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# Temperature Dependence of Triton X-100 Micelle Size and Hydration<sup>†</sup>

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Received May 3, 1994. In Final Form: September 19, 1994<sup>®</sup>

Quasi-elastic light scattering spectroscopy was used to measure the mutual diffusion coefficient,  $D_m$ , of Triton X-100 micelles in aqueous solution and the translational diffusion coefficient,  $D_p$ , of mesoscopic probes in the same solutions. We apply conventional hydrodynamic treatments of diffusion under the assumption that Triton X-100 minimal micelles are adequately represented as hard spheres.  $D_m$  and  $D_p$  measured at a series of surfactant concentrations are used to infer the micelle radius,  $a_m$ , aggregation number,  $N$ , and degree of hydration,  $\delta$ , for temperatures  $10 \leq T \leq 50$  °C. As  $T$  is increased toward the cloud point,  $a_m$  and  $N$  increase, the increase in  $N$  being especially dramatic above 40 °C.  $\delta$  at first increases but then tends to saturate with increasing  $T$ .

## Introduction

Triton X-100 [*p*-(1,1,3,3-tetramethylbutyl)phenoxy]poly(oxyethylene) glycol is a nonionic surfactant having a critical micellar concentration of ca. 0.6 g/L.<sup>1</sup> The physical properties of Triton X-100 micelles have been studied repeatedly by several authors using physical techniques including quasi-elastic light scattering,<sup>2</sup> viscometry,<sup>3</sup> X-ray scattering,<sup>4</sup> and pulsed field gradient NMR.<sup>5</sup> Brown et al.<sup>2</sup> used static and quasi-elastic light scattering and fluorescence quenching to examine aqueous solutions of Triton X-100 over a wide concentration range for temperatures between 10 and 45 °C. They inferred a dependence of micellar shape and size distributions on temperature and surfactant concentration.

This laboratory<sup>6</sup> has previously applied light scattering spectroscopy and optical probe diffusion to Triton X-100: water at 25 °C. In a conventional light scattering spectroscopy experiment, one infers the mutual diffusion coefficient of the scattering species from the temporal evolution of fluctuations in the intensity of the scattered light. In an optical probe experiment, one observes the diffusion of mesoscopic probes of given size through a complex fluid and determines the effect of the surrounding fluid on the probe motions. By measuring both the mutual diffusion coefficient,  $D_m$ , and the probe diffusion coefficient,  $D_p$ , at a series of surfactant concentrations, one may<sup>6</sup> obtain the probe radius,  $a_p$ , the radius of the micelles,  $a_m$ , and the mass,  $M_0$ , of the Triton X-100 in each micelle. From these parameters the aggregation number,  $N$ , and the degree of hydration,  $\delta$ , of the micelles can separately be inferred.

The next section describes the experimental equipment and techniques used in our experiments. Theoretical ideas used for our interpretation of the concentration dependences of  $D_m$  and  $D_p$  are summarized. Finally, we give our experimental results and an interpretation based on a

model of neutral micelles as diffusing hard spheres. A summary and comparison with the literature closes the paper.

## Experimental Methods

Quasi-elastic light scattering spectroscopy (QELSS)<sup>7</sup> was used to measure the mutual diffusion coefficient,  $D_m$ , of Triton X-100: water and the probe diffusion coefficient,  $D_p$ , of polystyrene latex spheres diffusing in Triton X-100:water. Physically, the concentration dependence of  $D_m$  is determined by the effect of intermicellar interactions on the translational diffusion of the micelles. The concentration dependence of  $D_p$  is determined by the effect of the micelles on the diffusion of the probe particles.

In a QELSS measurement, one characterizes the time evolution of Brownian-motion-driven fluctuations in the intensity  $I(q, t)$  of monochromatic light scattered by an equilibrium sample. Here  $q$  is the magnitude of the scattering vector,  $q$ ,

$$q = \frac{4\pi n}{\lambda} \sin(\theta/2) \quad (1)$$

where  $n$  is the index of refraction of the solution,  $\lambda$  is the light wavelength *in vacuo*, and  $\theta$  is the scattering angle (90° in our experiments). Operationally, one characterizes  $I(q, t)$  by dividing time into a series of adjoining intervals each having width  $s$  ( $s$  is the channel width or sample time). The number of photons received in each interval  $i$ ,  $n_i$ , is counted and used as a determination of  $I(q, t)$  during the interval. The digital correlator repeats this process for all moments,  $t$ , and computes the intensity-intensity correlation function

$$S(q, \tau) = \int_0^T dt I(q, t) I(q, t + \tau) \equiv \sum_{i=1}^M n_i n_{i+m} \quad (2)$$

where  $T = sM$ , the duration of the experiment, and  $\tau = sm$ , the delay time.

Spectra were analyzed by the method of cumulants,  $S(q, \tau)$  being fit to

$$\frac{1}{2}(\log(S(q, \tau) - B)) = \sum_{l=0}^N \frac{K_l(-\tau)^l}{l!} \quad (3)$$

Here  $B$  is the baseline (the time-independent part of the intensity-intensity correlation function), while the  $K_l$  are the cumulants and  $N$  is the order of the fit. In our experiments,  $B$  was determined by measuring  $S(q, \tau)$  at times well after ( $\tau$  values  $> 1 \cdot 10^3$  s beyond) the largest  $\tau$  used in the determination of the  $K_l$ .  $B$  may also be calculated as  $B = P^2/M$ , where  $P$  is the total number of photocounts recorded during the experiment. These two methods of determining  $B$  agreed to within the expected

<sup>†</sup> The partial support of this work by the National Science Foundation under Grant DMR91-15637 is gratefully acknowledged.

