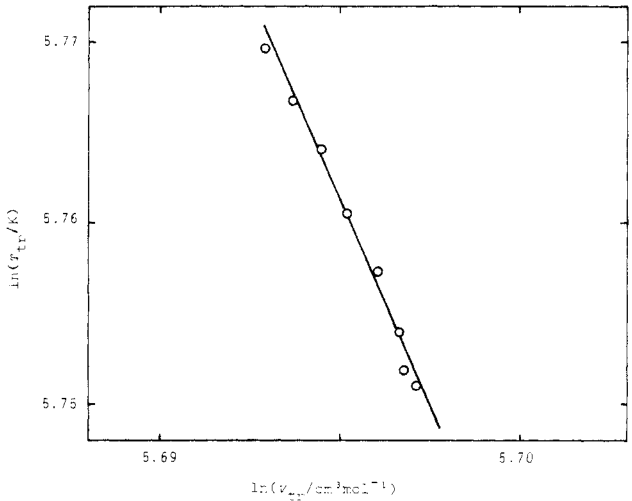

**Figure 4.** log–log plots of the molar volume at the transition points and the transition temperature for 8CB.

transition temperature was proportional to the molar volume at the transition points and the value d ln $T_{tr}$/d ln $V_{tr}$ = −2 was obtained by using eq 4. This value does not coincide with our observed value.

McColl and Shih[5] found the value to be −4 for 4,4′-dimethoxyazoxybenzene. In our previous measurement for 4,4′-propoxybenzylidenebutylaniline,[4] this value was found to be −3.76. These obtained values suggest that the repulsive part of the potential function plays an important role in the nematic–isotropic transition. Recently Keys and Daniels reported similar results for 4,4′-methoxybenzylidenebutylaniline.[6] For the melting of solid, many authors[7] suggest that the repulsive part of the potential energy plays an important role. In our experiments using 8CB, the value close to −4, which was calculated by employing the Pople–Karasz repulsion potential model, was obtained. Therefore, in the nematic–isotropic transition also the repulsion term plays and important role, as is seen in the melting of solids.

The value of d ln $T_{tr}$/d ln $V_{tr}$ is an excellent indicator to verify the role of the volume-dependent part of the potential energy function in the theory of nematics.

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# Micelle Formation of Ionic Surfactants. Tracer Self-Diffusion Studies and Theoretical Calculations for Sodium *p*-Octylbenzenesulfonate

**Björn Lindman,*[1a] Marie-Claude Puyal,[1b] Nicole Kamenka,[1b] Bernard Brun,[1b] and Gudmundur Gunnarsson[1c]**

*Divisions of Physical Chemistry 1 and 2, Chemical Center, S-220 07 Lund, Sweden, and Laboratoire des Interactions Moléculaires, Faculté des Sciences, U.S.T.L., Montpellier, France* *(Received: September 23, 1981; In Final Form: November 25, 1981)*

An investigation of association phenomena in aqueous solutions of a surfactant, sodium *p*-octylbenzenesulfonate (SOBS), was performed by self-diffusion measurements. Self-diffusion coefficients were obtained for amphiphile ions, sodium counterions, solubilized decanol molecules, water molecules, and chloride co-ions as a function of surfactant concentration by using the open-ended capillary tube method employing radioactive labeling. Decanol self-diffusion provides information on micellar translation and size. Surfactant ion self-diffusion gives the concentration of free surfactant ions. It is found that, at higher concentrations, free-surfactant concentration falls well below the critical micelle concentration. Counterion self-diffusion provides information on the concentration of free counterions and on $\beta$, the ratio of counterions and surfactant ions in the micelles. $\beta$ is invariant over wide concentration ranges corresponding to an ion condensation type behavior; however, at low concentrations $\beta$ decreases with increasing micelle concentration. The co-ion self-diffusion coefficients are used to deduce an effective excluded volume; the excluded volume per micelle decreases with increasing surfactant concentration. The water self-diffusion coefficients give information on micelle hydration; although hydration numbers are difficult to obtain (and to define), it may be shown that they are small and that there is no marked water penetration deep into the micelles. The various types of information obtained give an overall view of micellar solutions which is compared with current studies by other approaches, experimental and theoretical. Furthermore, various methodological problems and advantages of self-diffusion investigations of micelle formation are considered. Using a recently developed theory, which treats the electrostatic effects according to the Poisson–Boltzmann equation, we calculated the concentrations of free and micellized amphiphile ions and counterions. All of the features of the experimental observations were displayed also by the theoretical results, and for the amphiphile concentrations good quantitative agreement was found. For $\beta$, quantitative differences between experiment and theory were found which can be referred to the somewhat ambiguous division into free and micellar counterions.

## Introduction

Although the general picture of surfactant association into micelles was suggested quite some time ago, it is only recently that important aspects have been clearly established and that important molecular aspects have been touched on (recent reviews of the field are given by ref 2–4). Laser light scattering studies[5] have provided accu-

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(1) (a) Physical Chemistry 1, Lund; (b) Faculté des Sciences, Montpellier; (c) Physical Chemistry 2, Lund.

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rate information on micelle size and in particular on the growth from spherical to cylindrical micelles. Experimental and theoretical kinetic studies[6] in combination have provided a clear understanding of micellar kinetics and also of the molecular events involved in surfactant association and micelle dissociation. Various NMR studies[4,7-10] have given evidence for a liquidlike interior of the micelles and for a counterion binding mainly determined by the micellar charge density. Important theoretical studies[4,11-16] have dealt with the hydrophobic effect, with molecular-shape effects on aggregate structure, and with the electrostatic energy of micellization. Micellization is a loose association lacking a well-defined stoichiometry and directed short-range interactions as encountered in many other cases of chemical complex formation. The partitioning of a molecule between the micelles and the aqueous intermicellar medium then cannot be unambiguously defined but depends on criteria chosen, and these in turn depend on the experimental technique. Changes in spectroscopic parameters are often very useful in monitoring micelle formation, but one difficulty frequently encountered is to establish the value of the spectroscopic parameter in the micellar state; in NMR studies, e.g., with $^{13}C$ nuclei, this has been handled by iteration procedures.[17]

Since a micelle has a much lower translational mobility than a small molecule or ion in the bulk of the solution, the association of a species with a micelle leads to a rather marked change in the self-diffusion coefficient. Knowing the free-ion or -molecule self-diffusion coefficient as well as that of the micelle, one may quantitatively deduce the distribution between free and micellized states. It should then be possible to monitor such aspects as free-surfactant concentration, micelle hydration, counterion binding, and solubilizate partitioning. We previously made some attempts along these lines[18,19] but then had to resort to simplifying assumptions, because of incomplete experimental data. The present report describes a systematic self-diffusion study of the association of a surfactant, sodium *p*-octylbenzenesulfonate. On the basis of tracer self-diffusion coefficients of the surfactant ion, the counterion, a co-ion (of added salt), the water molecule, and a solubilized molecule, we deduce information on the micelle composition and present a discussion of possibilities and limitations of the method. The results confirm and extend current views on micelle formation and also provide some new insight.

A theoretical model for surfactant association into micelles with special emphasis on electrostatic effects has recently been presented.[13] In the present work we have performed calculations using this model for the self-association of sodium *p*-octylbenzenesulfonate. Thus, the theoretical values of the concentrations of free and micellized amphiphile ions and counterions as well as the degree of counterion binding may be compared with the experimental findings.

