**Figure 11.** Qualitative "cell" model.

A complete quantitative analysis of the phenomenon requires numerical solutions of the flow equations for rather lengthy times and use of a temperature-dependent absorption coefficient; this will be the subject of a second report from the thermal engineering department. It should be pointed out, however, that several qualitative features we observed support the mechanism outlined above. The period of oscillations should be determined by the slowest of the listed steps. This corresponds to heating of cell (2) which is in contact with the bottom window. An increase in radiation intensity or the addition of buffer gas should shorten that step and accordingly increase the oscillation frequencies, as observed. The 360° phase shift between the oscillations recorded at the center and bottom probes are also consistent with this mechanism. The complicated wave patterns with double peaks, observed at probes 3 which are absent in the off-axis locations suggest the development of more complicated flow patterns under some conditions. One possible explanation for this observation is the development of higher transverse convective modes which do not have axial symmetry. This possibility could be tested by inserting additional probes at a selected cell height.

Use of such gas cells and laser heating appears to be an attractive technique for studying convective phenomena because one can thus place the heat source within the fluid system in a controlled manner. On the other hand, appropriate cell design and proper operating conditions must be used for LPHP to minimize temperature oscillations. Mean temperatures derived from "chemical thermometers", incorporated as internal standards, were demonstrated to have kinetic significance.[1] But one may question whether temperatures derived from spectroscopic[14] or other sensors are adequate measures for kinetics investigations, in view of the complex patterns which develop under experimental conditions when convection plays a significant role.

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# Micelle Formation of Anionic and Cationic Surfactants from Fourier Transform Hydrogen-1 and Lithium-7 Nuclear Magnetic Resonance and Tracer Self-Diffusion Studies

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Multicomponent self-diffusion investigations were performed for a number of surfactant systems to provide a picture of the general aspects of the self-association in water of ionic surfactants with monovalent inorganic counterions. Surfactants studied were sodium *n*-octanesulfonate, sodium *n*-dodecyl sulfate, lithium *n*-dodecyl sulfate, hexadecyltrimethylammonium chloride, and hexadecyltrimethylammonium bromide. Self-diffusion coefficients were investigated in a wide concentration range for surfactant ions, counterions, water molecules, and solubilized molecules by the open-end capillary tube method employing radioactive labeling and/or the Fourier transform NMR pulsed-gradient spin-echo method. The latter used mainly $^1$H NMR but introduced as a novel feature the study of inorganic counterions by $^7$Li NMR. Using a two-site model, we deduced the concentrations of free and micellar surfactant ions, counterions, and water molecules. A general pattern independent of the surfactant system is found. The free-surfactant concentration has a broad maximum around the critical micelle concentration and decreases to values much below that at higher concentrations. The degree of counterion binding is for all systems nearly constant in a broad concentration range corresponding to an ion condensation behavior. The various results are in agreement with a recent theory of ionic surfactant systems, treating the electrostatic effects according to the Poisson–Boltzmann equation. The corresponding calculations were also performed for a bile salt sodium cholate and revealed a quite different self-association behavior.

## Introduction

While many general aspects of surfactant micellization are well established, other details of the self-association process, the role of electrostatic interactions, and the structure, dynamics, and interactions on a molecular level are in the focus of recent and current research. (For recent reviews on general aspects of surfactant self-association see ref 2-6) As a contribution in these

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efforts we have suggested multicomponent self-diffusion studies. Indeed, since the macroscopic translational mobility of an ion or a molecule is different by 1–2 orders of magnitude when diffusing with a micelle as a kinetic entity and when moving freely in the bulk solution, it is possible to quantify the populations of these two sites from an observed self-diffusion coefficient. Our previous studies have concerned one cationic surfactant with an organic counterion, decylammonium dichloroacetate,[7] and two anionic surfactants, sodium p-octylbenzenesulfonate[8] and sodium octanoate.[9] The most important results of the precious work were to demonstrate that the free-surfactant concentration decreases considerably above the critical micelle concentration (cmc), that the degree of counterion binding is quite invariant to changes in micelle concentration by orders of magnitude, and that the degree of micelle hydration is small, thus that there is significant hydrocarbon chain–water contact only close to the micelle surface.

In the present work we have investigated and analyzed the self-diffusion behavior of a series of cationic and anionic surfactants. In particular, four surfactants with much lower cmc's than in our previous studies have been studied and, furthermore, the effect of the nature of the inorganic counterion ($Cl^-/Br^-$ and $Li^+/Na^+$) has been investigated. Our study concerns both the capillary tracer tube method and Fourier transform nuclear magnetic resonance as experimental techniques; by parallel studies on the same systems using both techniques any experimental uncertainties are essentially eliminated. As a methodological progress, we also introduce self-diffusion studies of inorganic counterions by the FT NMR method, which thereby can be considerably broadened in scope. This is especially significant because of the limited range of applicability of the tracer techniques (inter alia are viscous micellar solutions or microemulsions and cubic liquid crystals excluded).

On the basis of the deduced concentrations of free and micellized ions and molecules, a discussion is presented on general and specific aspects of ionic surfactant micellization. In particular, we infer that most aspects of the self-association are invariant to changing the cmc by several orders of magnitude. For comparison we perform the corresponding analysis for a biological surfactant, sodium cholate, which is found to behave quite differently from the other surfactants investigated.

## Experimental Section

*Methods.* Two experimental techniques were employed to measure the self-diffusion coefficients, i.e., the open-ended capillary tube method using radioactive labeling and a recently developed Fourier transform pulsed field gradient spin-echo NMR technique. The latter method permits the simultaneous determination of the self-diffusion coefficients of several components. For the former approach the description in our previous papers[8,10] is applicable.

The FT NMR techniques for the determination of molecular self-diffusion coefficients have been outlined in ref 11 and 12. An unmodified JEOL FX-100 spectrometer operating at 2.3 T was utilized and the magnetic field gradients (typically 1 G cm$^{-1}$) were generated through the standard modulation coils (connected antiphase) in the probe. The dual 5-mm $^1H/^{13}C$ probe was utilized in the $^1H$-based measurements, while the $^7Li$ measurements were made on the JEOL 10-mm tunable multinuclear probe using 10-mm NMR tubes. Magnetic field gradient calibration was made on cyclohexane at 25 °C, as described previously.[11,12] Adequate signal/noise ratio on concentrated solutions was usually obtained

with only one transient for each field gradient parameter setting, while the most dilute (cf. the tables and figures) samples required overnight runs at each concentration. For $^7Li$, this is partly a result of the fairly long spin–lattice relaxation times of $Li^+$ ions in $D_2O$.

All NMR measurements were made on $D_2O$ solutions, by using internal deuterium lock for field/frequency stabilization.