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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, December 1, 1994.

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statistical error. The  $K_l$  were obtained from eq 3, using experimental values of  $S(q, \tau)$  and  $B$ , by means of weighted linear least-squares fits to  $\log(S(q, \tau) - B)$ . We calculated the  $K_l$  for each value of the truncation order  $N$  in the range 1–4; for our system an  $N$  of 2 or 3 was adequate.

The diffusion coefficient of the system is related to  $K_1$  via

$$D = \frac{K_1}{q^2} \quad (4)$$

$K_1$  was measured as a function of  $q$  in representative systems, finding that  $D$  is independent of  $q$ .

The second cumulant gives the degree of nonexponentiality of the spectrum in terms of the variance,  $V$ , namely

$$V = \frac{100S(K_2)\sqrt{|K_2|}}{K_1} \quad (5)$$

where  $S$  is the sign function, whose value is  $\pm 1$  to match the sign of its argument. We obtained  $V$  in the range 10–30%, with no trend apparent in  $V$  against concentration, except in the 200 g/L solution, in which  $V$  rose to  $\sim 55\%$ .

We also analyzed our spectra by fitting them via nonlinear least squares to a sum of two two-cumulant series, namely

$$(S(q, \tau) - B)^{1/2} = \sum_{l=0}^2 \frac{K_{1l}(-\tau)^l}{l!} + \sum_{l=0}^2 \frac{K_{2l}(-\tau)^l}{l!} \quad (6)$$

the  $K_{il}$  being the fitted cumulants. This fitting function allows isolation of  $D_p$  in the presence of nonzero scattering by the micelles. Fits to eq 6 yield slightly larger (5–8%) values of  $D_p$  than do fits to eq 3, but the same slope  $dD_p/dc$  is obtained from both sets of  $D_p$  values.

In our work, Triton X-100 (Aldrich) was prepared as stock solutions at 100 and 200 g/L using water purified by a Millipore Milli-Q water system. The resistivity of the purified water was 7–8 M $\Omega$ /cm. Other solutions were prepared from the stock solution by serial dilution. For the probe diffusion experiments, trace quantities (1–2  $\mu$ L/mL) of carboxylate-modified polystyrene latex spheres (PSL) (Seradyn), nominal diameter 0.067  $\mu$ m, were added to the sample. Scattering samples were clarified by passing them through 0.22  $\mu$ m pore size cellulose filters (Micron Separations) into precleaned light scattering cells. We used both disposable plastic and glass fluorimeter cells, with four sides polished (NSG Precision Cells).

This work involved two light scattering spectrometers. Three spectra were taken of each sample at each temperature. For the mutual diffusion measurements and the angular studies, we used a Spectra-Physics 2030 Ar<sup>+</sup> laser with a maximum power output of 1 W at 514.5 nm coupled to a Brookhaven Instruments Model BI-200SM photometer–goniometer. A 262-channel Brookhaven Instruments Model 2030AT digital correlator was used to measure  $S(q, t)$ . The temperature in the cells was maintained to within 0.1 °C using a Neslab RTE-110 circulator, heat exchange coils, and a decalin-filled index-matching vat.

For the probe diffusion measurements, a 30 mW Spectra-Physics Model 124B He-Ne laser with output at 632.8 nm was used. Light scattered through 90° was isolated with paired irises and detected by an RCA Model 7265 photomultiplier tube. After preamplification, discrimination, and pulse shaping, the detected signal was analyzed by a computer-controlled Langley-Ford 144-channel digital correlator. Temperature control was effected by placing the sample cells in a massive copper block; a computer-controlled Neslab RTE-100 circulating bath that held the temperature constant to within 0.1 °C was used to thermostat the block.

We studied the mutual diffusion coefficient of Triton X-100: water solutions for a series of Triton X-100 concentrations between 5 and 100 g/L and temperatures in the range 10–50 °C. The hydrodynamic radius,  $a_m$ , of the minimal micelles could be obtained from  $D_m$  by extrapolating  $D_m$  to its value  $D_{m0}$  in the limit of zero surfactant concentration and applying the Stokes–Einstein equation

$$D = \frac{k_B T}{6\pi\eta a} \quad (7)$$

to  $D_{m0}$ . Here  $T$  is the absolute temperature,  $k_B$  is Boltzmann's constant,  $\eta$  is the solvent viscosity, and  $a$  is the diffusant radius. Equation 7 works for highly dilute spheres in a simple solvent, which is the correct condition for our systems after extrapolation to the limit of zero surfactant concentration. At elevated surfactant concentrations, micelle–micelle interactions cause eq 7 to fail,  $D_m$  being larger or smaller than  $D_{m0}$ , depending on the details of the forces between the micelles. The Stokes–Einstein equation also links  $D_{p0}$  (the zero-surfactant-concentration limit of the probe diffusion coefficient  $D_p$ ) to  $a_p$  (the radius of the probe particles under the same conditions).

