  is the volume of the polar shell and  $V_w$  is the volume occupied by the water in the shell. In addition, ESR line shape studies yield the rotational correlation times,  $\tau_B$  and  $\tau_C$ , of the spin probe.<sup>11</sup>

We present results of measurements of aggregation number, hydration index,  $\tau_B$ , and  $\tau_C$  of SDS/heptane micelles in water with and without sodium chloride. The observed dependence of aggregation numbers on heptane and sodium chloride concentrations is largely in accord with earlier observations. The novel features of the present work are the introduction of the hydration index as a characteristic of micelles with solubilizates and the complementary interpretation of TRFQ and ESR data to define the micelle better both quantitatively and qualitatively. The main result of the experiments is that micelles grow linearly with the addition of heptane, but the volume fraction of water in the polar shell ( $H$ ) remains constant. Fitting our data to the core-shell model shows that the hydrocarbon density extends out into the polar shell. The derived features are consistent with expectations from molecular dynamics simulations.

### Experimental Section

**Samples.** TRFQ measurements were carried out with pyrene as probe (Aldrich) and dimethylbenzophenone (DMBP; Aldrich) as quencher. 5-Doxylstearic acid methyl ester (5-DSE, Sigma) was used as the spin probe. The surfactant studied was sodium dodecyl sulfate (Lancaster Synthesis, Inc., of purity 99%) with *n*-heptane (Fisher Scientific Co.) in the presence of sodium chloride (Aldrich). The materials were not purified further. Fresh doubly distilled water was used as the solvent. The SDS concentration in all samples was 100 mM. The various heptane concentrations studied were 6, 12, and 17 mM. For each of the SDS/heptane, measurements were conducted at NaCl concentrations in the range 0–500 mM, in incremental steps of about 25 mM. The pyrene concentration in the samples prepared for TRFQ experiments was kept at about 1/50 of the concentration of micelles. The average quencher concentration was about 1.25 quenchers per micelle for a 100 mM SDS solution in water in the absence of heptane and NaCl. The 5-DSE concentration in the samples for ESR was 1/500 of the total detergent concentration. TRFQ experiments were also carried out on selected SDS/heptane concentrations to check for dependence, if any, on quencher concentration.

**Methods. a. TRFQ.** The fluorescence decay curves of pyrene were obtained using an FL900 lifetime measurement spectrometer of Edinburgh Analytical Instruments (EAI). The decay curves were corrected for instrument response and fitted to the Infelta-Tachiya model,<sup>5,12,13</sup> using the Level 2 analysis software of EAI. The details of the experimental setup and the procedure for recovering the aggregation numbers are described in our previous

publication<sup>14</sup> and are not repeated here. All measurements were conducted at 25 °C.

**b. ESR.** ESR spectra were taken at X-band using a Bruker ESP 300 E spectrometer equipped with a Bruker variable temperature unit (model B-VT-2000). The details of sample configuration for ESR have been described previously.<sup>10</sup> The temperature of the sample was measured with an Omega temperature indicator (model DP41-TC-S2) and was kept constant at 25 °C within  $\pm 0.1$  °C. Three ESR spectra were acquired for each sample. Fittings of the experimental ESR lines to a Lorentzian-Gaussian sum function were performed using the program LOWFIT. This yields the position of the resonance fields of the three ESR lines with a precision of a few milligauss and also separates the Lorentzian and Gaussian contributions of the spin-label ESR lines. The spacing,  $A_+$ , between the first two lines in the ESR is a linear function of the hydration  $H$  (25 °C) as follows:<sup>10</sup>

$$A_+(H) = 14.210 + 1.552H(25\text{ }^\circ\text{C}) \quad (2)$$

for values of  $H(25\text{ }^\circ\text{C}) = 0.446\text{--}0.828$ . Thus, values of  $H(25\text{ }^\circ\text{C})$  can be found from the nitrogen hyperfine coupling constant  $A_+$ . The spectral fitting and the stability of the magnetic field gives high precision in  $A_+$  and hence in  $H$ .