For a number of cases, measurement series were performed by both experimental techniques (see below), while in others selected checks were made by the second method. Throughout, the two quite different approaches are in very good agreement, although in a few cases the tracer method gave results which seem to be systematically too low by a few percent. Long measuring times, laborious measurement procedures, and limited availability of relevant labeled compounds of sufficient activity are drawbacks for the tracer method. The requirement of a sufficiently long spin–spin relaxation time and an adequate receptivity of the nucleus studied are usually the problematic factors for the NMR method.

Measurements were generally performed at 25 °C. Since the Krafft point of pure hexadecyltrimethylammonium bromide is above 25 °C, these measurements, as well as those of the corresponding chloride, were performed at 33 °C.

*Materials.* Sodium octanesulfonate and sodium dodecyl sulfate were obtained from Merck, hexadecyltrimethylammonium bromide and decanol were obtained from BDH or Th. Schuchardt, and heavy water was obtained from Ciba-Geigy or Norsk Hydro. Hexadecyltrimethylammonium chloride, which was a kind gift from Dr. Ali Khan, was prepared from the $C_{16}TAB$ through an ion-exchange procedure as described previously.[13] Lithium dodecyl sulfate (BDH, biochemical grade) was used as supplied after drying under vacuum.

Concentrations are given in molality throughout, which for solutions with $D_2O$ as solvent implies the number of moles of solute per 55.5 mol of water.

The radioactively labeled products were the following: $^{14}C$-labeled decanol with a specific activity of 14 mCi mmol$^{-1}$ from Paris Labo; $^{22}Na$-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 μCi mg$^{-1}$ from Amersham; $^3H$-labeled water with a specific activity of 1 Ci mL$^{-1}$ from CEA, Département des Radioéléments, Gif sur Yvette, France; $^{82}Br$-labeled sodium bromide with a specific activity of 0.6 mCi mg$^{-1}$ from CEA; and $^{35}S$-labeled sodium n-dodecyl sulfate from Amersham.

## Results and Discussion

*Some General Comments on the Analysis of the Self-Diffusion Results.* A detailed account of the procedures of deducing information on the micelle-bulk distribution of different components has been given elsewhere[8] but some brief comments especially on the limitations are in order. In general, we use a simple two-site model, the two sites being the micelles and the free species in the bulk solution. The observed self-diffusion coefficients are population-weighted averages of the self-diffusion coefficients of the different sites. The free-ion or -molecular self-diffusion coefficients are obtained from measurements on micelle-free systems. Corrections are made for molecular interactions in the bulk (empirically) and, in particular, for the micelle obstruction effect, the latter correction using the obstruction theory of Jönsson et al.[14] The micelle self-diffusion coefficients are obtained from measurements on solutions where a small amount of solubilized and essentially bulk-insoluble compound is introduced to label the micelles. There are a number of quantities which can be deduced from the self-diffusion data. In this work, emphasis will be on three parameters, i.e., the free-surfactant concentration, the degree of counterion binding, and the micelle hydration, and a brief mention of the precision of these quantities under different conditions is appropriate.

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The self-diffusion approach for the determination of micellar aggregation, as compared to other techniques, is particularly sensitive to the amount of nonaggregated ions, since their fraction is amplified by the diffusion coefficient ratio when analyzing the time-averaged self-diffusion coefficients.

The free-surfactant concentration is accurately obtained in quite a wide range of concentration but there are two limitations, both concerning the high surfactant concentration region: The free-surfactant concentration, $m_f{}^a$, is mainly determined by the difference between the measured surfactant self-diffusion coefficient, $D^a$, and the micelle self-diffusion coefficient, $D_m$. As the total surfactant concentration, $m_t{}^a$, increases to concentrations much above the cmc, the fraction of free surfactant decreases and $D^a$ approaches $D_m$. Therefore, the relative error in the difference $D^a - D_m$ increases and thus also the relative (but not the absolute) error in $m_f{}^a$. There is also another effect which may produce errors in $m_f{}^a$: namely, errors in $D_m$ due to a small dissociation of the solubilized label. This effect is insignificant in a broad range above the cmc (say, up to ca. 10(cmc)) because here this error is small compared to the difference $D^a - D_m$. However, for measurements at high concentrations for a surfactant with a low cmc, the solubility of even rather hydrophobic compounds is no longer negligible compared to the free-surfactant concentration. In extreme cases, we even observed the solubilizate self-diffusion coefficient, $D^s$, to equal or exceed $D^a$. One solution to this problem is, of course, to select a suitable solubilizate with lower bulk solubility. To eliminate this effect as far as possible we then undertook measurements of $D^s$ for some additional solubilizate for some systems. The choice is rather limited, however, mainly because of unsuitable NMR spectra of the solubilizates and the limited availability of radioactively labeled compounds.

As concerns $m_m{}^a$, the micellized-surfactant concentration, it is mainly determined by the difference between the free-surfactant self-diffusion coefficient, $D_f{}^a$, and $D^a$. This difference is small around the cmc, thus producing large *relative* errors in $m_m{}^a$ in this concentration region while the relative error in $m_m{}^a$ decreases rapidly with increasing surfactant concentration.

The counterion binding can be characterized by $m_m{}^c$, the concentration of counterions diffusing with the micelles, but it is more useful to introduce the degree of counterion binding, $\beta$, defined as the ratio $m_m{}^c/m_m{}^a$. $\beta$ can be accurately deduced over a concentration range spanning over orders of magnitude (being independent of problems in determining $D_m$) but has a large relative error just above the cmc. This arises because here neither $m_m{}^c$ nor $m_m{}^m$ can be precisely obtained.

Information on micelle hydration is deduced from the difference between the free-water self-diffusion coefficient, $D_f{}^w$, and the observed water self-diffusion coefficient, $D^w$. The micelle hydration number can therefore be obtained with any accuracy only at quite high surfactant concentrations since only then is an appreciable fraction of the water molecules translating with the micelles as a kinetic entity. Furthermore, since the hydration numbers of these ionic surfactant micelles are quite small, they have large relative errors.