It is important to emphasize that the Stokes–Einstein equation is only accurate in simple solvents. Even though our probe particles are much larger than our micelles, data on systems hydrodynamically similar to those studied here show that eq 7 should not be expected to describe probe diffusion through nondilute micellar fluids, no matter whether  $\eta$  is the solvent or solution viscosity. For example, Ullmann et al.<sup>8</sup> measured  $D_p$  of polystyrene spheres in bovine serum albumin (BSA):physiological saline. They found that the dependences of  $D_p$  and  $\eta$  on BSA concentration deviate from eq 7 by as much as 35% at elevated BSA concentration.

Measurements of the diffusion of optical probes were made for Triton X-100 concentrations in the range 5–200 g/L at temperatures covering the range used to observe  $D_m$ . We used large probes (which are hard spheres to an excellent approximation), thereby ensuring that light scattering by the micelles is negligibly small compared to light scattering by the probes. Control experiments comparing spectra of Triton X-100:water and PSL: Triton X-100:water solutions taken under identical conditions (same laser power, iris openings, sample times, and experiment durations) confirm that probe scattering completely dominates scattering due to the micelles. Furthermore, probe spectra are readily observed at surfactant concentrations below the critical micelle concentration (cmc), where there are no micelles, confirming that we are studying probe and not micelle diffusion.

Since PSL is a very good scatterer, only trace concentrations (volume fraction under 0.001) of probes were needed. Complications arising from interactions between pairs of probe particles were effectively eliminated by using very dilute probes.

## Theory

Here the probe particles and the micelles are modeled as uncharged hard spheres diffusing through a simple Newtonian fluid. Experimental data supporting this approximation are discussed below. The model, which was presented in more detail in our previous paper,<sup>6</sup> recognizes two sorts of forces, direct and hydrodynamic. The direct micelle–micelle and micelle–probe forces are excluded-volume interactions. Denoting the micelle and probe radii by  $a_m$  and  $a_p$ , respectively, hard-sphere interactions limit micelle–micelle and micelle–probe distances of closest approach to  $2a_m$  and  $a_m + a_p$ , respectively. Hydrodynamic forces represent correlations between Brownian forces on different macroparticles and are described by extensions<sup>9</sup> of the Oseen tensor.

The first-order concentration correction to the mutual diffusion coefficient  $D_m$  of a solution of monodisperse hard spheres was evaluated by Carter and Phillies.<sup>10</sup> The corresponding correction to  $D_p$  for a large sphere diffusing through a solution of smaller spheres was evaluated by ref 6. In summary,

$$D_m = D_{m0}(1 + \alpha_m \phi) \quad (8)$$

and

(8) Ullmann, K.; Ullmann, G. S.; Phillies, G. D. J. *J. Colloid Interf. Sci.* **1985**, *105*, 315.

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(10) Carter, J. M.; Phillies, G. D. J. *J. Phys. Chem.* **1985**, *89*, 5118.

$$D_p = D_{p0}(1 + \alpha_p \phi) \quad (9)$$

where  $D_{m0}$  and  $D_{p0}$  are the mutual and probe diffusion coefficients in the limit of low surfactant concentration, and where  $\alpha_m$  and  $\alpha_p$  are the linear slopes. The micelle concentration has been expressed in terms of the volume fraction

$$\phi = \frac{4\pi a_m^3}{3} \frac{c}{M_0} \quad (10)$$

Here  $4\pi a_m^3/3$  is the volume,  $V_o$ , of a single micelle,  $c$  is the mass concentration of surfactant, and  $M_0$  is the mass of Triton X-100 per micelle. Surfactant concentrations here were always far above cmc of Triton X-100, so we approximate the concentration of surfactant in micelles as being the total surfactant concentration. Carter and Phillies<sup>10</sup> demonstrate

$$\alpha_m = -0.9 \quad (11)$$

while Phillies et al.<sup>6</sup> give

$$\alpha_p = -\left(\frac{15}{4} \frac{a_p}{a_p + a_m} - \left(\frac{5}{2} - \frac{11}{8} \left(\frac{a_m}{a_p}\right)^2\right) \left(\frac{a_p}{a_p + a_m}\right)^3\right) \quad (12)$$

for probe diffusion.

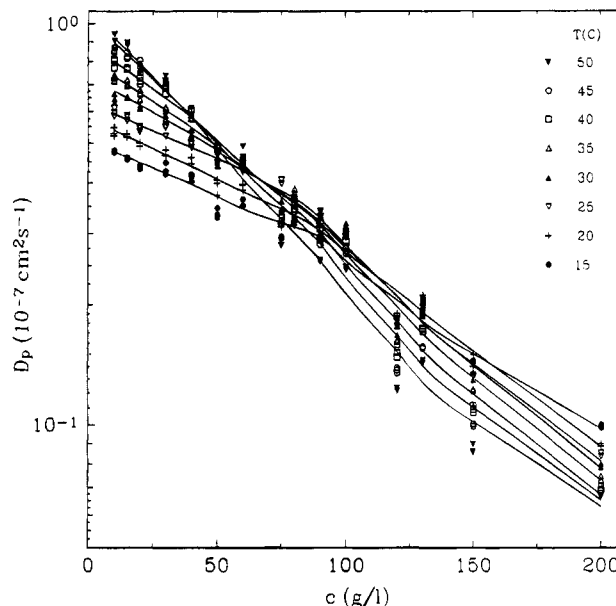
The value of  $\alpha_m$  is in some dispute in the literature. Batchelor<sup>11</sup> and Felderhof<sup>12</sup> propose that  $\alpha_m \approx +1.6$  instead of  $\alpha_m \approx -0.9$ . One of us has identified apparent difficulties<sup>13</sup> with the Batchelor<sup>11</sup> and Felderhof<sup>12</sup> derivations, difficulties that account for the discrepancy between their results and those of Carter et al.<sup>10</sup> It is important to emphasize that the differences refer only to  $\alpha_m$ , not to  $\alpha_p$ . There is no disagreement as to the concentration dependence of  $D_p$ . Furthermore,  $\alpha_p$  is much less sensitive than  $\alpha_m$  to small deviations of the intramicellar interactions from simple hard-sphere behavior or form.