## Experimental Section

The experimental technique used was the open-ended capillary tube method with radioactive labeling, essentially as described in previous papers.[18,20] This technique requires considerable experimental work since the experiments are time-consuming and a separate experiment is usually required for each component (surfactant, counterion, etc.) at each concentration. The diffusion time is typically of the order of a few days. Another difficulty may be the availability of labeled compounds; often synthetic work is required. Furthermore, for certain systems (although not for that considered here) one may have adsorption effects causing systematic errors. The recently developed Fourier transform pulsed gradient NMR spin-echo self-diffusion method[21,22] provides simultaneously data for several $^1H$ (or $^{13}C$)-containing compounds in the same solution in a short time and is generally to be preferred for complex surfactant systems. However, since it cannot monitor the diffusion of many inorganic ions ($Na^+$ and $Cl^-$ in the present case), a combination of the two techniques is usually most advantageous.

Because of the relatively high Krafft point (18 °C) of sodium *p*-octylbenzenesulfonate (SOBS), all of the measurements were made at 33 ± 0.5 °C. Capillary lengths varied between 1 and 3 cm depending on the value of the self-diffusion coefficient measured. Care was taken to avoid any macroscopic concentration gradients. Radioactivity measurements used a Packard Tri-Carb liquid scintillation spectrometer equipped with a Packard Auto-Gamma spectrometer. $\gamma$ emitters were measured directly in the capillaries (after some waiting time to achieve solution homogeneity in the capillary), while for $\beta$ emitters the capillary content was transferred to an Instagel Packard scintillator solution before counting.

SOBS was synthesized according to a synthesis proposed by Gray et al.[23] To phenyloctane is added dropwise 20% $H_2SO_4$, the temperature being kept below 30 °C. The temperature is then kept at 55 °C for 1.5 h, after which 10% NaOH is added and the pH finally adjusted to 7. The desired surfactant is filtered off and purified by recrystallization in water. $^{35}S$-labeled SOBS was obtained analogously in a microsynthesis which was developed starting with 98% $^{35}S$-labeled sulfuric acid (from CEA, Département des Radioéléments, Gif sur Yvette, France; specific activity, 59 mCi mmol$^{-1}$). The activity of the obtained product is 1 mCi mmol$^{-1}$. $^{14}C$-labeled decanol

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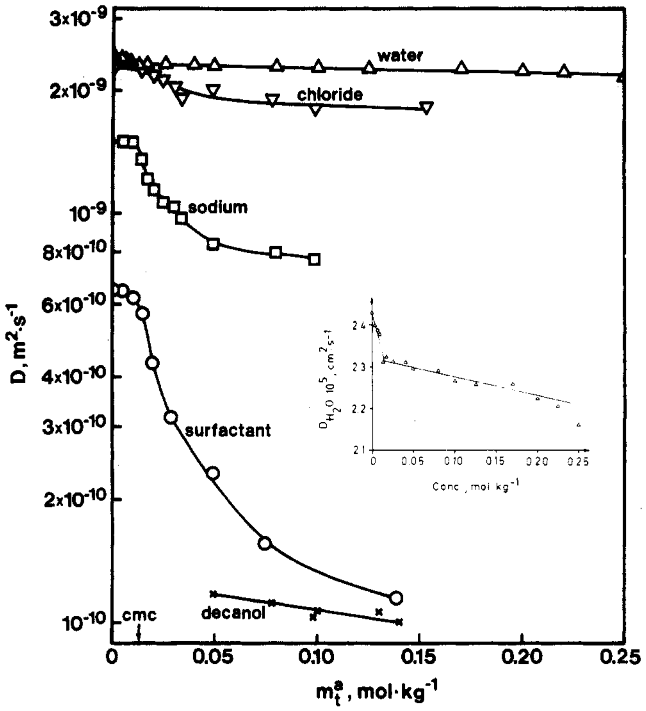

**Figure 1.** Surfactant concentration dependence of the self-diffusion coefficients of water (△), chloride ions (▽), sodium ions (□), surfactant ions (○), and decanol (×) for aqueous solutions of sodium *p*-octylbenzenesulfonate (temperature, 33 °C). (Chloride ions and decanol were added in small amounts; cf. text.) The insert shows the water self-diffusion coefficients; here, the *D* values are given on a linear scale, while in the main figure a logarithmic scale is used.

with a specific activity of 14 mCi mmol$^{-1}$ was obtained from Paris Labo, Paris, $^{22}$Na-labeled sodium chloride with a specific activity of 30 mCi mg$^{-1}$ from Amersham, Radiochemical Center, Buckinghamshire, England, $^{36}$Cl-labeled sodium chloride with a specific activity of 7 $\mu$Ci mg$^{-1}$ from Amersham, and $^{3}$H-labeled water with a specific activity of 1 Ci mL$^{-1}$ from C.E.A.

## Experimental Results

Self-diffusion coefficients of octylbenzenesulfonate ions, of sodium ions, of chloride ions (from added small amounts of NaCl), of decanol molecules (added small amounts of decanol), and of water molecules were obtained as a function of surfactant concentration at 33 °C. In the decanol diffusion measurements the decanol-to-surfactant molar ratio was in the range 0.04–0.08, except for the lowest surfactant concentration where it was 0.113. In the chloride diffusion studies the Cl$^-$ concentration was ca. 0.002 mol kg$^{-1}$.

The experimental self-diffusion coefficients are plotted vs. the surfactant concentration in Figure 1. Plots of the surfactant and counterion diffusion coefficients vs. the inverse surfactant concentration give essentially two straight lines intersecting at the cmc (0.0128 *m*) as suggested by the phase separation model (and a constant counterion binding).[18] Throughout the concentration range covered, the self-diffusion coefficients decrease in the sequence water (self-diffusion coefficient denoted $D^{\mathrm{w}}$), chloride ($D^{\mathrm{Cl}}$), sodium ($D^{\mathrm{Na}}$), surfactant ($D^{\mathrm{a}}$), and solubilizate ($D^{\mathrm{s}}$). $D^{\mathrm{w}}$ decreases monotonously with increasing surfactant concentration, but the decrease is more than a factor of 10 more rapid below than above the cmc (see insert of Figure 1). $D^{\mathrm{Cl}}$ decreases rather regularly over the entire concentration range and is (not unexpectedly) the only self-diffusion coefficient not displaying clearly the cmc. $D^{\mathrm{Na}}$ starts to decrease rapidly at the cmc, and at the highest concentrations it levels off at a value which is about half that observed below the cmc. Decanol diffusion is very slow and decreases slowly with increasing surfactant concentration. $D^{\mathrm{s}}$ could not be measured below the cmc for solubility reasons (the solubility of decanol in water is about 1.5 × 10$^{-7}$ mol kg$^{-1}$), but the self-diffusion coefficient of decanol in water can be expected[24] to be ca. 6 × 10$^{-10}$ m$^2$ s$^{-1}$.

## Discussion of the Self-Diffusion Results

*General Aspects of the Method.* The self-diffusion coefficients to be discussed refer to experiments in which the diffusion time is very long; i.e., the study concerns diffusion over macroscopic distances, several orders of magnitude larger than the extension of any aggregate in the solutions. It may be useful to distinguish between effects of confinement and effects related to the partitioning between different aggregates. If the solution is microscopically inhomogeneous and contains closed domains and a certain molecule or ion is confined to such domains, its self-diffusion coefficient will be very low. For example, in a micellar solution a solubilizate with a very low aqueous solubility will be confined to the micelles and therefore have a very low self-diffusion coefficient, corresponding to the motion of the whole micelle. On the basis of this simple principle, it is possible in studies of hydrophobic and hydrophilic molecules or ions to establish whether a certain solution is water or "oil" continuous, or bicontinuous or neither oil nor water continuous. Although it is well accepted, it is clearly borne out by the present experimental data (Figure 1) that micellar solutions are water continuous and oil discontinuous. However, for phases with unknown structure like microemulsions and various liquid crystalline phases, the self-diffusion method may give structural information.[20,25–28]