The correctness of the self-diffusion coefficients was checked in a number of cases by performing experiments with the two completely different experimental techniques and agreement was very good. The low-concentration data can be compared with self-diffusion coefficients calculated from limiting equivalent conductivities using the Nernst expression.[15] The tracer method was found in a couple of cases to give values which are systematically low by a few percent. This was not further investigated (but may be due to the fact that the solutions were not stirred) since the relative changes (which determine the deduced quantities of interest in this work) were found to be accurate. When comparing with literature data obtained at a slightly different temperature (25 °C instead of 33 °C, or 30 °C instead of 33 °C) we made a recalculation on the basis of the viscosity of pure water at different temperatures.[15] Similarly, conversion of data between
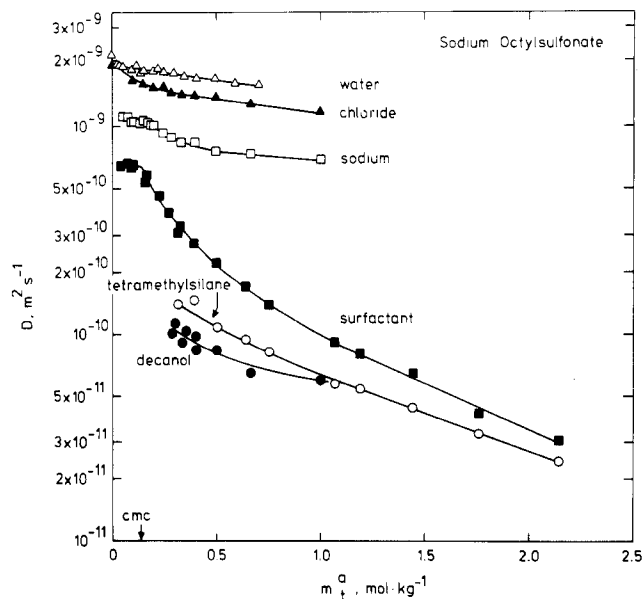


**Figure 1.** Self-diffusion behavior of sodium octanesulfonate solutions. Water (△), (small amount of added) chloride (▲), sodium (□), surfactant (■), solubilized-tetramethylsilane (○), and decanol (●) self-diffusion coefficients ($D$ in $m^2\ s^{-1}$) are shown as a function of surfactant concentration ($m_t{}^a$). Surfactant and tetramethylsilane self-diffusion coefficients were studied in $D_2O$ and have been recalculated to normal water solution. Temperature, 25 °C.

$H_2O$ and $D_2O$ as solvent was made by using the viscosity ratio (1.23).[16] These conversion factors were confirmed experimentally within our experimental error.

The critical micelle concentration, even if it is strictly defined only in the phase separation model of micelle formation shown to be inaccurate (inter alia in the present type of study), still can serve as a useful characteristic of a surfactant system. Therefore, we provide estimates of the cmc's as obtained from plots of $D$ ($D^a$ or $D^c$) vs. the inverse surfactant concentration.[17]

*Sodium n-Octanesulfonate.* For solutions of sodium *n*-octanesulfonate, self-diffusion coefficients were determined at 25 °C in the concentration range 0–2.15 mol kg$^{-1}$. Self-diffusion coefficients of the surfactant ion and of solubilized tetramethylsilane (in low concentrations) were obtained by using the $^1H$ FT NMR technique (solvent $D_2O$) while those of sodium ions, water and small amounts of added chloride ions and decanol were measured by the capillary tube method. The experimental results presented in Figure 1 show the rapid decrease of surfactant diffusion in the micellar region, the slower decrease of counterion diffusion, and the relative insensitivity of water diffusion to the micelle concentration. Our infinite-dilution value for surfactant ion self-diffusion of 0.66 × 10$^{-9}$ m$^2$ s$^{-1}$ is slightly lower than that calculated from the limiting conductivity[18] (0.696 × 10$^{-9}$ m$^2$ s$^{-1}$) and as noted in previous work the same applies to sodium ion diffusion. The tetramethylsilane self-diffusion coefficient is at low surfactant concentrations significantly higher than that of decanol. The reasons for this are not clear but the effect was not further investigated since (because of the high cmc) the calculations were rather little affected. In the calculations of micellized- and free-component concentrations, the decanol diffusion coefficients were used throughout.

The cmc values obtained from plots of surfactant ion and counterion self-diffusion coefficients vs. the inverse surfactant concentration are 0.14–0.15 mol kg$^{-1}$ (literature[19] values are ca. 0.155 *m*).

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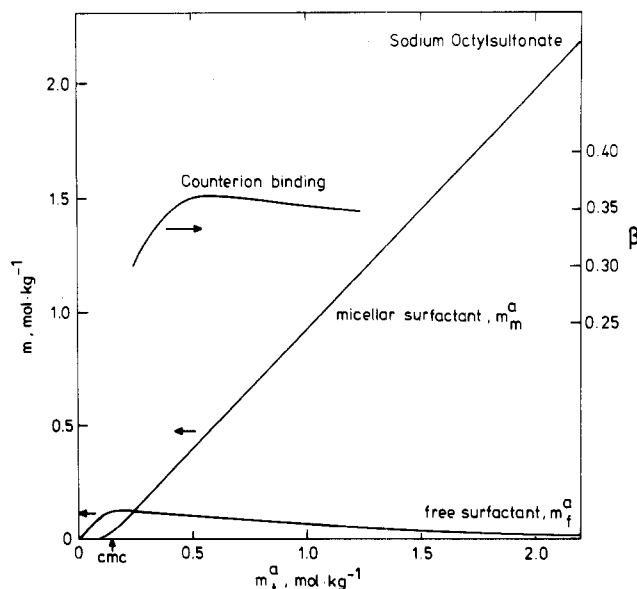(19) Mukerjee, P.; Mysels, K. J. *Natl. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1971**, *No. 36*.

**Figure 2.** Self-association in solutions of sodium octanesulfonate. Concentrations of free $(m_f^a)$ and micellar $(m_m^a)$ surfactant and the degree of counterion binding $(\beta)$ as a function of the total surfactant concentration.



**Figure 3.** Self-diffusion behavior of sodium dodecyl sulfate solutions. Water (△, ref 20), sodium (■, ref 21; □, ref 22, 23), surfactant (○, this work, $D_2O$ solution recalculated to normal water; ●, ref 20), and solubilized-azobenzene (◓, ref 24) self-diffusion coefficients are shown as a function of the surfactant concentration (temperature, 25 °C).

From the experimental self-diffusion coefficients, the concentrations of free and micellar surfactant ions and counterions, and the micelle hydration numbers, were calculated as indicated above and as described in detail in ref 8. As can be inferred from Figure 2, the free-surfactant concentration has a broad maximum around the cmc and decreases to values much below the cmc at high surfactant concentrations. The micellized-surfactant concentration starts to be significant slightly below the cmc and increases linearly with total surfactant concentration at higher concentrations. The degree of counterion binding lies between 0.30 and 0.35 and is in most of the concentration range studied close to 0.35. The micelle hydration number is obtained to be 7–10 water molecules per surfactant molecule in the concentration range 0.4–0.7 mol $kg^{-1}$.