The four phenomenological quantities  $D_{m0}$ ,  $D_{p0}$ ,  $\alpha_p$ , and  $\alpha_m$  are physically independent and experimentally measurable. These four phenomenological quantities are determined by three fundamental physical parameters, namely  $a_p$ ,  $a_m$ , and  $M_0$ . Because there are more independent measurables than there are underlying physical parameters, the problem is potentially overspecified. Comparison of experimental data on  $D_m(c)$  and  $D_p(c)$  then yields  $a_p$ ,  $a_m$ , and  $M_0$  and simultaneously tests the proposed hard-sphere model for Triton X-100 micelles.

In the following, we used two schemes for analyzing our data. One scheme took  $a_m$  from a phenomenological extrapolation of  $D_m$  to  $c = 0$ , avoiding all question as to the correct theoretical treatment of  $\alpha_m$ , while the other scheme incorporated the more-controversial eq 11. These two methods yielded parameters that are in good agreement with each other.

### Experimental Results

This section reports  $D_p$  and  $D_m$  against surfactant concentration at temperatures between 10 and 50 °C. Figure 1 shows  $D_p$ . For all temperatures studied, over a wide range of Triton X-100 concentrations,  $D_p$  decreases linearly with increasing  $c$ . For  $10 \leq T \leq 25$  °C,  $D_p$  remains linear in  $c$  for  $c < 150$  g/L. At higher temperatures, the linear regime becomes narrower; at 45 or 50 °C the linear decrease of  $D_p$  extends from extreme dilution to concen-



**Figure 1.** Probe diffusion coefficient,  $D_p$ , in Triton X-100:water as a function of surfactant concentration and temperature. The probes were  $0.067 \mu\text{m}$  polystyrene spheres, observed with quasi-elastic light scattering. Lines are guides for the eye.

trations no larger than 60 g/L. Theoretical analysis based on eqs 8–12 is limited to the low-concentration linear regime. At surfactant concentrations above the linear regime,  $dD_p/dc$  depends on  $c$ . At these larger concentrations, either micelles change size or shape or three-body micelle–micelle–probe interactions become important. The nonlinear behavior at larger  $c$ , especially at higher  $T$ , may be associated with the approaching cloud point at large  $T$ .

Data in Figure 1 are consistent with the results of Phillies et al.<sup>6</sup> for this system at 25 °C. We obtain virtually the same zero-concentration intercept as did Phillies et al.,<sup>6</sup> viz.  $6.3 \cdot 10^{-8}$  and  $6.75 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ , respectively. We also obtained very nearly (within 15%) the same slope,  $dD_p/dc$ , that Phillies et al.<sup>6</sup> obtained in the same system for  $0.1 < c < 65$  g/L.

Figure 2 focuses on the temperature dependence of  $D_p$  by plotting  $D_p$  against  $T/\eta$  at various fixed surfactant concentrations. Here  $\eta$  is the viscosity of pure water. For  $c \leq 30$  g/L (Figure 2a) and all but the highest temperatures (i.e.,  $T > 40$  °C),  $D_p$  is linear in  $T/\eta$ , consistent with the Stokes–Einstein equation (eq 7).  $D_{p0}$  also depends linearly on  $T/\eta$ .