In a solution where a certain species can occur in different kinetic entities, normally different chemical complexes, the self-diffusion coefficient observed for this species is given by the probabilities for it to occur in the different environments as well as the intrinsic self-diffusion coefficients of the different kinetic entities. The simple relation is

$$D = \sum p_i D_i \qquad (1)$$

Here $D$ is the observed self-diffusion coefficient, $p_i$ is the fraction of the observed molecules or ions in a complex i, and $D_i$ is the self-diffusion coefficient of this complex. Equation 1 presupposes that the lifetime of the studied species in a site i is much shorter than the measuring time, which is no limitation in the present case. However, there are other complications, arising for the present problem, for example, from an effective translational motion within an aggregate combined with a very short lifetime in the aggregate.[29]

We are interested in this work in the distribution of the different molecules and ions between the micelles and the intermicellar solution. It is reasonable to describe the system in terms of a two-site model, with the two environments or sites referred to by subscripts m and f. Equation 1 then reads

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$$D^x = p_f^x D_f^x + p_m^x D_m = D_f^x - p_m^x(D_f^x - D_m) \qquad (2)$$

Here x is w, Cl, Na, a, or s. $p_m^x$ and $p_f^x$ are the fractions of micellized and free x, $D_f^x$ the self-diffusion coefficient of free x, and $D_m$ the micelle self-diffusion coefficient. Apparently, with information on $D_f^x$ and $D_m$, a measured value of $D^x$ directly gives $p_m^x$ at the concentration studied. Therefore the data in Figure 1 should give the concentration dependence of $p_m^x$ (and, of course, also of the concentration of micellized x, $m_m^x$) provided that $D_f^x$ and $D_m$ are known. $D_m$ can be measured directly in the actual solution by studying the diffusion of a molecule confined completely to the micelles; in the present case the diffusion of small amounts of added decanol was studied. Moreover, $D_m \ll D_f^x$ for all cases so that errors in $D_m$ have a quite small influence on the calculated $p_m^x$ values; in fact, it is often a useful first approximation to neglect $D_m$.

To deduce the various $D_f^x$ values at different concentrations is a much more delicate problem, and in the course of this study several different procedures have been tried. The $D_f^x$ values differ from the corresponding values, $D_0^x$, at infinite dilution in water (the $D_0^x$ values can easily be obtained by extrapolation of low-concentration data or calculated from limiting conductances) for two principal reasons. Firstly, ion–ion and ion–solvent interactions among the free ions and molecules decrease the translational mobilities, as is well-known for simple nonassociated electrolyte solutions where this has been considered in detail both experimentally and theoretically.[30,31] If one knows the composition of the intermicellar solution, $D_f^x$ values may be estimated empirically or from theoretical expressions. Since the intermicellar concentrations are deduced by using $D_f^x$ values, an iteration procedure (with rapid convergence, however) is required. However, the present situation differs from that previously treated in that the intermicellar solution is not symmetric with respect to anion and cation concentrations; typically the free-counterion concentration is 1 order of magnitude higher than the free-surfactant concentration. In the present case, however, the cmc is rather low, so that corrections are small and no significant error is introduced. The second source of concentration dependence in $D_f^x$ is an obstruction effect due to the micelles which act as an excluded volume for certain molecules or ions, thus lengthening their diffusion paths. Knowing the shape and volume fraction of the micelles, one may use the results of Wang[32] to correct for this effect. (As an example, at 0.14 *m* SOBS, the upper limit of most of the measurements in this work, the correction amounts to 4.9%. At 0.25 *m* it amounts to 8.7%.) However, for ionic surfactant solutions, electrostatic interactions[13,14] are very important and of long range, and therefore the effective excluded volume could conceivably depend markedly on the molecular charge (positive, negative, or uncharged).[33] To treat this, one may either attempt electrostatic calculations of the effects or make empirical corrections based on measurements of species not associated with the micelles. However, neither approach is easy and objection-free.

*Micelle Self-Diffusion.* For a compound in a micellar solution which is entirely confined to the micelles and has a negligible solubility in the intermicellar solution, the observed self-diffusion coefficient will be the same as the self-diffusion coefficient of the micelles. One must realize that the added solubilizate may perturb the micelles in some way, i.e., by reducing the critical micelle concentration or affecting micelle size (and/or shape), or it may preferably sample part of the micelle distribution curve. Therefore, the micellar self-diffusion coefficient obtained in the presence of a solubilizate may differ somewhat from that of the solubilizate-free micellar solution. On the other hand, there exists to our knowledge no other method to determine the self-diffusion coefficient of micelles.[34] The errors inherent in the procedure may be reduced as far as possible by working at low solubilizate concentrations and making measurements at several solubilizate concentrations and extrapolating to zero solubilizate concentration.

We obtained the micelle self-diffusion coefficient, $D_m$ from measurements on $^{14}$C-labeled decanol; decanol has a very strong preference for the micelles, and the nonsolubilized fraction is negligible.[38] Observed values of $D_m \simeq D_s$ are given as a function of the total surfactant concentration in Figure 1. A plot of $1/D_m$ vs. the concentration of micellized surfactant (deduced as described below from the amphiphile self-diffusion) is approximately linear with an extrapolated $D_m$ value at zero micelle concentration of $1.23 \times 10^{-10}$ m$^2$ s$^{-1}$ and a slope of $1.17 \times 10^{10}$ s kg m$^{-2}$ mol$^{-1}$; for sodium dodecyl sulfate we found previously[19] (at 25 °C) from a less rigorous treatment the extrapolated value $1.5 \times 10^{-10}$ m$^2$ s$^{-1}$ and the slope $0.78 \times 10^{10}$ s kg m$^{-2}$ mol$^{-1}$.

The reduction in $D_m$ with increasing micelle concentration is probably due mainly to electrostatic intermicellar repulsion. A theoretical account of this effect has been given by Mazo,[39] who obtains an initial linear relation between $D_m^{-1}$ and the micellar concentration in approximate agreement with the present findings. We find no further reduction in $D_m$ at higher concentrations (up to 0.15 mol kg$^{-1}$) as would be expected for a micellar shape transition, and the micelles can therefore be considered to remain approximately spherical throughout the concentration range studied.[40] Theoretical arguments as well as experimental results suggest that the optimal micellar radius corresponds approximately to the extended amphiphilic molecule;[4] in the present case the radius of the "dry" micelle should then be 20 Å. Because of hydration, the hydrodynamic radius (calculated from $D_m$ by using the Stokes–Einstein equation) will be slightly larger. The

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[33] The problem is apparently to achieve a separation into (attractive) interaction and excluded-volume effects, which is not unambiguous. An alternative way of expressing the problem is in terms of attractive and repulsive interactions, the obstruction effect being a hard-core interaction. For co-ions, for example, we consider only repulsive interactions, while for the amphiphile ions these are relatively insignificant.

[34] The mutual diffusion coefficients measured with quasi-elastic light scattering (QLS)[5,35] equal the self-diffusion coefficients for the case where intermicellar interactions are negligible, as for infinite dilution. Mazer et al.,[5,36,37] in their extremely valuable studies of sodium dodecyl sulfate micelles, have eliminated intermicellar interactions by adding high concentrations of electrolyte. When comparing micellar diffusion coefficients obtained by different experimental methods, one should realize that different averages are encountered. In our self-diffusion studies it is the probability of decanol solubilization which weights different micellar sizes, while in quasi-elastic light scattering the amount of scattered light is decisive. For the rather low-disperse spherical micelles studied here, the difference should be negligible.

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[38] From the work of Stilbs[24] one may estimate that for decanol in sodium dodecyl sulfate solutions the degree of solubilization is, as an example, ≳99.5% at 0.1 mol kg$^{-1}$.

[39] R. M. Mazo, *J. Chem. Phys.*, 43, 2873 (1965).