The ESR line widths yield the rotational correlation times  $\tau_C$  and  $\tau_B$  of the spin-label.<sup>15</sup> These times are a measure of the rates of rotational motion of the spin-label<sup>11</sup> and depend on the viscosity of its environment referred to here as the microviscosity of the polar shell.<sup>15</sup> The rotational correlation times derived from the spectra refer to the rotation of the spin-label in the laboratory frame, and this includes both the effects of the rotation of the spin-label itself and the rotation of the micelle as a whole. The microviscosity is calculated from the mean rotational correlation time,  $\tau_m$ , defined as  $(\tau_C\tau_B)^{1/2}$ , after correcting for micelle rotation,<sup>15</sup> using the Debye-Stokes-Einstein equation

$$\tau_m = \frac{4\pi\eta R^3}{3kT} \quad (3)$$

where  $\eta$  is the microviscosity of the spin-label neighborhood,  $R$  is the hydrodynamic radius of the spin-label ( $=4.68$  Å for 5-DSE),<sup>15</sup>  $k$  is the Boltzmann constant, and  $T$  is the sample temperature.

### Core-Shell Model and Calculations

The hydrocarbon volume in a micelle of aggregation number  $N$  is the sum of the contributions from the surfactants and heptane. In our calculations we take the micelle core to be a fraction  $(1 - f)$  of this total volume, while the rest of it is in the shell region. Molecular dynamics simulations for SDS micelles of  $N = 60$  show that there is an overlapping region in which the micelle carbon density decreases and the sulfate and water density increase.<sup>16</sup> Thus

$$V_{\text{core}} = (NV_{\text{tail}} + N_{\text{hep}}V_{\text{hep}})(1 - f) = \left(NV_{\text{tail}} + \frac{[\text{heptane}]}{[\text{micelles}]}V_{\text{hep}}\right)(1 - f) \quad (4)$$

where  $V_{\text{tail}}$  is the volume of the dodecyl chain of SDS (taken as  $350$  Å<sup>3</sup>)<sup>10</sup> and  $V_{\text{hep}}$  is the molecular volume of heptane ( $=246$  Å<sup>3</sup>).<sup>3</sup> The number of heptane molecules,  $N_{\text{hep}}$ , per micelle is given by

$$N_{\text{hep}} = \frac{[\text{heptane}]}{[\text{micelles}]} = \frac{[\text{heptane}]N}{[\text{SDS}] - [\text{SDS}_{\text{free}}]}$$

For a spherical micelle of radius  $R_{\text{mic}}$ , core radius  $R_{\text{core}}$ ,

(11) Schreier, S.; Polnaszek, C. F.; Smith, I. C. P. *Biochim. Biophys. Acta* **1978**, *515*, 375.

(12) Infelta, P. P.; Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1974**, *78*, 190.

(13) Tachiya, M. *Chem. Phys. Lett.* **1975**, *33*, 289.

(14) Ranganathan, R.; Tran, L.; Bales, B. L. *J. Phys. Chem. B* **2000**, *104*, 2260.

(15) Bales, B. L.; Stenland, C. *J. Phys. Chem.* **1993**, *97*, 3418.

(16) MacKerell, A. D. *J. Phys. Chem.* **1995**, *99*, 1846.

and polar shell thickness  $s$ , the total micelle volume,  $V_{\text{mic}}$ , is

$$V_{\text{mic}} = \frac{4\pi}{3} R_{\text{mic}}^3 = \frac{4\pi}{3} (R_{\text{core}} + s)^3 = \frac{4\pi}{3} \left( \left( \frac{3}{4\pi} V_{\text{core}} \right)^{1/3} + s \right)^3 \quad (5)$$

The polar shell volume is then

$$V_{\text{shell}} = V_{\text{mic}} - V_{\text{core}} \quad (6)$$

With the measured value of  $H$  from ESR, the total volume occupied by water in the polar shell may be written as  $HV_{\text{shell}}$ , eq 1. The number of water molecules per headgroup is then

$$\frac{N_w}{N} = \frac{V_w}{30N} = \frac{HV_{\text{shell}}}{30N} \quad (7)$$

The quantity  $V_w$  is in units of  $\text{\AA}^3$ . The number 30 is the volume of a water molecule in  $\text{\AA}^3$ . In addition to  $N_w$  or  $V_w$  other features of the polar shell may be derived. The polar shell comprises the headgroups with an almost constant fraction of the counterions that are required to neutralize the surfactant charges, water of hydration, and the overlapping hydrocarbon fraction  $f$  of  $V_{\text{core}}$ . Therefore,  $V_{\text{shell}}$  may also be written as