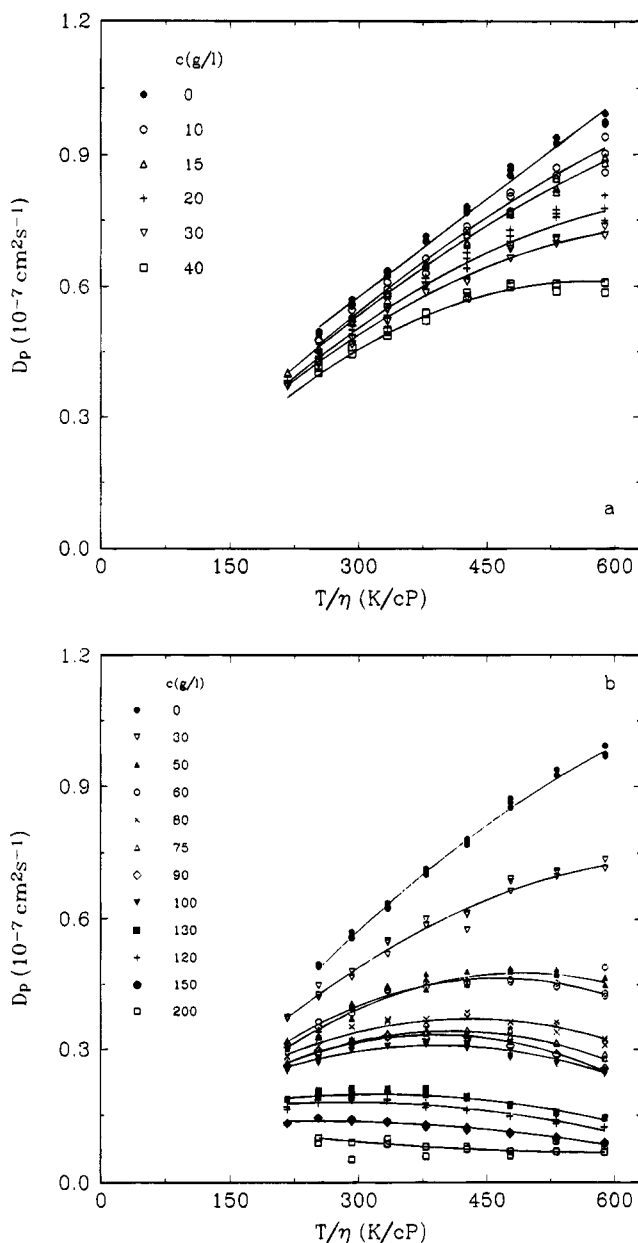
At surfactant concentrations  $\geq 30$  g/L,  $D_p$  ceases to be linear in  $T/\eta$ . At 75 g/L  $D_p$  has a clear maximum at 30 °C, further increases in temperature leading to a decrease in  $D_p$ . At  $c \geq 120$  g/L we find that  $D_p$  is nearly independent of  $T/\eta$ , a slight decrease of  $D_p$  with increasing  $T/\eta$  being apparent in the data. This correlation between  $D_p$  and  $T/\eta$  cannot be explained as a consequence of hydrodynamic interactions, because  $D_p$  only depends on  $T$  and  $\eta$  through  $D_{p0}$ ;  $\alpha_p$  and  $\alpha_m$  are independent of  $\eta$ . The observed nonlinear dependence of  $D$  on  $T/\eta$  at large  $c$  must arise from temperature- and concentration-induced changes in micelle size, shape, or hydration at large  $c$ . Such changes in micelle properties are also implicit in the static light scattering data of Brown et al.<sup>2</sup> and are consistent with an approach to a cloud point in the Triton X-100 solutions.

Figure 3 presents  $D_m$  of Triton X-100 micelles as a function of Triton X-100 concentration and temperature. At all temperatures,  $D_m$  shows a very weak dependence on  $c$ . For  $c < 30$  g/L,  $D_m$  decreases;  $D_m$  increases again at higher surfactant concentrations. Micelles are much

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

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(13) Phillies, G. D. *J. Colloid Interf. Sci.* **1987**, *119*, 518.

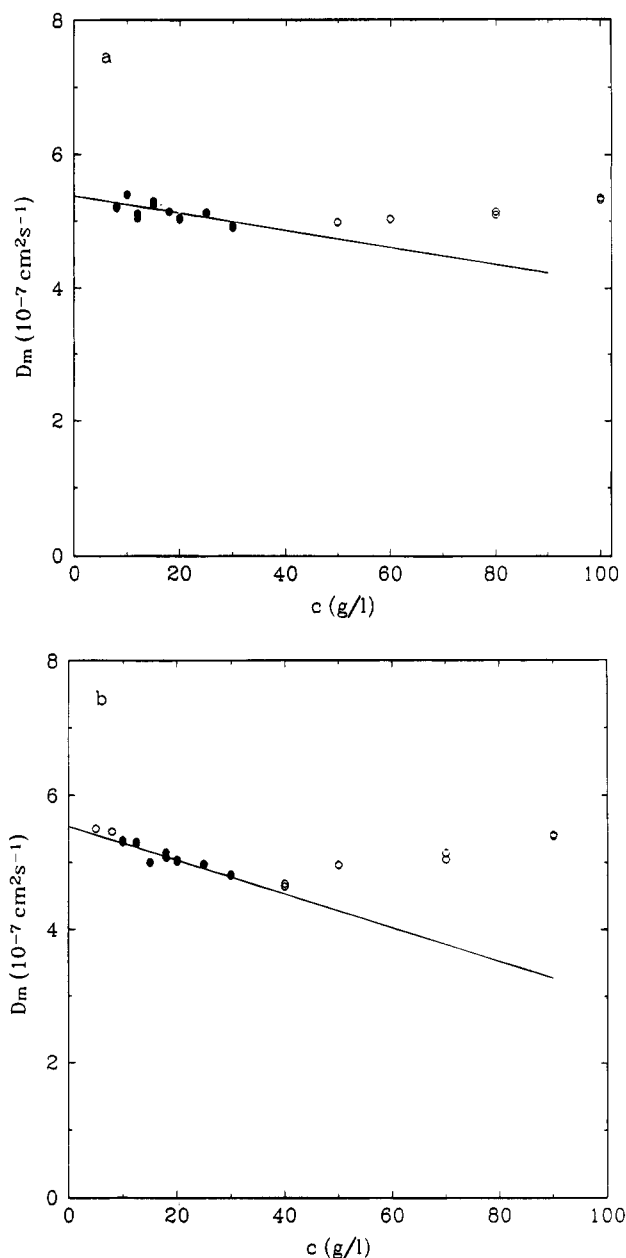


**Figure 2.** Temperature dependence of probe diffusion coefficient,  $D_p$ , plotted against  $T/\eta$  ( $\eta$  being the solvent viscosity) at (a) low and (b) elevated surfactant concentrations. Note the lack of Walden's rule behavior at elevated  $c$  and  $T$ .

more massive than individual Triton X-100 molecules. As shown below, a typical micelle contains more than 100 surfactant molecules. Except perhaps very close to or below the cmc, micelle scattering dominates scattering by individual monomers. Just as scattering from PSL: Triton X-100:water solutions gives the  $D_p$  of PSL, light scattering from Triton X-100:water solutions also gives the  $D_m$  of the micelles. We made measurements of  $D_m$  at concentrations as low as 5 g/L, but reliable data was obtained only for  $c \geq 10$  g/L. At concentrations  $c < 10$  g/L, scattering by the micelles is inadequate to give high-quality spectra. We show data points in this low- $c$  regime in Figure 3, but did not include them in our further analysis. In contrast, optical probe measurements can be made without difficulty for surfactant concentrations down to and below the cmc.