[40] Viscosity data also show that there is no significant growth of the micelles at higher concentrations. The intrinsic viscosity is determined to be 0.87 L mol$^{-1}$ (at 40 °C), which, assuming spherical shape, gives a partial molar volume for the micellized surfactant of 1.19 mL g$^{-1}$, a value close to those obtained for other cases.

difference obtained in the present study, ca. 3 Å, is in agreement with several experimental techniques finding one layer of water molecules being appreciably perturbed and moving with the micelle.[41-45] However, the figure obtained is rather imprecise, and deducing information on hydration from hydrodynamic data is far from being objection-free, in general, and in the present case the effects of micellar surface roughness and dynamic amphiphile protrusion are difficult to account for.

A few measurements of $D_m$ in the presence of added salt were also performed. On addition of $50 \times 10^{-3}$ *m* NaCl to a $50 \times 10^{-3}$ *m* SOBS solution, $D_m$ changes insignificantly ($1.17 \times 10^{-10}$ to $1.19 \times 10^{-10}$ m$^2$ s$^{-1}$). (It should be recalled that there is some increase in the micellar concentration on addition of salt.) Corresponding additions of the other alkali chlorides give $1.10 \times 10^{-10}$ m$^2$ s$^{-1}$ for LiCl, $1.05 \times 10^{-10}$ m$^2$ s$^{-1}$ for KCl, and $1.11 \times 10^{-10}$ m$^2$ s$^{-1}$ for CsCl. Hence, there seem to be no significant counterion effects on SOBS micelle size at these concentrations.

*Surfactant Self-Diffusion.* Surfactant self-diffusion coefficients were measured to obtain information on the cooperative self-association process. The surfactant ions have rather long residence times in the micelles,[6] and a description with two distinct states is a good approximation. Thus

$$D^a = p_f^a D_f^a + p_m^a D_m \tag{3}$$

from which one may deduce for the concentration of free (nonassociated) amphiphile

$$m_f^a = m_t^a - m_m^a = \frac{D^a - D_m}{D_f^a - D_m} m_t^a \tag{4}$$

$m_t^a$ being the total amphiphile concentration. The problem in deducing $m_f^a$ from the experimental $D^a$ and $D_m$ values lies in estimating $D_f^a$. $D_f^a$ can be thought to affected by ion–ion (and ion–solvent–ion) interactions in the intermicellar medium and by an obstruction effect due to the micelles. Calculations of $m_f^a$ were performed with various estimates of $D_f^a$: taking a constant infinite-dilution value; making an empirical correction for the intermicellar ion concentrations (in an iterative procedure); correcting these values for an excluded-volume effect due to the micelles. Another idea was that the mobility of the free surfactant should be mimicked by an anion not associated with the micelles; therefore, the diffusion of added small amounts of chloride ions was investigated. However, it can be argued that hydrophilic and hydrophobic anions must have quite different short-range interactions with the micelles. A hydrophilic ion of the same charge as the micelles should, because of electrostatic repulsion, experience a large excluded volume due to the micelles while, for a hydrophobic ion, in view of the liquidlike character of micelles,[4,7] it is not appropriate to correct for an excluded-volume effect. The retardation of motion due to being part of a micelle is taken into account by the last term of eq 3.

Calculations of $m_f^a$ as a function of $m_t^a$ were performed[46] with each of the aforementioned estimates of $D_f^a$. Qualitatively the same behavior of $m_f^a$ was deduced in all cases: At low concentrations $m_f^a$ equals $m_t^a$, then around the cmc it has a broad maximum, and, when $m_t^a$ is much larger than the cmc, the free-amphiphile concentration falls well below the cmc. To illustrate the effects of different modes of calculation, one can mention that the maximal $m_f^a$ may vary at most between $12 \times 10^{-3}$ and $15 \times 10^{-3}$ *m*. At higher total concentrations, the difference between different procedures is smaller. Since $D^a$ and $D_m$ approach each other at higher concentrations, experimental errors then produce large *relative* errors in $m_f^a$. Similarly, at low concentrations the large error in $D_f^a - D^a$ propagates to $m_m^a$. The experimental uncertainty is estimated to introduce errors in $m_f^a$ and $m_m^a$ which are $\pm(1 \times 10^{-3}$–$2 \times 10^{-3})$ *m* over the entire concentration range.

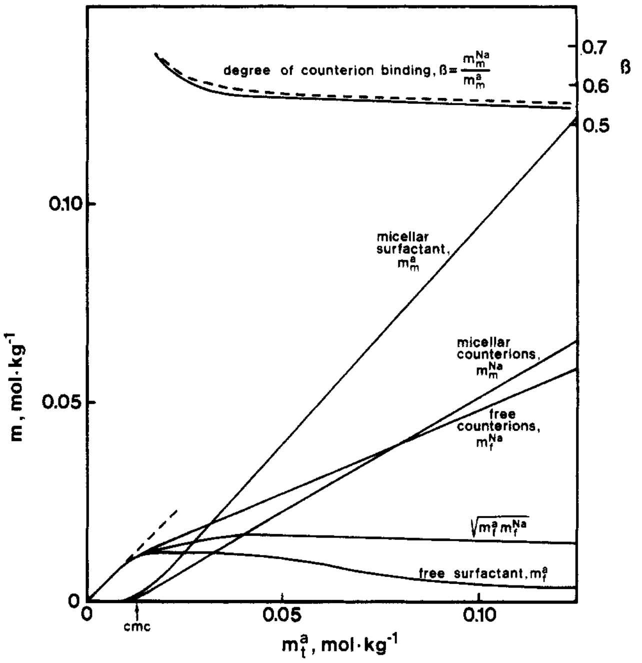

**Figure 2.** Deduced concentrations of free and micellized amphiphile ions and counterions vs. the total surfactant concentration for aqueous solutions of sodium *p*-octylbenzenesulfonate: $m_f^a$ = free surfactant ion concentration; $m_f^{Na}$ = free sodium ion concentration; $m_m^a$ = micellized-surfactant concentration; $m_m^{Na}$ = micellar sodium ion concentration; $\beta$ = degree of counterion binding (dashed line, no obstruction-effect correction, cf. text).

In Figure 2 we present the concentrations of free and micellized surfactant as obtained in a calculation where $D_f^a$ was corrected only for the intermicellar ion concentrations; although the problem of estimating $D_f^a$ is not completely solved, we believe that this is the most satisfactory approach. It can be seen that $m_f^a$ increases as $m_t^a$ at low concentrations, starts to deviate well below the cmc, has a maximum approximating the cmc, and decreases monotonously to values well below the cmc at higher concentrations. $m_m^a$ starts to be significant below the cmc and increases after the cmc approximately linearly with $m_t$.

*Counterion Self-Diffusion.* The application of a two-state model for the counterions can certainly be questioned since it is known that micelle–counterion interactions are nonspecific and long-range.[4] However, retaining a two-state approximation in spite of the fact that a continuous ion distribution is a preferable description can be defended for two reasons. Firstly, a two-state model gives a very convenient description of the counterion binding, for example, as a function of concentration, solubilization, added salt, etc. Secondly, recent theoretical calculations of the Poisson–Boltzmann[13] and the Monte Carlo type[48,49] dem-

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(41) P. Mukerjee, *J. Colloid Sci.*, 19, 722 (1964).

(42) P. Ekwall and P. Holmberg, *Acta Chem. Scand.*, 19, 455 (1965).

(43) D. Stigter, *J. Phys. Chem.*, 78, 2480 (1974).

(44) B. Halle and G. Carlström, *J. Phys. Chem.*, 85, 2142 (1981).

(45) B. Lindman, H. Wennerström, H. Gustavsson, N. Kamenka, and B. Brun, *Pure Appl. Chem.*, 52, 1307 (1980).

(46) Since we did not choose to measure all of the self-diffusion coefficients at exactly the same concentrations, interpolated values were generally used in the calculations. (In FT NMR self-diffusion investigations, this problem is not at hand.[47]) For this reason, deduced quantities are represented in the figures by continuous curves.