*Sodium n-Dodecyl Sulfate.* As regards the self-diffusion behavior of solutions of sodium dodecyl sulfate some aspects are covered by studies reported in the literature while some further aspects were investigated in this work. Partly, the experimental data available are deficient and, although a general picture of the association is provided, the analysis must leave uncertain points.

Self-diffusion coefficients of the surfactant ion and of small amounts of solubilized tetramethylsilane were determined by the $^1H$ FT NMR technique for $D_2O$ solutions at 25 °C. The dodecyl sulfate results are presented in Figure 3 together with some literature data; the $Me_4Si$ self-diffusion coefficient (not shown) is a bit below the surfactant self-diffusion coefficient at concentrations below ca. 0.05 mol $kg^{-1}$ while at higher concentrations the two self-diffusion coefficients are essentially equal. We have previously determined $D^a$ by the tracer technique.[20] Accounting for the difference in solvent, the two sets of data are, in general, in good agreement; the FT NMR data are more detailed and have a higher precision. Counterion self-diffusion was not studied in the present work. Instead, the calculations of counterion binding were based on the tracer self-diffusion data of Clifford and Pethica[21] and a few previous tracer data from our group.[22,23] It seems that agreement between the two sets of data is good except at low concentrations. Unfortunately, each of the different series
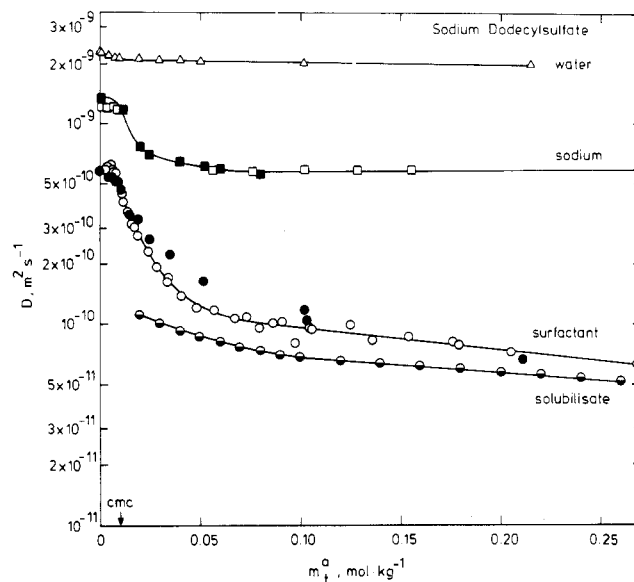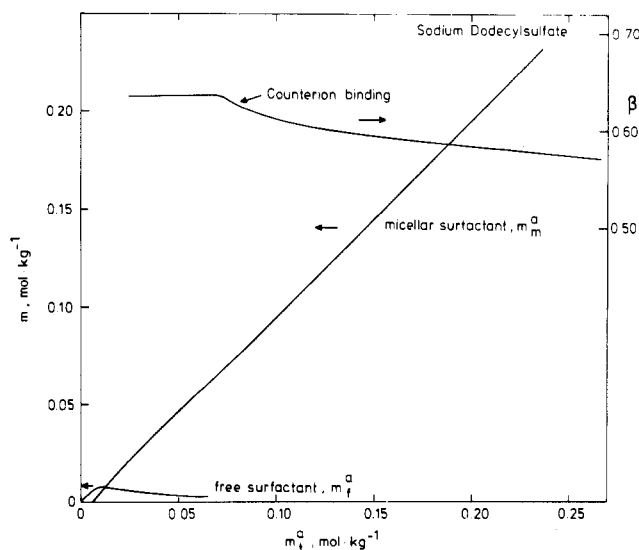


**Figure 4.** Self-association in solutions of sodium dodecyl sulfate. Concentrations of free $(m_f^a)$ and micellar $(m_m^a)$ surfactant and the degree of counterion binding $(\beta)$ as a function of the total surfactant concentration.

of experiments on counterion diffusion concerns only a rather small concentration range. Water self-diffusion was studied in our previous work.[20] As regards the micelle self-diffusion coefficients there are some problems. Thus, as already noted, the extent to which $Me_4Si$ is confined to the micelles is not high enough and $Me_4Si$ self-diffusion data are inapplicable. Instead we used the azobenzene self-diffusion data of Clifford and Pethica.[24] The various self-diffusion data for $C_{12}SO_4Na$ solutions are summarized in Figure 3, recalculated to $H_2O$ as solvent when appropriate. Our value for dodecyl sulfate self-diffusion at low concentrations of ca. $0.61 \times 10^{-9}$ $m^2$ $s^{-1}$ is close to the infinite-dilution value deduced from limiting conductivity[18] (($0.57–0.64) \times 10^{-9}$ $m^2$ $s^{-1}$). The cmc value deduced from the concentration dependence of the surfactant self-diffusion coefficient (ca. $8 \times 10^{-3}$ mol $kg^{-1}$ from FT NMR and $8.7 \times 10^{-3}$ mol $kg^{-1}$ from tracer self-diffusion) is in agreement with literature values.[19]

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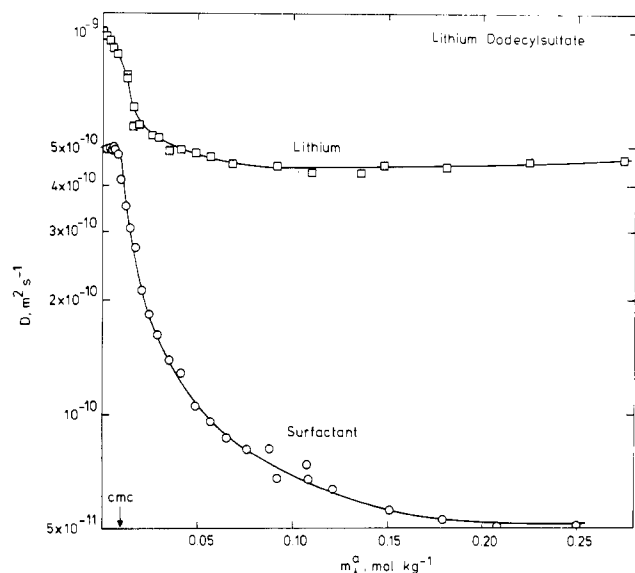(24) Clifford, J.; Pethica, B. A. *J. Phys. Chem.* **1966**, *70*, 3345.

**Figure 5.** Counterion (□) and surfactant ion (O) self-diffusion coefficients in lithium dodecyl sulfate solution (in $D_2O$; temperature, 25 °C) as a function of surfactant molality.



**Figure 6.** Self-association in solutions of lithium dodecyl sulfate. Concentrations of free ($m_f^a$) and micellar ($m_m^a$) surfactant and the degree of counterion binding ($\beta$) as a function of the total surfactant concentration.