### Analysis

Before applying the theoretical scheme sketched above, one must first ask if it is appropriate to treat Triton X-100



**Figure 3.** Mutual diffusion coefficient,  $D_m$ , of Triton X-100 micelles in water as a function of  $c$  and  $T$ . Filled points and solid lines indicate the low-concentration linear regime and the linear fit to  $D_m$  in that regime. Lowest-concentration points (open circles) have inferior signal-to-noise ratios and were not included in the analysis. (a) 10 °C; (b) 45 °C.

micelles as hard spheres. Data bearing on this question is provided by Brown et al.,<sup>2</sup> who measured the reduced scattering intensity ( $Kc/R_\theta$ ) of Triton X-100 solutions and calculated therefrom the inverse osmotic compressibility

$$\frac{\partial \pi}{\partial c} = \frac{Kc}{R_\theta} RT \quad (13)$$

Brown et al.<sup>2</sup> found that  $\partial \pi / \partial c$  exhibits hard sphere behavior for  $c < 50$  g/L at all temperatures ( $10.3 < T < 44.1$  °C) studied. At higher concentrations,  $\partial \pi / \partial c$  deviates from a hard sphere model.

The experiments of Brown et al.<sup>2</sup> show a decrease of the second virial coefficient,  $A_2$ , with increasing temperature, indicating that intermicellar interactions become less repulsive at higher  $T$ . At 45 °C,  $A_2$  goes to zero, corresponding to a cancellation between the excluded volume potential and an attractive pair potential between

**Table 1. Micelle Radii  $a_m$  and Surfactant Molar Masses (kDa of Triton X-100 per micelle) as a Function of Temperature, Showing Values Obtained by Two Different Methods**

$T$ (°C)	$a_m$ (Å)		$M_0$ (kDa)	
	I <sup>a</sup>	II <sup>b</sup>	I <sup>a</sup>	II <sup>b</sup>
50	85	83	283	278
45	71	71	179	174
35	54	54	89	87
30	47	49	64	65
25	43	44	56	61
20	38	38	38	34
15	40	37	49	39
10	29	30	18	25

<sup>a</sup> Extrapolation of  $D_m$  to  $c = 0$  to obtain  $a_m$  and then determination of  $M_0$  from the slope of  $D_p$  against  $c$ . <sup>b</sup> Simultaneous nonlinear least-squares fit of all data to determine  $a_m$ ,  $a_p$ , and  $M_0$ .

micelles. Above 45 °C, the attractive pair potential dominates and  $A_2$  becomes negative. Brown et al.<sup>2</sup> propose that the increase in the attractive pair potential promotes rapid micellar growth and/or aggregation, leading to the observed cloud point in Triton X-100:water solutions.

How do the results of Brown et al. compare with ours?  $D_m$  is directly sensitive to the inverse osmotic compressibility via the approximate generalized Stokes–Einstein equation<sup>19</sup>

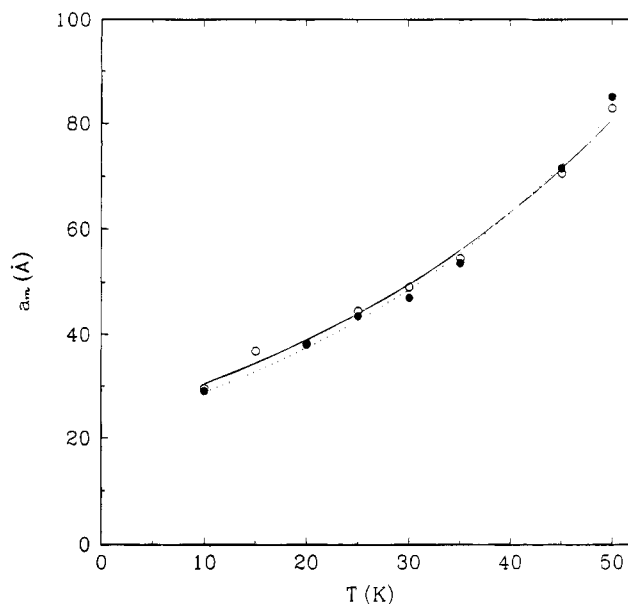
$$D_m = \frac{\partial \pi}{\partial c} \frac{1}{f_m k_B T} (1 - \phi) \quad (14)$$

where  $f_m$  is a drag coefficient corresponding to mutual diffusion. Our  $D_m$  data depart from linear hard sphere behavior at approximately the  $c \approx 50$  g/L at which Brown et al. saw a deviation from hard sphere behavior in their light scattering intensity data. Static and dynamic light scattering data are thus both consistent with the existence of a low-concentration regime in which micelles act as hard spheres and a higher-concentration regime in which the forces driving the system toward its cloud point lead to substantial deviations from hard sphere behavior, as seen in  $\partial \pi / \partial c$ ,  $D_m$ , and  $D_p$ .