(47) P. Stilbs and B. Lindman, *J. Phys. Chem.*, 85, 2587 (1981).

onstrate that the counterion distribution is sharp enough to make a two-state model a good approximation; bound ions are in these calculations taken to be those which are attracted by the micelle by more than 1 kT.

With a two-site model the concentration of bound counterions is

$$m_m^{Na} = m_t^{Na} - m_f^{Na} = \frac{D_f^{Na} - D^{Na}}{D_f^{Na} - D_m} m_t^{Na} \quad (5)$$

where $m_t^{Na}$ is the total counterion concentration (allowing for a case of added salt, see below). It is useful to introduce the degree $\beta$ of counterion binding as

$$\beta = m_m^{Na}/m_m^a$$

The effective charge per micellized monomer is $1 - \beta$.

The problem of calculating $m_m^{Na}$ lies mainly in establishing how to estimate $D_f^{Na}$. It is evident that for the counterions the micelles constitute an excluded volume which by an obstruction effect reduces $D_f^{Na}$; this obstruction effect was taken according to Wang.[32] On the other hand, the effect of interionic interactions was empirically found to be negligible. The values of $m_f^{Na}$, $m_m^{Na}$, and $\beta$ so obtained are given in Figure 2. Included are also $\beta$ values obtained without the obstruction-effect correction. As with the amphiphile, alternative ways of estimating $D_f^{Na}$ were also tried, but qualitatively the same results were obtained. The error in $\beta$ is very large around the cmc because of large relative errors in both $D_f^{Na} - D^{Na}$ and $D_f^a - D^a$. However, the reduction in $\beta$ with increasing surfactant concentration at low micelle concentrations is certainly significant.

Considering Figure 2, the increase in $m_f^{Na}$ above the cmc and the slower increase of $m_m^{Na}$ than of $m_m^a$ are according to expectation and without particular interest. What should be noted is firstly that $\beta$ is quite constant (at 0.55–0.60) over a wide concentration range (0.03–0.12 mol kg$^{-1}$) and that $\beta$ is somewhat higher at low than at high micelle concentrations.

Additionally, we studied the effect on counterion diffusion of adding NaCl, of ion competition (addition of different alkali chlorides), and of solubilization of cyclohexane, benzene, and octanol. Although micellar self-diffusion was only studied in part of these conditions, the concentration of bound and free counterions could be rather reliably deduced. However, since amphiphile diffusion was not studied, the concentration of micellar and free amphiphile is unknown and $\beta$ could not be reliably obtained. In view of these limitations, these investigations will only be briefly considered.

In Figure 3 we have plotted observed values of $D^{Na}$ as a function of the surfactant concentration for three concentrations of added NaCl, i.e., 0.001 *m* (cmc = 0.0125 *m*), 0.01 *m* (0.0113 *m*), and 0.05 *m* (0.083 *m*). Given are also the concentrations of free and micellar counterions calculated as above by using a simple obstruction correction to obtain $D_f^{Na}$. The general appearance of $m_f^{Na}$ and $m_m^{Na}$ is similar to that observed without added salt taking into consideration the change in cmc. Calculations of $\beta$ give ca. 0.5 for high surfactant concentrations for all three NaCl concentrations irrespective of how $m_m^a$ is chosen. At lower surfactant concentrations, $\beta$ is ca. 0.5 throughout if a sharp decrease in free-surfactant concentration is assumed at the two higher NaCl concentrations. If a similar behavior of $m_f^a$ is assumed as for the salt-free case, rather high (0.8–0.9) and sharply decreasing (with surfactant concentration) $\beta$'s are found for low surfactant concentrations. A choice between these two possibilities cannot be made at present.

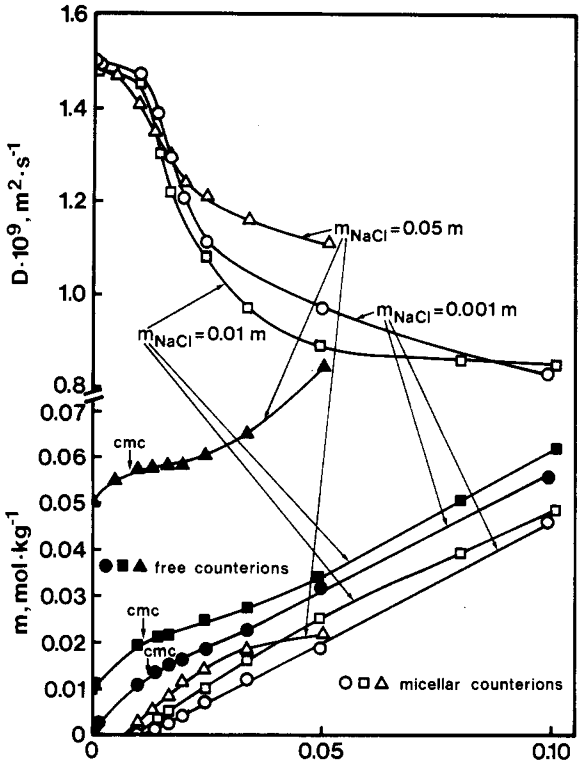

**Figure 3.** Sodium ion self-diffusion coefficients in solutions containing sodium octylbenzenesulfonate and sodium chloride (fixed at 0.001, 0.01 or 0.05 *m*) as a function of surfactant concentration. Lower part gives the concentrations of free (filled symbols) and micellar counterions (open symbols) at 0.001 (●, ○), 0.01 (■, □), and 0.05 (▲, △) *m*.

TABLE I: Effect of Adding 0.050 *m* Alkali Chloride to a 0.050 *m* Sodium Octylbenzenesulfonate Solution on the Sodium Ion Self-Diffusion Coefficient ($D^{Na}$) and on the Degree of Counterion Binding to the Micelles ($\beta$)

| salt added | $10^9 D^{Na}$, m$^2$ s$^{-1}$ | $\beta^{Na}$ | bound Na$^+$ ions, % |
|---|---|---|---|
| none | 0.844 | 0.60 | |
| LiCl | 1.04 | 0.35 | 30.3 |
| NaCl | 1.11 | 0.59 (0.29)[a] | 25.3 |
| KCl | 1.13 | 0.27 | 23.6 |
| RbCl | 1.17 | 0.24 | 20.7 |
| CsCl | 1.30 | 0.13 | 11.4 |

[a] In this experiment twice as many Na$^+$ ions are bound as under equibalent binding conditions for the other cases. Therefore, the observed figure should be divided by two in the comparison.

Results of additions of 0.050 *m* of the different alkali chlorides to a solution containing 0.050 *m* SOBS are given in Table I. $m_m^{Na}$ and $\beta$ were calculated by using measured values of $D_m$, $D_f^{Na}$ values obtained by making a simple obstruction-effect correction and assuming $m_m^a$ to be 0.0043 *m* throughout. (The latter assumption is without greater importance in comparing the different counterions.) There are only small differences in cmc among the different counterions, but there are marked ion-competition effects. The larger the added bare ion, the lower is the degree of Na$^+$ binding observed; i.e., ion binding increases monotonously going from Li$^+$ to Cs$^+$ in the alkali series.

In the solubilization studies, $D^{Na}$ was measured as a function of added cyclohexane, benzene, and octanol for

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(48) B. Jönsson, H. Wennerström, and B. Halle, *J. Phys. Chem.*, 84, 2179 (1980).

(49) P. Linse, G. Gunnarsson, and B. Jönsson, *J. Phys. Chem.*, 86, 413 (1982).