The deduced information on surfactant ion partitioning and on counterion binding is shown in Figure 4. The general features are the same as for sodium octanesulfonate with a decreased free surfactant ion concentration above the cmc ($m_f^a$ remains low in the high-concentration region but here precision is low) and a degree of counterion binding which is rather invariant to concentration (in the range 0.55–0.65). As noted there are some problems with the counterion data (leading inter alia to an uncertainty not in the concentration dependence but in the level of the high-concentration data by a few percentage units). The water self-diffusion data are not detailed enough to provide reliable hydration numbers but demonstrate above all a very extensive dehydration of the surfactant on micellization.

*Lithium n-Dodecyl Sulfate.* The studies of lithium dodecyl sulfate (all at 25 °C in $D_2O$) included as a novel feature measurements on an inorganic counterion by the FT NMR method. Self-diffusion coefficients were also obtained for the surfactant anion and for solubilized $Me_4Si$ by the same method. To illustrate possibilities and precision of the FT NMR method these data are given in Table I as well as in Figure 5. Again $Me_4Si$ self-diffusion gives an unreliable measure of micelle self-diffusion at higher surfactant concentrations; in the calculations we therefore used the same $D_m$ values as used for sodium dodecyl sulfate. The surfactant ion self-diffusion coefficient at low concentration is $0.604 \times 10^{-9}$ $m^2$ $s^{-1}$, in agreement with both the value for sodium dodecyl sulfate solutions and that calculated from the limiting conductivity (see above). The infinite-dilution $Li^+$ self-diffusion coefficient obtained from measurements on LiCl solutions is 0.86 $\times 10^{-9}$ $m^2$ $s^{-1}$, which converted to normal water solution gives 1.06 $\times 10^{-9}$ $m^2$ $s^{-1}$ to be compared with the value $1.029 \times 10^{-9}$ $m^2$ $s^{-1}$ given by the limiting conductivity. (The low-concentration surfactant solutions give significantly higher lithium ion self-diffusion coefficients, indicating experimental difficulties for millimolar concentrations.) The cmc value deduced from the concentration dependence of surfactant ion or counterion self-diffusion is ca. $(8.5–9.0) \times 10^{-3}$ mol $kg^{-1}$, thus in agreement with literature data.[19]

The deduced quantities presented in Figure 6 show the same pattern as for the other systems. There is again an approximately constant counterion binding over a wide range but the $\beta$ value of $Li^+$ is significantly lower than that of $Na^+$ at all concentrations.

*Hexadecyltrimethylammonium Chloride.* Self-diffusion coefficients of the surfactant ion were obtained in this work over a wide concentration range (from below $5 \times 10^{-4}$ mol $kg^{-1}$ to above 0.5 mol $kg^{-1}$) for solutions of cetyltrimethylammonium chloride (33 °C in $D_2O$) by the $^1H$ FT NMR technique. We also determined by the same method the self-diffusion coefficient of solubilized isooctane; because of the difficulties with $Me_4Si$,
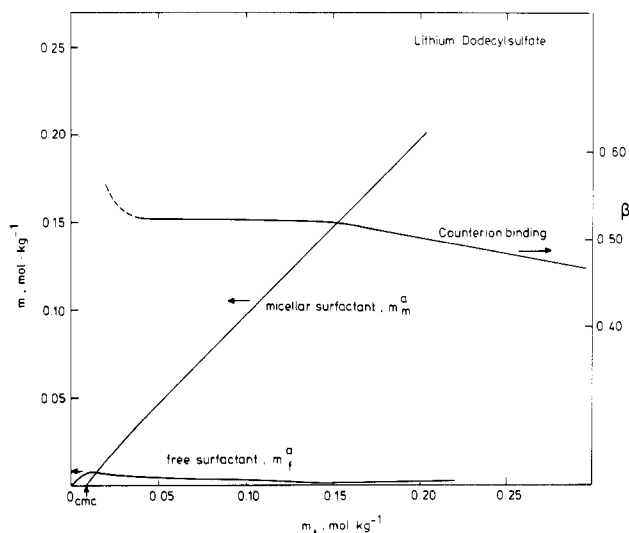


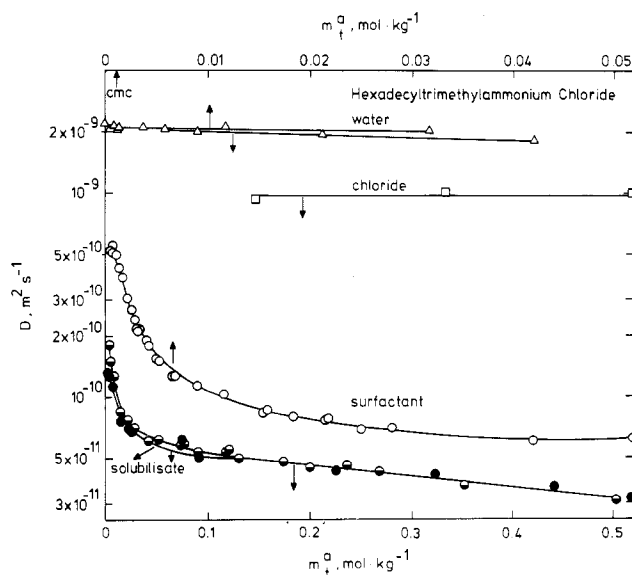**Figure 7.** Self-diffusion behavior of hexadecyltrimethylammonium chloride solutions. Water (△, ref 23, 25 °C), chloride (□, ref 13, 33 °C), surfactant (O and ◐, this work, 33 °C in $D_2O$), and solubilized-isooctane (●, this work, 33 °C in $D_2O$) self-diffusion coefficients are shown as a function of the surfactant concentration. Note upper and lower concentration scales and referring arrows.

isooctane was chosen to give better values of $D_m$. The experimentally obtained results are given in Table II and in Figure 7 and here we include also some previous tracer results from our group since these were used in the calculations. The previous data concern the counterion self-diffusion coefficient[13] (but only at three high concentrations), the self-diffusion coefficient of solubilized decanol,[13] and, in more detail, the water self-diffusion coefficient.[23] Chloride and decanol self-diffusion were studied at 33 °C and water at 25 °C. The surfactant ion self-diffusion coefficient at low concentrations (well below the cmc), $0.529 \times 10^{-9}$ $m^2$ $s^{-1}$, recalculated to $H_2O$ at 25 °C gives $0.547 \times 10^{-9}$ $m^2$ $s^{-1}$ to be compared with $0.554 \times 10^{-9}$ $m^2$ $s^{-1}$ calculated from the limiting conductivity.[18] The cmc obtained from the concentration dependence of the surfactant ion self-diffusion is ca. $1.1 \times 10^{-3}$ mol $kg^{-1}$, in agreement with the literature value.[19]