There are two routes from  $D_m$  and  $D_p$  to  $a_m$ ,  $a_p$ , and  $M_0$ . First, one can extrapolate the measured  $D_m$  and  $D_p$  to zero concentration to obtain  $a_m$  and  $a_p$  from eq 7 and then use either or both slopes and the calculated radii to infer  $\phi$  and  $M_0$ . By using the  $a_m$  and  $a_p$  as calculated from  $D_{m0}$  and  $D_{p0}$ , respectively, together with the slope of  $D_p$  against  $c$ , one avoids all questions as to a preferred theoretical value for  $\alpha_m$ . Second, one may follow Phillies et al.<sup>6</sup> and simultaneously fit eqs 8–12 to all experimental data on  $D_p$  and  $D_m$  at one  $T$  via nonlinear least squares.

Table 1 compares these approaches, presenting  $a_m$  and  $M_0$  from each approach at each  $T$ . The  $a_m$  data also appear in Figure 4. The approaches give very nearly the same quantitative results for  $a_m$  and  $M_0$  at most temperatures, as expected if the hard sphere assumption and our treatment of  $\alpha_m$  are valid. Parameters from the second approach show a somewhat smoother dependence on  $T$  than do parameters from the first approach.

Under the first approach, we obtained  $D_{m0}$  at each  $T$  by linear extrapolation of  $D_m$  at low concentrations ( $10 \leq c \leq 30$  g/L). From  $D_{m0}$  and eq 7, the minimal-micelle  $a_m$  was computed at different temperatures. This value of  $a_m$  is independent of one's choice of treatment of the slope  $\alpha_m$ , because  $a_m$  is obtained from an empirical extrapolation of  $D_m$  to  $c = 0$ . As seen in Figure 4,  $a_m$  from  $D_{m0}$  increases with increasing temperature, from 29 Å at 10 °C to 85 Å at 50 °C. Our values for  $a_m$  are consistent with direct



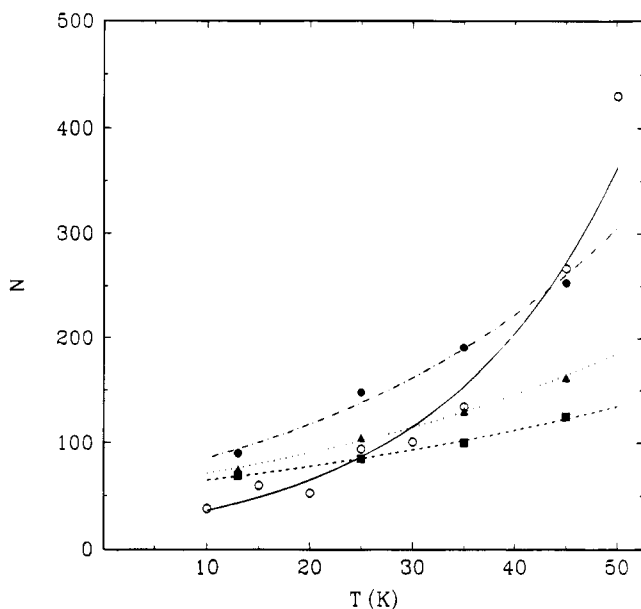
**Figure 4.** Radius  $a_m$  of Triton X-100 micelles in the limit of low surfactant concentration as a function of  $T$ : filled circles,  $a_m$  via extrapolation of  $D_m$  to zero  $c$  and use of the Stokes–Einstein equation; open circles, simultaneous nonlinear least-squares fit of eqs 8–12 to all data at each  $T$ .

extrapolation at the QELSS spectra of Brown et al.<sup>2</sup> which indicated that  $a_m$  varies from 45 to 92 Å over  $10.3 \leq T \leq 44.1$  °C. Our results show a linear growth of  $a_m$  with  $T$  for temperature  $T < 40$  °C and an upward deviation from a linear dependence of  $a_m$  for  $T > 40$  °C.

Under the second approach, we made a simultaneous fit of  $D_m$  and  $D_p$  at each  $T$  to eqs 8–12, using  $a_m$ ,  $a_p$ , and the aggregation number  $M_0$  as simultaneous free parameters. The data to be fit was limited to the low-concentration linear regime, namely  $10 \leq c \leq 30$  g/L for  $D_m$  and  $c \leq 60$  (at low  $T$ , 75) g/L for  $D_p$ . From this three-parameter ( $a_m$ ,  $a_p$ ,  $M_0$ ) nonlinear least squares fit, we obtained  $a_m$  of 30 Å at 10 °C, increasing to 83 Å at 50 °C. At 25 °C we obtain 44.4 Å for  $a_m$ , in excellent agreement with the data of Phillies et al.,<sup>6</sup> who found 45 Å at the same temperature.

The simultaneous fit to 8–12 also yields the molar mass  $M_0$  of surfactant in each micelle, and hence the aggregation number  $N$ . Figure 5 shows  $N$  as a function of temperature. At 25 °C we find  $N = 97$ , consistent with  $N \approx 100$  from Phillies et al.<sup>6</sup> and  $N \approx 105$  from Brown et al. at this temperature.  $N$  increases with increasing  $T$ , slowly below 40 °C, but much more rapidly above 40 °C. The rapid increase of hydration number indicates micelle growth with increasing temperature, especially as the cloud temperature (64 or 68.5 °C)<sup>2,14</sup> is approached. Brown et al.<sup>2</sup> determined  $N$  with fluorescence quenching experiments. They report an appreciable concentration dependence, but only a limited temperature dependence, of  $N$ , especially at concentrations much larger than those used in this analysis. For purpose of comparison, the findings of Brown et al.<sup>2</sup> appear in Figure 5.