$$V_{\text{shell}} = V_w + V_{\text{hg}}N + fV_{\text{core}} \quad (8)$$

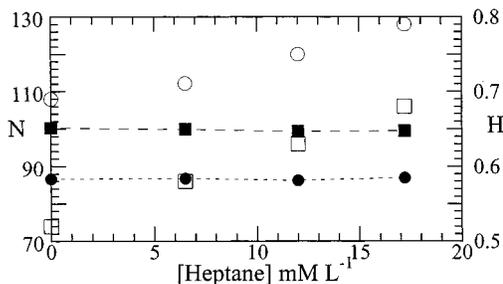
or equivalently

$$1 = H + \frac{NV_{\text{hg}}}{V_{\text{shell}}} + \frac{fV_{\text{core}}}{V_{\text{shell}}} \quad (9)$$

The volume per headgroup  $V_{\text{hg}}$  includes the headgroup volume plus a fraction of the volume of a counterion. The volume contributions from the counterions, and the apparent equivalence of hydration water and free water, have been discussed.<sup>17,18</sup> In our calculations the polar shell thickness,  $s$ , is set to be 5  $\text{\AA}$ , a value that fits the small-angle neutron scattering data,<sup>19,20</sup> the sulfur atom density distribution obtained in an MD simulation,<sup>16</sup> and the size of the sulfate group. Then letting  $V_{\text{hg}} = 66 \text{\AA}^3$  (the volume of the sulfate ion),  $V_{\text{shell}}$  may be obtained from eqs 4–6 and hence the fraction  $f$  from eq 9.

## Results and Discussion

Our main observation is presented in Figure 1. Numerical values are provided in Table 1. The precision in  $N$  is  $\pm 5\%$  and is determined from our measurements of  $N$  on several samples used in this and past studies. The aggregation number increases with [heptane], while the hydration remains constant for SDS/heptane micelles in water in the absence or presence of a fixed amount of NaCl. This behavior, shown only for  $[\text{NaCl}] = 0$  and  $[\text{NaCl}] = 150 \text{ mM}$ , is found at all  $[\text{NaCl}] \leq 375 \text{ mM}$ . The fraction  $f$  changes from 0.17 for 100 mM SDS with no heptane to 0.13 with 17 mM heptane. This is about the volume of two methylene groups. The numbers for SDS micelles compare very well with a molecular dynamics simulation.<sup>16</sup> From the graph of the density distributions of various atoms of an SDS micelle of aggregation number = 60, in the work referred to, the fraction of the total micelle carbon density

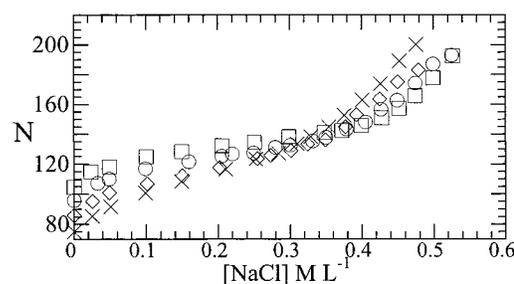


**Figure 1.** Dependence of aggregation numbers,  $N$  (open symbols, left side axis), and hydration index,  $H$  (filled symbols, right side axis), of SDS/heptane micelles on the concentration of heptane, for  $[\text{SDS}] = 100 \text{ mM}$ : (a) in the absence of NaCl ( $\square$ ,  $N$ ;  $\blacksquare$ ,  $H$ ) and (b) with  $[\text{NaCl}] = 150 \text{ mM}$  ( $\circ$ ,  $N$ ;  $\bullet$ ,  $H$ ). The dashed lines are meant to serve as a guide to the eye to show the invariance property of  $H$ .