The deduced quantities on CTAC micellization shown in Figure 8 have the same general behavior as in the other systems. Although briefly studied, the essential constancy of counterion binding with increasing concentration seems well supported. The

**TABLE I: Measured Self-Diffusion Coefficients[a] of Lithium Dodecyl Sulfate in $D_2O$ at 25 °C**

| concn, m | $D^a$ | $D^s$ | concn, m | $D^c$ |
|---|---|---|---|---|
| 0.00250 | $0.488 \pm 0.040$[b] | | 0.00167 | $1.000^{+0.045}_{-0.080}$ |
| 0.00386 | $0.493 \pm 0.030$ | | 0.00284 | $0.990^{+0.035}_{-0.051}$ |
| 0.00447 | $0.488 \pm 0.017$ | | 0.00392 | $0.950^{+0.011}_{-0.088}$ |
| 0.00528 | $0.492 \pm 0.030$ | | 0.00392 | $0.945^{+0.053}_{-0.073}$ |
| 0.00637 | $0.491 \pm 0.012$ | | 0.00578 | $0.910^{+0.062}_{-0.034}$ |
| 0.00609 | $0.503 \pm 0.023$ | | 0.00778 | $0.880^{+0.034}_{-0.021}$ |
| 0.00836 | $0.482 \pm 0.016$ | | 0.0133 | $0.760^{+0.026}_{-0.015}$ |
| 0.0102 | $0.415 \pm 0.007$ | | 0.0134 | $0.762^{+0.032}_{-0.056}$ |
| 0.0127 | $0.353 \pm 0.007$ | | 0.0164 | $0.637^{+0.076}_{-0.087}$ |
| 0.0147 | $0.0308^{+0.014}_{-0.005}$ | | 0.0170 | $0.571 \pm 0.016$ |
| 0.0174 | $0.275 \pm 0.010$ | | 0.0193 | $0.576 \pm 0.028$ |
| 0.0205 | $0.212 \pm 0.019$ | | 0.0259 | $0.539^{+0.020}_{-0.016}$ |
| 0.0244 | $0.183 \pm 0.011$ | | 0.0300 | $0.532 \pm 0.017$ |
| 0.0292 | $0.162 \pm 0.007$ | | 0.0349 | $0.491 \pm 0.033$ |
| 0.0350 | $0.139 \pm 0.003$ | | 0.0411 | $0.497^{+0.013}_{-0.022}$ |
| 0.0413 | $0.129 \pm 0.003$ | $0.115 \pm 0.015$ | 0.489 | $0.484 \pm 0.017$ |
| 0.0486 | $0.105 \pm 0.002$ | $0.099 \pm 0.010$ | 0.0568 | $0.474^{+0.014}_{-0.031}$ |
| 0.0568 | $0.096 \pm 0.002$ | $0.111 \pm 0.006$ | 0.0678 | $0.454 \pm 0.030$ |
| 0.0665 | $0.087 \pm 0.002$ | $0.089 \pm 0.005$ | 0.0921 | $0.448 \pm 0.018$ |
| 0.0761 | $0.081 \pm 0.001$ | $0.084 \pm 0.003$ | 0.110 | $0.433 \pm 0.007$ |
| 0.0882 | $0.082 \pm 0.002$ | | 0.136 | $0.433 \pm 0.006$ |
| 0.0921 | $0.0679 \pm 0.0007$ | $0.076 \pm 0.002$ | 0.148 | $0.453 \pm 0.006$ |
| 0.107 | $0.074 \pm 0.001$ | | 0.181 | $0.447 \pm 0.008$ |
| 0.108 | $0.0676 \pm 0.0009$ | $0.077 \pm 0.002$ | 0.225 | $0.461 \pm 0.003$ |
| 0.121 | $0.0636 \pm 0.0005$ | $0.067 \pm 0.001$ | 0.275 | $0.467 \pm 0.004$ |
| 0.151 | $0.0559 \pm 0.0003$ | $0.063 \pm 0.001$ | | |
| 0.179 | $0.0528 \pm 0.0006$ | $0.055 \pm 0.001$ | | |
| 0.208 | $0.0506 \pm 0.007$ | $0.060 \pm 0.002$ | | |
| 0.251 | $0.051 \pm 0.001$ | $0.062 \pm 0.002$ | | |

[a] All self-diffusion coefficients given in units of $10^{-9}$ $m^2$ $s^{-1}$. $D^a$, $D^s$, and $D^c$ are diffusion coefficients of surfactant ion, of solubilized tetramethylsilane, and of counterion, respectively. [b] Error limits correspond to 80% statistical confidence intervals, regarding random errors only.
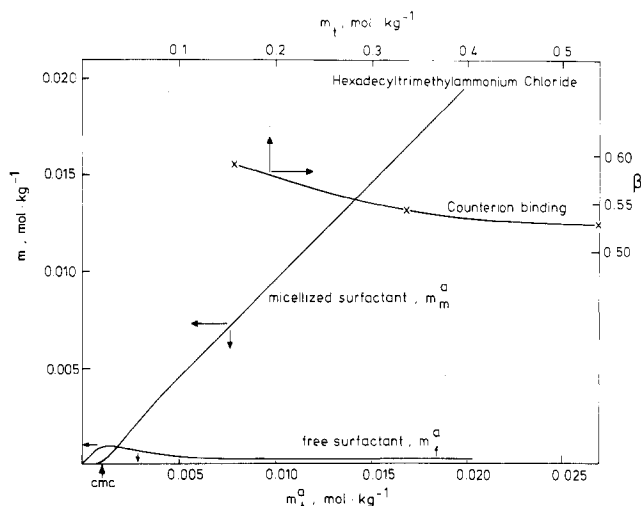


**Figure 8.** Self-association in solutions of hexadecyltrimethylammonium chloride. Concentrations of free ($m_f{}^a$) and micellar ($m_m{}^a$) surfactant and the degree of counterion binding ($\beta$) as a function of the total surfactant concentration.

micelle hydration numbers are low, 5–10 water molecules per surfactant ion in a wide concentration range (0.05 mol $kg^{-1}$ essentially up to saturation).