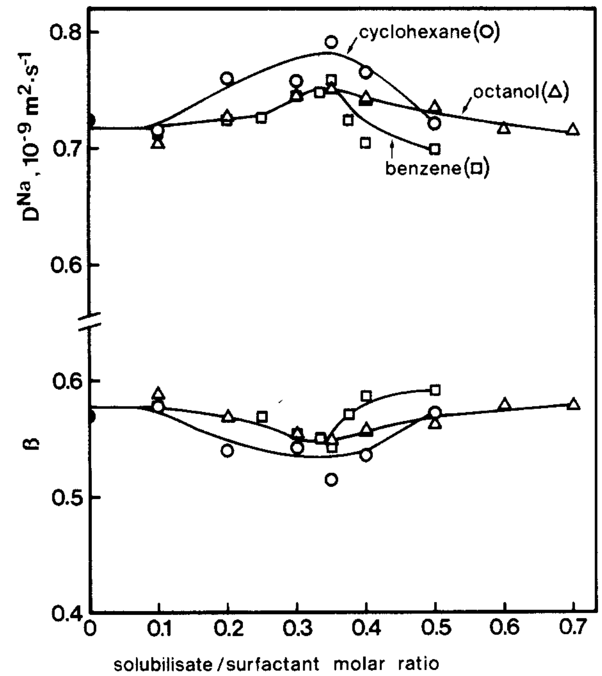

**Figure 4.** Sodium ion self-diffusion coefficients (31 °C) as a function of added cyclohexane (O), benzene (□), and octanol (Δ) for 0.08 *m* solutions of sodium octylbenzenesulfonate. Lower part shows β, the degree of counterion binding.

0.080 *m* SOBS solutions. (These measurements were performed at 31 °C, while all others were made at 33 °C.) β values were calculated as above by assuming $D_f^{Na}$ to be $1.41 \times 10^{-9}$ m$^2$ s$^{-1}$ and $m_f^a$ to have a constant value of 0.0059 mol kg$^{-1}$. The $D^{Na}$ and β values presented in Figure 4 show above all that $D^{Na}$, and thus also β, is almost independent of solubilization. One is really on the limit of being able to discern any significant changes in β. However, there seems in all three cases to be a slight decrease in β for intermediate amounts of solubilizate (molar ratio around 0.3). The increase in β at higher solubilizate concentration may at least partly be an artifact due to the assumption of a constant value of $m_f^a$; in fact, $m_f^a$ is expected to decrease slightly on solubilization since solubilization should stabilize the micelles.

*Water Self-Diffusion.* The translational motion of the water molecules is retarded by the micelles by two mechanisms: the bulk of the micelles obstruct water translation and water molecules have their mobility reduced because of an "association" with the micelles. Water being the solvent, it is not straightforward (and perhaps not even meaningful) to make a separation into free and micelle-bound water molecules. Thus, solvent molecules are close to solutes even in the absence of strong attraction; cf. water structuring around hydrophobic solutes. We may also recall that there are many different ways of defining hydration numbers and many experimental techniques which can provide hydration numbers. On the other hand, it is very difficult to interpret the hydration numbers obtained. However, simple calculations from the self-diffusion data may give limits of the hydration and therefore help in deducing, for example, whether water penetrates into micelles or not.

In a plot of $D^w$ vs. $m_t$, the slope is about 15 times as large below as above the cmc. Using the phase separation model of micelle formation, one infers that the nonassociated amphiphile is ca. 15 times as effective as the micellized amphiphile in reducing water mobility. Recalling in addition that the nonassociated amphiphile has a mobility about 6 times as high as the micellized one, we may estimate that the effective hydration number of an amphiphile ion in a micelle is almost a factor of 100 below that of the free amphiphile. This simple estimate indicates that on micellization the hydrocarbon chains of the amphiphile are almost completely withdrawn from water contact. In order to more quantitatively study this problem, we have made calculations for the simple two-site model, i.e.

$$D^w = D_f^w - (n m_m^a / 55.5)(D_f^w - D_m) \qquad (6)$$

Here *n* is the average hydration number per amphiphile ion of the micelle. The term referring to the nonmicellar water molecules can be split into terms corresponding to free water molecules, water molecules hydrating the free amphiphile ions, and water molecules hydrating the free sodium ions.[50] The two latter effects were taken into account empirically. Thus, in the calculations we used the deduced concentrations of free amphiphile ions and of counterions (cf. above) to empirically correct $D_f^w$ on the basis of the pre-cmc data and the water self-diffusion data of McCall and Douglass.[52] Furthermore, the simple obstruction effect was taken into account according to Wang[32] using the micelle concentrations deduced above. The calculations so performed gave hydration numbers in the range 5–12 over the entire concentration range without any significant variation with total amphiphile concentration; however, the precision in the hydration number was found to be quite low. Since the polar exterior of the micelle is accessible to water and since varying degrees of water penetration have been proposed in the literature (see below), calculations were performed with different values of the excluded volume, but this did not influence the general picture obtained.

Although in our opinion the water self-diffusion results give rather compelling evidence for a quite low micelle hydration, it is essential to point out two major difficulties in this type of study preventing us from obtaining any more detailed insight. Firstly, one is monitoring a very small relative change in water self-diffusion in the micellar region (less than 10% up to 20 times the cmc) making the experimental error quite significant in the calculations; on the other hand, one can of course note that, had there been a significant amount of water deep in the micelles, one would have observed quite large effects. Secondly, water being the solvent, its association with the micelles in terms of a hydration number cannot be interpreted unambiguously.

*Co-ion Self-Diffusion.* The concentration dependence of $D^{Cl}$ is naturally much weaker than for the amphiphile ions and the counterions and should mainly reflect retardation of motion firstly through an interaction with free counterions and secondly through an obstruction effect of the micelles; because of electrostatic repulsions, one expects the effective excluded volume sensed by $Cl^-$ ions to be greater than the actual micellar volume. We have been interested in estimating the radius of this excluded volume of a micelle. To obtain this, we have deduced the former effect, which is rather small, from $Cl^-$ self-diffusion data[53] of solutions of NaCl. Then we have calculated the volume fraction excluded by using Wang's equation.[32] Finally, our deduced values of $m_m^a$ and of the average micelle aggregation number have provided us with information on the micelle concentration and then with the effective excluded

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(50) The dramatic effect of free alkyl chains in retarding water diffusion, which has been noted previously (for example, ref 18, 19, and 51), corresponds to very large effective hydration numbers.

(51) H. G. Hertz, B. Lindman, and V. Siepe, *Ber. Bunsenges. Phys. Chem.*, **73**, 542 (1969).

(52) D. W. McCall and D. C. Douglass, *J. Phys. Chem.*, **69**, 2001 (1965).

(53) B. Brun, Thesis, Faculté des Sciences, Montpellier, France, 1967.

volume and radius of the micelle. Values of the radius so obtained[54] are around 35 Å at the lowest concentrations and decrease monotonously to around 25 Å at the highest concentrations studied (0.15 mol kg$^{-1}$). These values should be compared with the radius of the "dry" micelle estimated to be ca. 20 Å and the radius of the hydrated one estimated to be ca. 23 Å.

## Theoretical Calculations

One of the more interesting results of this study is the decrease observed in free-amphiphile concentration above the cmc. A theory, based on the Poisson–Boltzmann equation and the cell model of polyelectrolyte solutions, which gives the same behavior has recently been presented.[13] In order to compare the experimental results reported here with the above-mentioned theory, hereafter called the PB theory, we have done some calculations on a model of salt-free $p$-octylbenzenesulfonate solutions.