**Table 1. Results of Calculations Based on the Core–Shell Model for the Data in Figure 1<sup>a</sup>**

[heptane], mM	$N$	$H$	$A/N, \text{\AA}^2$ <sup>b</sup>	$fV_{\text{core}}/V_{\text{shell}}^c$	$N_w/N^d$	$N$ at transition <sup>e</sup>
0	$74 \pm 4$	0.651	$50.3 \pm 2.2$	0.18	7	130
6.5	$86 \pm 4$	0.650	$50.2 \pm 2.1$	0.17	7	140
12.0	$96 \pm 5$	0.647	$50.1 \pm 2.1$	0.17	7	145
17.2	$105 \pm 6$	0.648	$50.2 \pm 2.0$	0.17	7	150

<sup>a</sup>  $[\text{SDS}] = 100 \text{ mM}$ ;  $[\text{NaCl}] = 0$ ;  $T = 25 \text{ }^\circ\text{C}$ . Also listed, in the final column, are the aggregation numbers at the sphere-to-rod transition that occurs at some added NaCl concentration. A change in the rate of variation of the micelle hydration is believed to be a sign of the onset of transformation to rodlike micelles.<sup>b</sup> Area per headgroup <sup>c</sup> Fractional volume of hydrocarbon in the polar shell. The fraction of total available hydrocarbon in the shell is  $f$ . <sup>d</sup> Number of water molecules per headgroup. <sup>e</sup> The aggregation number derived from TRFQ at that NaCl concentration when  $H$  begins to change from a monotonically decreasing to constant behavior.



**Figure 2.** Variation of aggregation numbers of SDS/heptane micelles with  $[\text{NaCl}]$ . The concentration of SDS is 100 mM. Symbols used identify the different heptane concentrations and are for  $[\text{heptane}] =$  (a) 0 ( $\times$ ), (b) 6.5 ( $\diamond$ ), (c) 12.0 ( $\circ$ ), and (d) 17.2 mM ( $\square$ ).

in the shell is estimated to be  $\approx 10\%$ . The hydrocarbon volume fraction in the shell, given by  $fV_{\text{core}}/V_{\text{shell}}$ , is found to vary only slightly with heptane. The calculated values of the area per headgroup,  $A/N$ , in the present study are also presented in Table 1 for  $[\text{NaCl}] = 0$ . While the same pattern of behavior, for  $N$  and  $H$ , as in Figure 1 is exhibited at other fixed salt concentrations, the calculated values of  $A/N$  do not remain invariant with heptane.

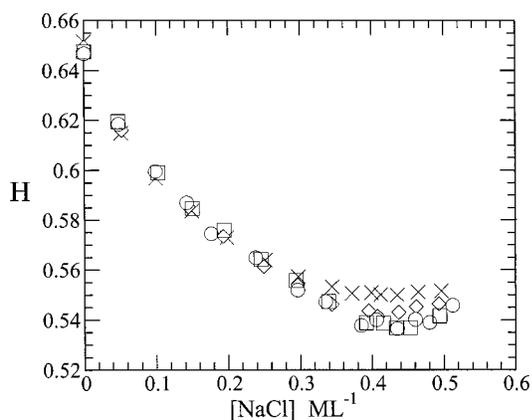
The growth of  $N$  with  $[\text{NaCl}]$  for four fixed concentrations of heptane is shown in Figure 2 and the corresponding values of the hydration index in Figure 3. Two distinct regions of growth and hydration are clearly exhibited. An initial slow growth accompanied by a decrease in hydration is followed by a rapid growth during which  $H$  is comparatively constant. The radius of the hydrophobic core is limited by the length of the stretched surfactant tail

(17) Lianos, P.; Zana, R. *J. Phys. Chem.* **1980**, *84*, 3339.

(18) Lianos, P.; Lang, J.; Zana, R. *J. Phys. Chem.* **1982**, *86*, 4809.

(19) Cabane, B.; Duplessix, R.; Zemb, T. *J. Phys. (Paris)* **1985**, *46*, 2161.

(20) Vass, S. *J. Phys. Chem. B* **2001**, *105*, 455.

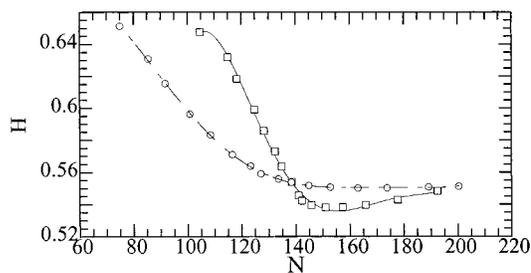


**Figure 3.** Variation of the micelle hydration index,  $H$ , of SDS/heptane micelles with  $[\text{NaCl}]$ . The concentration of SDS is 100 mM. Symbols used identify the different heptane concentrations and are for [heptane] (a) 0 (x), (b) 6.5 (◊), (c) 12.0 (○), and (d) 17.2 mM (◻).