*Hexadecyltrimethylammonium Bromide.* Since cetyltrimethylammonium bromide (CTAB) is probably the most studied cationic surfactant, it often serves as an important reference system, making a detailed mapping of its association behavior particularly interesting. In this work we have studied in a broad concentration range (5 × 10⁻⁴ mol $kg^{-1}$ to above 0.4 mol $kg^{-1}$) the self-diffusion of the surfactant ion by the ¹H FT NMR method (33 °C in $D_2O$) and the same method was used to measure (less extensively) the self-diffusion of solubilized isooctane. ($Me_4Si$ self-diffusion was studied but an appreciable (compared to the surfactant) dissociation from the micelles is apparent from higher $Me_4Si$ than surfactant self-diffusion coefficients at higher concentrations.) The sub-cmc value of 0.54 × 10⁻⁹ $m^2$ $s^{-1}$ is in
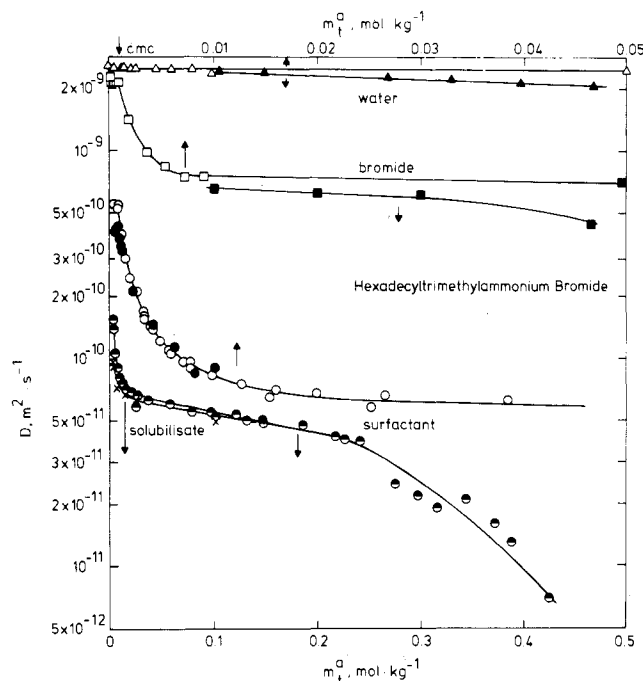


**Figure 9.** Self-diffusion behavior of hexadecyltrimethylammonium bromide solutions (33 °C except where otherwise noted). Water (△ and ▲, ref 23, $H_2O$ solution), bromide (□, ref 25, 25 °C recalculated to 33 °C; ■ ref 23), surfactant (○ and ◐, this work, $D_2O$ solution; ●, ref 25, 25 °C, $H_2O$ solution recalculated to $D_2O$ solution and 33 °C), and solubilized-isooctane (×, this work) self-diffusion coefficients are shown as a function of the surfactant concentration. Note upper and lower concentration scales and referring arrows.

excellent agreement with the value of 0.536 × 10⁻⁹ $m^2$ $s^{-1}$ estimated from the limiting conductivity.[18] Earlier data[25] (included in Figure 9) from this group obtained by the tracer method are in very good

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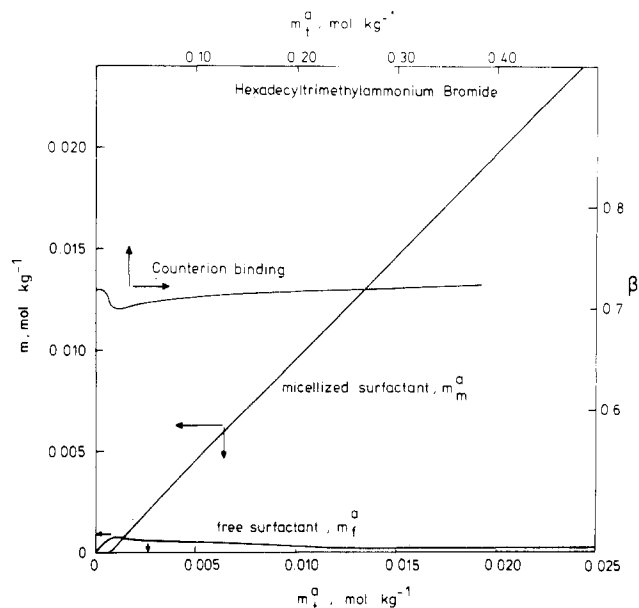
**Figure 10.** Self-association in solutions of hexadecyltrimethylammonium bromide. Concentrations of free ($m_f^a$) and micellar ($m_m^a$) surfactant and the degree of counterion binding ($\beta$) as a function of the total surfactant concentration.

agreement with the present NMR data (accounting for differences in solvent and temperature) except that the earlier results are systematically lower at the lowest concentrations (possibly due to adsorption). In addition, various aspects of the bromide ion self-diffusion in this system have been covered by studies in the literature; these data are partly used in the calculations in this work and partly discarded (see below). Bromide self-diffusion in CTAB solutions has been investigated in our group by the tracer technique in two studies[13,23,25] at 25 and 33 °C in the low- and high-concentration regions, respectively; these data were used in evaluating the counterion binding. The low-concentration self-diffusion coefficient of ref 25 is $1.83 \times 10^{-9}$ m$^2$ s$^{-1}$, which is a bit lower than $2.08 \times 10^{-9}$ m$^2$ s$^{-1}$ obtained from the limiting conductivity.[15] Another report of Br$^-$ self-diffusion in CTAB solutions is due to Smith,[26] who used a radiometric porous-frit method. These data disagree strongly with ours as regards both the absolute magnitude of the Br$^-$ self-diffusion coefficient and the concentration dependence. Smith's low-concentration data differ by a factor of 2–3 from those deduced from the limiting conductivity. We have, therefore, not based any calculations on these results. Water self-diffusion in CTAB solutions has previously been studied[23] in great detail in our group by the tracer technique (33 °C) and these results are included in Figure 1. From our surfactant diffusion data we deduce a cmc of ca. $9 \times 10^{-4}$ mol kg$^{-1}$ while in ref 25 cmc's of $9.1 \times 10^{-4}$ and $9.6 \times 10^{-1}$ were deduced from the cation and anion results, respectively. All these values are close to the accepted cmc value.[19]

It is clear from Figure 10 that CTAB self-association shows the same features as the other surfactants studied. One may particularly note the constant counterion binding ($\beta = 0.71 \pm 0.02$) up to concentrations more than 400 times the cmc. The slight increase at higher concentrations is probably associated with the gradual transition from spherical to rodlike micelles. Hydration amounts to ca. 10 water molecules per surfactant or below in a wide concentration range.