For the sake of simplicity, we shall take the micellar size distribution to be monodisperse, with micelles of aggregation number 50. The micelle is assumed to be spherical with a radius of 20 Å. The micellar solution is divided into spherical cells of equal size, radius $r_c$, each cell containing a micelle at its center. Because of the high micellar charge, there will be an accumulation of counterions (sodium ions) near the micelle and the free amphiphile ions will be repelled. The distribution of the small ions is given by

$$m^i(r) = m_0^i e \frac{-z_i e\psi(r)}{kT} \tag{7}$$

where $m_0^i$ is the concentration of ion i at the surface of the cell and $z_i$ its valence. $\psi(r)$ is the electrostatic potential at $r$, where $r$ is the radial distance from the center of the cell. Under given boundary conditions $m^i(r)$ is obtained from a solution of the Poisson–Boltzmann equation; for details see ref 13.

The nonuniform ion distribution will influence the free energy of a micellar solution and therefore also the chemical potential of each species. The chemical potentials of free amphiphile, $\mu_a^f$, and micellar amphiphile, $\mu_a^m$, can be expressed as

$$\mu_a^f = \mu_a^{f,O} + kT \ln (m_0^a M_{H_2O}) \tag{8}$$

$$\mu_a^m = \mu_a^{m,O} + \mu_a^m(\text{el}) + kT \ln X_m \tag{9}$$

where $\mu_a^{f,O}$ and $\mu_a^{m,O}$ are standard chemical potentials, $M_{H_2O}$ is the molecular weight of water, and $X_m$ is the mole fraction of micelle in a cell. $\mu_a^m(\text{el})$ is the electrostatic contribution to the chemical potential of a micellar amphiphile, and it varies with both the cell radius and the concentration of free amphiphile. For a detailed expression for $\mu_a^m(\text{el})$ see ref 13.

After the chemical potentials of the free and micellar amphiphiles are equated, the following equation is derived:

$$kT \ln X_m + (\mu_a^{m,O} - \mu_a^{f,O}) = kT \ln (m_0^a M_{H_2O}) - \mu_a^m(\text{el}) \tag{10}$$

For a given cell radius, $X_m$ is given. Assume that the value of $\mu_a^{m,O} - \mu_a^{f,O}$ is given. Both terms on the right-hand side of eq 10 vary with the total concentration of free amphiphile, $m_f^a$. $m_f^a$ and $m_0^a$ are related by

$$m_f^a = m_0^a \int \exp(-e\psi/kT)\, dV \tag{11}$$

where the integral is over the whole volume of the cell. $m_f^a$ (or $m_0^a$) is now varied until eq 10 is fulfilled. The free-amphiphile concentration $m_f^a$ and the total amphiphile concentration $m_t$ can now be calculated.

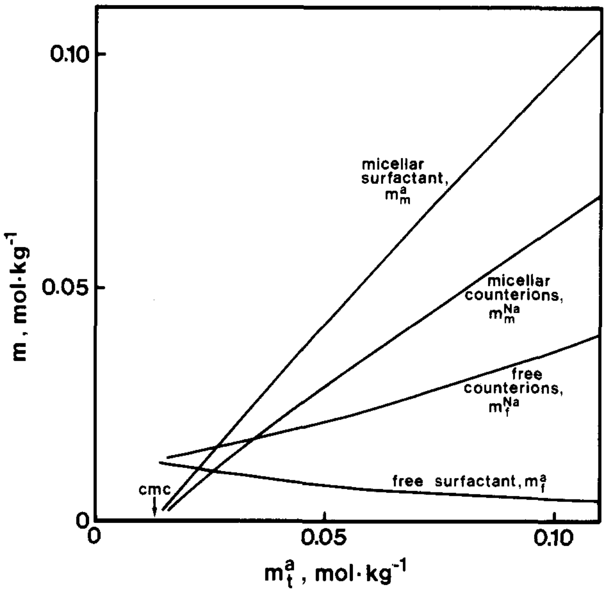

**Figure 5.** Calculated concentrations of free and micellized amphiphile ions and counterions vs. the total surfactant concentration as obtained from the theoretical model (see text) using the Poisson–Boltzmann equation for the electrostatic effects. (Notations as in Figure 2.)

This procedure is repeated for several values of $r_c$, the value of $\mu_a^{m,O} - \mu_a^{f,O}$ being kept constant. $m_m^a$ vs. $m_t^a$ is then plotted, and the intercept (extrapolated) is taken as a value of the cmc. The cmc will depend on the value of $\mu_a^{m,O} - \mu_a^{f,O}$. The value of $\mu_a^{m,O} - \mu_a^{f,O}$ is varied until agreement with the experimental cmc is obtained. The resulting plots of $m_f^a$ and $m_m^a$ vs. $m_t^a$ are shown in Figure 5. It is seen that the decrease in $m_f^a$ above the cmc is in nearly quantitative agreement with experiments. It has previously been shown[13] that, once the value of $\mu_a^{m,O} - \mu_a^{f,O}$ has been fixed, it is possible to reproduce the changes in cmc with salt concentration and with the change in counterion valency.

An estimate of the degree of ion binding to a micelle, $\beta$, can be obtained from the ion distribution. However, the separation into free and bound ions is not unambiguous, but different reasonable criteria can be utilized. These criteria in turn depend on the experimental technique considered. For the degree of ion binding as measured through a transport property, $\beta_{tr}$, such as self-diffusion coefficients, it is reasonable to consider ions with an electrical energy, $z_i e\psi$, larger than the thermal one, $kT$, as moving with the micelle and bound. In a thermodynamic measurement one measures the activity of the counterion, which within the PB theory is $m_0^{Na}$. The degree of ion binding as measured through a thermodynamic property, $\beta_{th}$, can be written

$$\beta_{th} = (m_t^a - m_0^{Na})/m_m^a \tag{12}$$

In spectroscopic measurements like NMR, it is only ions in the direct vicinity of the micelle that have spectroscopic properties different from those of a micelle-free solution. We therefore consider ions within a distance $\Delta$ from the micelle as bound, and the degree of ion association defined in this way is denoted $\beta_{sp}$.

In Figure 6 we show how $\beta_{tr}$, $\beta_{th}$, and $\beta_{sp}$ vary with total amphiphile concentration. Whichever definition of $\beta$ is used, we see that the variation in $\beta$ with $m_t^a$ is quite weak, thus justifying the assumption of a constant $\beta$ often used in the literature. (Theoretical calculations using the

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(54) Examples of values are as follows: $m_t < 0.05$ mol kg$^{-1}$, 35 Å; $m_t = 0.06$, 33 Å; $m_t = 0.08$, 30 Å; $m_t = 0.10$, 28 Å; $m_t = 0.12$, 27 Å; $m_t = 0.15$, 25 Å.

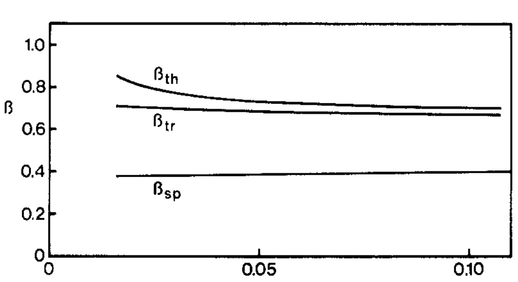

**Figure 6.** Calculated degree of ion binding, $\beta$, vs. the total surfactant concentration for solutions of sodium *p*-octylbenzenesulfonate. Theoretical model used as in Figure 5; see text. Three different $\beta$'s are given to mimic experimental conditions, i.e., $\beta_{th}$ (thermodynamic measurements), $\beta_{tr}$ (transport properties), and $\beta_{sp}$ (spectroscopic studies). For details, see text.

Poisson–Boltzmann equation have indeed demonstrated a so-called counterion condensation behavior for spherical, cylindrical, and planar surfaces having a high charge density.[13,55]) The decrease in $\beta_{tr}$ obtained is in agreement with experimental observations.

In conclusion, it is thus clear that the PB theory reproduces well the main features of the experimental results presented in this paper. For $\beta$ there is some quantitative difference between experiment and theory. This is not surprising in view of the rather ambiguous separation into free and bound ions. We have defined bound ions as those for which $z_i e\psi/kT \geq 1$, but this limit can certainly be discussed.