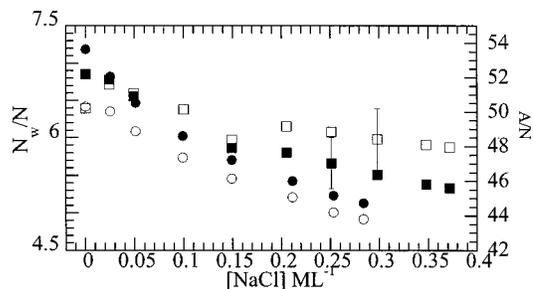
(i.e., 16.7 Å for the  $\text{C}_{12}$  tail of SDS<sup>21</sup>). A simple calculation shows that this corresponds to an aggregation number of 56, which means that the SDS micelles are not perfect spheres, not even in the absence of salt. If the micelles are to remain spherical, then the growth is limited by the need for filling the center of the micelle. There could be a number of rationales for this, without the need to invoke a specific nonspherical shape. The micelles are dynamic entities, and the average shape may well be spherical, even if each instantaneous shape is similar to an amoeba. The SDS molecule has an ether O between C and S, which is not strongly polar. It is possible that one of the monomers has this ether O buried in the core; this effect alone would increase the possible radius by 1.2 Å and the aggregation number to 69. Such effects may explain the finding from this and other studies, that the SDS micelle seems to grow slowly, presumably as a more or less globular entity, up to an aggregation number of 110–130 (radius 21–22 Å). In this range a change of behavior is observed, taken as a transition to rodlike micelles that grow more rapidly than spherical micelles. This change is seen as a sudden transition to a constant hydration index.

The rate of growth is observed to be smaller in the presence of heptane. As a result, there is a crossover in the behavior at about  $[\text{NaCl}] = 400$  mM. The aggregation number at higher salt concentrations actually decreases with addition of heptane. At these salt concentrations micelles are rodlike and probably quite polydisperse and the absolute values for the aggregation numbers derived from TRFQ may be invalid.<sup>22</sup> At the high salt concentrations, the relative values of  $N$ , however, are still useful in gathering the trends.

We can understand the effect of heptane as follows. As long as the globular micelles are far from the transition to rods, the presence of heptane in the core provides more hydrophobic volume and induces the uptake of more monomers while retaining the optimal volume fraction of water. On the other hand, when the micelles are rodlike at high salt concentrations, the effect of added heptane is to allow a transition to swollen micelles of spherical shape. Nonpolar solutes like heptane release the geometrical constraint, allowing the micelle to remain globular up to larger aggregation numbers, and thus shift the sphere-to-rod transformation to higher  $[\text{NaCl}]$  or aggregation numbers.



**Figure 4.**  $H$  decreases with micelle growth for globular micelles and becomes almost constant upon transformation to cylindrical micelles. The aggregation number at the transition is higher when heptane is included in the micelles.  $H$  vs  $N$  for SDS micelles (○) and for SDS with 17.2 mM heptane (◻). The lines are drawn just to guide the eye.



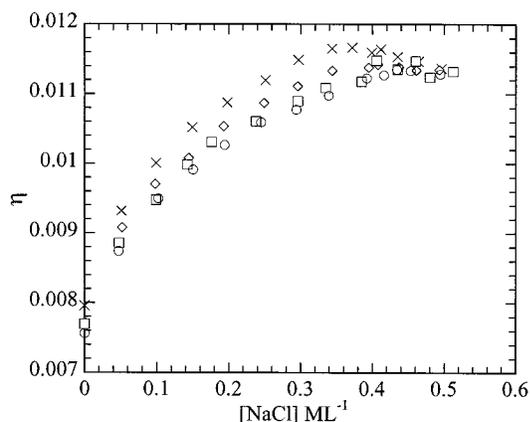
**Figure 5.** Number of water molecules (the filled symbols) and the area per headgroup (open symbols) for SDS with 17.2 mM heptane (■, ◻) and without heptane (●, ○) at various salt concentrations. Representative error bars are shown on one data point only for each of the ordinate variables. The error bars are calculated and due to the  $\pm 5\%$  error in  $N$  and  $0.5\%$  in  $H$ .