If one assumes that Triton X-100 and water exist within micelles at approximately their neat liquid densities, it is possible to compute the degree of hydration of a micelle from the micelle volume  $4\pi a_m^3/3$ , the mass and density of Triton X-100 in a micelle, and the density of water. Results are presented in Figure 6, which gives the degree of hydration,  $\delta$  (in grams of H<sub>2</sub>O per grams of Triton X-100), as a function of  $T$ . The degree of hydration of the micelles



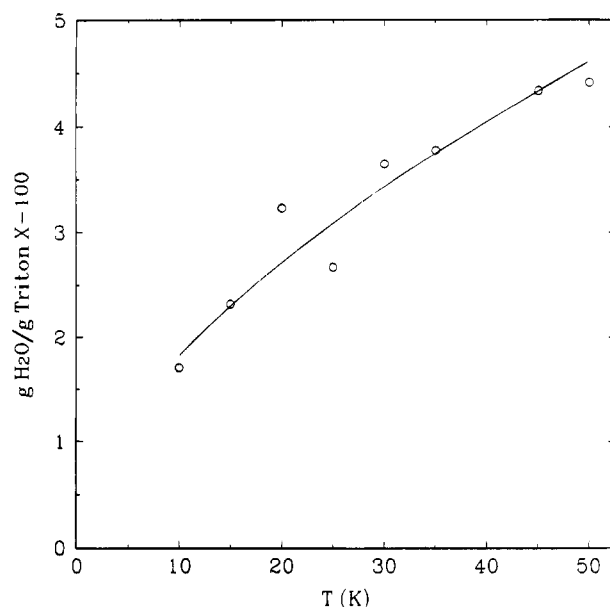
**Figure 5.** Aggregation number,  $N$ , of Triton X-100 micelles as a function of  $T$ , based on (open circles) simultaneous fit of eqs 8–12 to all data at one  $T$ , and on (filled circles) fluorescence-quenching studies of Brown et al.<sup>2</sup> at 10, 50, and 299 g/L.

increases with increasing temperature. At 25 °C we find  $\delta = 2.7$  (smooth line gives  $\delta = 3.2$ ), in good agreement with the  $\delta = 2.6$  obtained by Phillies et al.<sup>6</sup> at this temperature.

### Summary and Discussion

Here we have reported a study of micelle formation in Triton X-100 water. By employing optical probe diffusion as well as conventional light scattering spectroscopy, we determined two independent hydrodynamic properties of these solutions. Application of modern theories of mesoparticle dynamics<sup>6,9,10</sup> in solution allowed interpretation of these properties in terms of micelle radius, aggregation number, and hydration. Our determinations of  $\alpha_m$  and  $N$  are in reasonable agreement with literature,<sup>2–5</sup> providing a strong argument for the validity of our underlying model and for the correctness of our plausible assumption that minimal Triton X-100 micelles behave much like hard spheres.

It is important to question whether this agreement between our data, theory, and the literature is fundamental or whether the agreement results from a coincidence unique to Triton X-100:water. This laboratory has recently made studies on mutual and probe diffusion in



**Figure 6.** Degree of hydration,  $\delta$  (gram of  $\text{H}_2\text{O}$  per gram of Triton X-100), of Triton X-100 micelles at various temperatures, based on the data in the preceding figures and the approximation that water and Triton X-100 are present in micelles at their neat liquid densities.

Brij-35:water,<sup>15</sup> sodium dodecylsulfate:NaCl:water,<sup>16</sup> and cetyltrimethylammonium bromide:NaBr:water.<sup>17</sup> For the neutral Brij-35 micelles, good agreement with literature values<sup>18</sup> of  $N$  was obtained. With charged micelles, refinement of micelle–micelle and micelle–probe potentials beyond the familiar Debye–Huckel potential is required to gain a fully quantitative interpretation of the data.

Unlike previous work, we were also able to obtain the degree of hydration of a Triton X-100 micelle, showing that in a hydrodynamic sense a great deal of solvent is associated with each micelle, especially at higher temperatures. This water is not necessarily the same as the water bound thermodynamically to each micelle. Water might readily be dynamically trapped within large surface folds of a micelle, even if there was no significant thermodynamic interaction between water and surfactant.

At higher concentrations, we observe clear evidence for changes in micelle size with increasing temperature. As seen in Figure 2, at low  $c$   $D_p$  is linear in  $T/\eta$ . At elevated surfactant concentrations,  $D_p$  becomes independent of  $T/\eta$ , or even falls as  $T/\eta$  is increased. However, hydrodynamic models<sup>10,6</sup> have the important feature that they depend on  $T/\eta$  only through  $D_{m0}$  and  $D_{p0}$ , the slopes  $\alpha_p$  and  $\alpha_m$  being independent of  $T$  and  $\eta$ . In consequence, any deviation of  $D_p$  from a simple linear dependence on  $T/\eta$  must arise from a change in micelle–probe direct and hydrodynamic interactions attendant to changes in micelle sizes or shapes.

LA9403688

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