## Concluding Remarks

The self-diffusion method can be seen to provide significant information on several aspects of micelles. In summarizing the different results obtained, we will correlate them with results obtained by other methods.

The magnitude of the micelle self-diffusion coefficient and its concentration dependence show that the micelles are approximately spherical with a radius corresponding to the length of the extended surfactant ion and with a hydration corresponding to about one layer of water molecules. This is in agreement with determinations of micelle size by various techniques (for reviews, see ref 2–5). The transformation from spherical to rodlike micelles is now well established and has been shown to occur in the presence of high concentrations of added salt[37] (for example, $C_{12}SO_4Na + NaCl$) or in the absence of added salt for surfactants with long alkyl chains[56] (for example, $C_{16}N^+(CH_3)_3Br$).

The self-diffusion technique probably gives the first direct demonstration that the concentration of free amphiphile ions decreases substantially above the cmc.[47] From kinetic studies, Aniansson et al.[6] have previously deduced a decreased monomer concentration above the cmc. Several authors have used surfactant-sensitive electrodes to demonstrate a decreasing surfactant monomer activity above the cmc.[57,58] This decreased monomer concentration and activity is explained by the change in the counterion distribution.[13] Thus, an enhanced concentration of free counterions stabilizes the micellar state by leveling out the uneven counterion distribution. (This is probably a better description than one in terms of the free counterions screening the unfavorable electrostatic repulsions.) The theoretical analysis based on the Poisson–Boltzmann equation is indeed able to predict the various features of Figure 2. Of these, that of a decreasing monomer activity and concentration above the cmc for ionic surfactants is not yet spread to a wider audience. The large fall in free-monomer concentration above the cmc is an effect that should be strongest in the absence of added salt and would decrease considerably in the presence of appreciable salt concentrations.

The free-counterion concentration increases naturally at a slower rate above than below the cmc. The degree of counterion binding, $\beta$, is approximately constant over wide concentration ranges as predicted by simple ion condensation theory.[59] Many different NMR experiments have also demonstrated an ion condensation behavior for surfactant systems.[4,10] Interestingly, we observe, perhaps for the first time, $\beta$ to be significantly higher at low than at high micelle concentration. This is exactly as predicted by the theoretical calculations based on PB theory and may be explained by an increasing total free-ion concentration screening the ionic repulsions at the micellar surface. With increasing free-ion concentration, the range of the decreased electrostatic potential is reduced, and thus the volume in which the interaction energy exceeds the thermal energy is also reduced. The closer approach of micelles to each other at higher concentration also reduces the electric potentital differences between the micellar vicinity and the bulk of the solution; this effect should, however, be insignificant at the concentrations of interest here.

The strong competition between the different alkali ions (Table I) is interesting. To understand this, one has to go beyond the simple theoretical model used and consider ion size and ion hydration. In the present case, binding increases with decreasing counterion hydration. A similar dependence on hydrated counterion size has been noted for alkali dodecyl sulfates concerning both the cmc[60] and the sphere-to-rod transition.[61]

The generally accepted picture of a micelle is one with a liquidlike hydrocarbon interior and with water contact for the surfactant only for the outermost methylenes. The water self-diffusion data of this study, although not providing precise hydration numbers, gives very direct support for this view, while it is inconsistent with suggestions[62,63] of a significant water penetration deep (several methylenes)[64] into micelles. Several other recent studies using a variety of experimental methods are also in conflict with this water penetration.[4] Two recent NMR studies have particularly provided insight into these matters, one looking from the alkyl-chain side and one from the water side. Cabane,[66] in studies of the effect of paramagnetic ions on the $^{13}C$ and $^1H$ nuclei of amphiphile alkyl chains, could demonstrate that the water–hydrocarbon contact is

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limited to the surface of the micelles.[67] (Furthermore, this study[66] nicely demonstrated the liquidlike interior of micelles in contrast to a recent proposal[68] to the contrary.) Halle and Carlström,[44] from water $^{17}O$ relaxation data, could demonstrate that the water–hydrocarbon contact in several ionic micelles is equivalent to less than two fully exposed methylene groups. $^{19}F$ relaxation in $H_2O$ and $D_2O$ of fluorinated chains is also inconsistent with a deep water penetration into micelles.[69]

At low amphiphile concentrations co-ions stay away from the micelles, while at higher concentration the effective excluded volume decreases markedly. This is in qualitative agreement (and should be amenable to quantitative tests) with results of theoretical calculations on the basis of the Poisson–Boltzmann equation and can be interpreted as a combination of two effects: (a) with increasing free-counterion concentration (and thus total free-ion concentration), the range of the electric interactions is reduced and the co-ions are repelled to a smaller extent; (b) with decreasing distance between the micelles, the depths of the potential minima between micelles become smaller, which might be called an electric double layer repulsion.

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# Isotope Effects in Aqueous Systems. 13. The Hydrophobic Interaction. Some Thermodynamic Properties of Benzene/Water and Toluene/Water Solutions and Their Isotope Effects

**Malay K. Dutta-Choudhury, Nada Miljevic,[†] and W. Alexander Van Hook***

*Chemistry Department, University of Tennessee at Knoxville, Knoxville, Tennessee 37996* *(Received: September 25, 1981; In Final Form: December 1, 1981)*

Henry's law constants, $K_H = K° + K_1X$, have been measured as a function of concentration for the water-rich and benzene-rich solutions $C_6H_6/H_2O$ and $C_6H_6/D_2O$ and for the water-rich solutions $C_6D_6/H_2O$ and $C_6D_6/D_2O$ at several temperatures. The constants $K°$ and $K_1$ are sensitive to temperature and to isotopic label. The vapor pressure results have been supplemented with measurements of the apparent molar volumes of the solutions listed above, as well as for $H_2O$- and $D_2O$-rich solutions of toluene and deuteriotoluene, and with determinations of the solubilities and solubility isotope effects of the toluene solutions. The data have been interpreted in the context of the theory of isotope effects in condensed-phase systems. That analysis indicates that a significant dynamical vibrational coupling between solute and solvent normal modes occurs in these solutions. The result is of interest particularly as it pertains to models of the hydrophobic interaction.

## Introduction

A number of the solute–solute and solute–solvent interactions which occur in aqueous solutions of hydrocarbons or solutions of molecules containing hydrocarbon groups are broadly described, rather labeled, as the "hydrophobic effect".[1] A proper and quantitative understanding of solutions exhibiting the hydrophobic interaction is of importance in the application of physicochemical theory to some important problems, including the determination of conformation of biopolymers in aqueous solution, the thermodynamics of hydrocarbon/detergent/water systems found in oil recovery, and others. Tucker and Christian[2a] (TC) have pointed out that the benzene/water system forms an excellent prototype model for the hydrophobic interaction. These authors reported vapor pressure measurements for the $C_6H_6/H_2O$ system at 35 °C together with the Henry's law constants derived from them, finding $K_H = 3.527 \times 10^5 - (3.07 \times 10^7)X_B$ in pressure units of torr. The contribution of the term describing the first-order deviation from Henry's law, $f_B = K_HX_B$, amounts to nearly 4% at saturation ($4.4 \times 10^{-4} = X_B$). The result is mildly surprising in view of earlier claims that Henry's law is obeyed reasonably well as far as the solubility limit.[3-6] Rossky and Friedman[7] (RF) have published an interpretation of the observations reported by TC and concluded that the experimental results are in reasonable accord with model calculations earlier reported.[8] In view of widespread interest in the hydrophobic effect, and because of the conflict between the results of TC and the earlier claims,[3-6] we concluded that independent con-

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[†] N.M. is responsible for the major part of the work on toluene/water systems.

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