The hydration,  $H$ , has been shown to be very useful and reliable in identifying the sphere-to-rod transformation point.<sup>10</sup> A decrease in the hydration of surfactant ions is known to accompany micellar growth and transformation of spherical into rodlike micelles.<sup>23,24</sup> For SDS micelles without heptane,  $H$  decreases as the micelle increases in size and levels to a constant at a certain salt concentration (see Figure 3). This point is indicative of a transformation to rodlike micelles.<sup>10</sup> The results mean that, as long as micelles are globular,  $H$  decreases with growth. Upon complete transformation to rods, the micelles approach a constant value of  $H$ . The effect of heptane is to shift the transition to higher aggregation numbers. A comparison of the transition behavior of  $H$  with respect to  $N$  in the presence and absence of heptane is shown in Figure 4. The slight upturn in  $H$  after the transition could be because of a polydisperse mixture of spherical and cylindrical micelles in the transition region.  $H$  is representative purely of the headgroup environment. Rodlike micelles have constant  $H$  because they can grow lengthwise, without any change in the headgroup environment or geometrical constraints. The aggregation number at the sphere-rod transition are provided in the last column of Table 1.

Figure 5 shows the calculated values of  $A/N$  and  $N_w/N$  for the region of growth with NaCl. A comparison with Figure 3 shows that, unlike  $H$ , the optimal area per headgroup does not remain constant with heptane in the presence of added salt. The number of water molecules per headgroup is constant to within one molecule. This means that the hydration, as defined by the fractional

(21) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membrane*, 2nd ed.; Wiley-Interscience: New York, 1980.  
(22) Almgren, M.; Löfroth, J. E. *J. Chem. Phys.* **1982**, *76*, 2734.

(23) Ikeda, S. *Colloid Polym. Sci.* **1991**, *269*, 49–61.  
(24) Zieliński, R.; Ikeda, S.; Nomura, H.; Kato, S. *J. Colloid Interface Sci.* **1988**, *125*, 497.



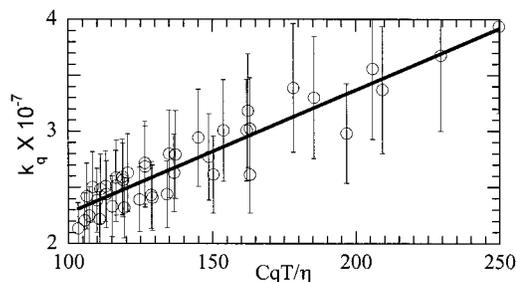
**Figure 6.** Microviscosity of the polar shell, in units of Pa-s, as sensed by the spin probe in SDS/heptane micelles at various [NaCl]. The concentration of SDS is 100 mM. Symbols used identify the different heptane concentrations and are for [heptane] = (a) 0 (x), (b) 6.5 ( $\diamond$ ), (c) 12.0 ( $\circ$ ), and (d) 17.2 mM ( $\square$ ).

interface volume occupied by water, is the relevant physical quantity. Being independent of any assumptions of shape,  $H$  is more reliable as the property to test for when seeking invariance behavior.

In the quest to characterize micelles as reaction media, it is important to establish the parameters that determine the bimolecular collision rates between additive molecules. One such parameter is the viscosity of the medium. The microviscosity data calculated from the ESR line shapes by using eqs 27–33 of Bales and Stenland<sup>15</sup> is therefore presented first. Figure 6 shows the microviscosity of the polar shell as a function of [NaCl] for four fixed concentrations of heptane. The microviscosity, at any fixed [heptane], increases with [NaCl] along with a “drying up” (reduction of  $H$ , see Figure 3) of the micelle surface. The number of water molecules  $N_w/N$  decreases from 7 to 5 (see Figure 5). Viscosity is a phenomenological quantity and lacks a microscopic description and one can only speculate on the trend of its variations. A larger  $N_w/N$ , at lower NaCl, facilitates easier rotational motion is a possible argument for an increase in  $\eta$  with NaCl. At the low salt concentrations the microviscosity decreases slightly with [heptane] although the hydration remains constant. In this case the presence of heptane in the interior of the micelle could be argued to increase the fluidity in the core and allow more facile movements of the anchoring tails of both probe and surfactant molecules. The polar part of the probe can then execute faster motion in the polar region as well. A characteristic change in behavior, encountered previously in the case of  $H$  (Figure 3), occurs also for the microviscosity at the higher salt concentrations. A nonchanging microviscosity reflects the nonchanging composition of the environment of the spin probe—a situation that occurs when globular micelles transform to rods and start growing lengthwise as illustrated by  $H$ .

Finally, we present data on the collision rate between probes and quenchers obtained by TRFQ. The Stokes–Einstein hydrodynamic description, which is a simple, well founded formulation in bulk solvents, seems to describe diffusion processes in the polar shell of SDS micelles containing a fraction of heptane molecules quite well. On the basis of such a description,

$$k_q = PC_q \frac{8R_0T}{3000\eta} \quad (10)$$



**Figure 7.** Bimolecular collision rate given by the quenching rate  $k_q$  of pyrene by DMBP vs  $C_q T/\eta$  for all of the SDS/heptane micelles with and without salt at 25 °C. The straight line is a linear least-squares fit to the Stokes–Einstein equation (eq 10). From the slope the probability,  $P$ , of quenching per collision is 0.5.

With,  $k_q$  being the quenching rate due one quencher, the molar concentration of quenchers,  $C_q$ , is given by

$$C_q = \frac{10^{27}}{N_0 V_{\text{shell}}}$$

where  $N_0$  is the Avogadro number. These equations have been presented and discussed in previous publications.<sup>4</sup> The quantity  $P$  is the probability that quenching occurs upon collision. For mixed micelles of SDS and dodecylmalonobis( $N$ -methylglucamide) (DBNMG, a sugar-based nonionic detergent) of varying compositions, a dependence such as that in eq 10 was shown to hold over a wide range in which  $k_q$  varied by an order of magnitude. From the slope of the line for  $k_q$  vs  $C_q T/\eta$ ,  $P$  was determined to be 0.5. A similar plot for the present system of SDS/heptane is shown in Figure 7. The slope yields again  $P = 0.5$ , independent of the medium, as it should be, because the relevant property of the medium, namely  $\eta$ , has been accounted for separately in eq 10.

### Summary and Conclusions

The micelle–water interface, of SDS/heptane micelles in NaCl solutions, can be characterized using TRFQ and ESR. Specifically, the aggregation number and the volume fraction of water (hydration) in the polar shell are obtained. These numbers are very useful in developing a physical model and in the determination of the geometrical features of the micelle. SDS micelles respond, upon solubilization of heptane, by growing until the volume fraction of water in the polar shell is the same as that in the micelle before addition of heptane. This invariance property of the micelle interface hydration is an experimental observation, and this conclusion is independent of any model. Application of a core–shell geometry to SDS/heptane micelles shows that about 17% of the micelle carbon density overlaps with the headgroup sulfate and hydration water in the polar shell. This corresponds to about the volume of two methylene groups. Heptane dissolves in the micelle core, thereby providing a larger core volume. This allows the micelle to retain its favorable globular shape up until higher aggregation numbers.

For any given detergent, micelle hydration depends only on the added salt concentration. Effect of other linear hydrocarbons on hydration should not be different from that of heptane. The sphere-to-rod transformation will however be different. The longer the hydrocarbons, the larger will be the aggregation number at which the transformation occurs. A mismatch in the length of the added hydrocarbon and the detergent chain length may influence the fluidity of the core and thereby the micro-

viscosity. A smaller mismatch could result in more rigidity or higher microviscosity.

The same equations that describe diffusion and collision of molecules in bulk solvents also describe bimolecular collision in the polar shell. This is an interesting result, which means that the polar shell, a restricted region of high ion concentration, appears to have the properties of a bulk solvent.

**Acknowledgment.** Support from the National Institute of General Medical Sciences under Contracts

GM00667-01 (for R.R.) is gratefully acknowledged. R.R. thanks the Uppsala University, Department of Physical Chemistry, for supporting her extended visits there and acknowledges valuable discussions with colleagues at UU, in particular Dr. Per Hansson. The College of Science and Mathematics and the Research and Sponsored Programs office of the California State University Northridge provided reassigned time to R.R. and M.P. for conducting this research.

LA010231Z