*Sodium Cholate.* The surfactants discussed so far form a rather homogeneous class of amphiphilic substances: The polar character is confined to a small group separated from the nonpolar part which in all cases is a *n*-alkyl chain. Micellization is also discussed in connection with other types of compounds and one way of gaining a better understanding of the mechanism of micellization is to analyze the self-association behavior as a function of chemical
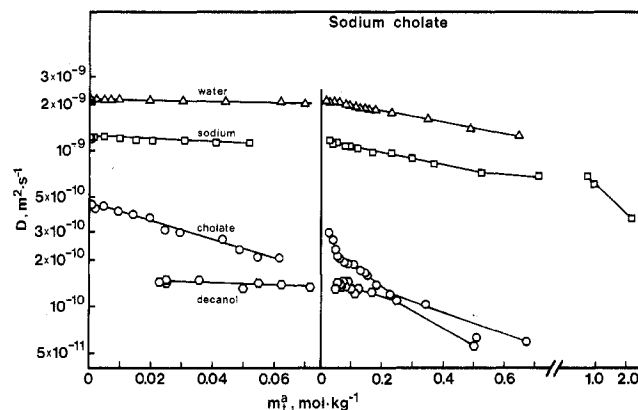
(26) Smith, D. H. *J. Colloid Interface Sci.* **1979**, *68*, 70.



**Figure 11.** Self-diffusion behavior (25 °C) of sodium cholate solutions according to data presented in ref 33. Water ($\triangle$), sodium ($\square$), cholate ($\bigcirc$), and solubilized-decanol ($\bigcirc$) self-diffusion coefficients are shown as a function of the surfactant concentration.
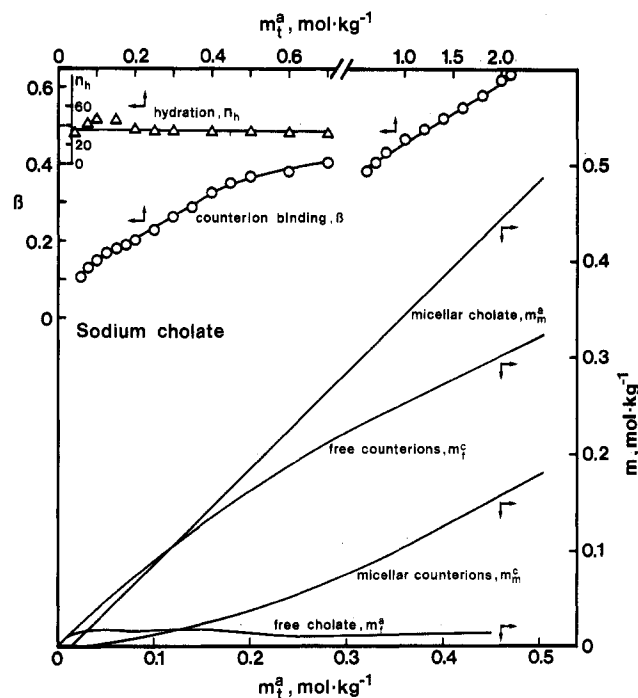


**Figure 12.** Self-association in solutions of sodium cholate. Concentrations of free and micellar cholate ions and counterions and the degree of counterion binding ($\beta$) and hydration number ($n_h$) as a function of the total sodium cholate concentration.

structure. One class of biosurfactants of much current interest is given by the bile salts,[27-32] built up essentially of a steroid skeleton with the polar groups (hydroxyls and carboxylate or sulfonate) spread out over one side of the rather flat molecules. We have previously[33] obtained rather complete multicomponent self-diffusion data for sodium cholate and it was of interest to apply the present type of analysis to these results. The self-diffusion coefficients are given in Figure 11 while the deduced quantities are presented in Figure 12. One notes an appreciable self-association but important features differ from those of the simple surfactants: Firstly, there is no marked decrease in free-cholate

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**TABLE II: Measured Self-Diffusion Coefficients[a] of Hexadecyltrimethylammonium Chloride and Hexadecyltrimethylammonium Bromide in $D_2O$ at 33 °C**

| concn, $m$ | $D^a$ | $D^s$ | concn, $m$ | $D^a$ | $D^s$ |
|---|---|---|---|---|---|
| | CTAC | | | CTAB | |
| 0.000492 | $0.538^{+0.071}_{-0.067}$[b] | | 0.000503 | $0.550^{+0.028}_{-0.052}$ | |
| 0.000637 | $0.519^{+0.057}_{-0.089}$ | | 0.000639 | 0.550 ± 0.062 | |
| 0.000748 | $0.560^{+0.107}_{-0.063}$ | | 0.000823 | 0.527 ± 0.027 | |
| 0.00101 | $0.498^{+0.040}_{0.008}$ | | 0.00115 | $0.406^{0.063}_{-0.008}$ | |
| 0.00130 | $0.430^{0.027}_{-00.050}$ | | 0.00148 | $0.305^{0.007}_{0.018}$ | |
| 0.00171 | 0.387 ± 0.007 | | 0.00200 | 0.245 ± 0.005 | |
| 0.00210 | 0.306 ± 0.008 | | 0.00247 | 0.212 ± 0.004 | |
| 0.00248 | $0.269^{0.012}_{-0.014}$ | | 0.00326 | 0.168 ± 0.003 | |
| 0.00273 | 0.239 ± 0.005 | | 0.00328 | 0.156 ± 0.004 | 0.097 ± 0.004 |
| 0.00278 | $0.279^{0.005}_{0.008}$ | | 0.00334 | $0.165^{+0.007}_{-0.003}$ | |
| 0.00312 | 0.212 ± 0.10 | | 0.00404 | 0.145 ± 0.002 | |
| 0.00315 | 0.217 ± 0.10 | | 0.00415 | 0.138 ± 0.010 | 0.092 ± 0.002 |
| 0.00336 | 0.217 ± 0.14 | | 0.00484 | 0.123 ± 0.002 | |
| 0.00398 | $0.192^{0.003}_{-0.006}$ | | 0.00578 | 0.107 ± 0.002 | 0.072 ± 0.002 |
| 0.00410 | 0.181 ± 0.006 | 0.132 ± 0.005 | 0.00585 | 0.110 ± 0.001 | |
| 0.00500 | 0.153 ± 0.002 | | 0.00702 | 0.098 ± 0.001 | |
| 0.00520 | 0.149 ± 0.002 | 0.130 ± 0.010 | 0.00763 | 0.091 ± 0.002 | 0.074 ± 0.001 |
| 0.00668 | 0.127 ± 0.002 | | 0.00780 | 0.098 ± 0.002 | |
| 0.00674 | 0.127 ± 0.001 | 0.112 ± 0.001 | 0.00988 | 0.084 ± 0.001 | |
| 0.00902 | 0.114 ± 0.002 | | 0.0127 | 0.076 ± 0.001 | |
| 0.0115 | 0.104 ± 0.002 | | 0.0154 | 0.065 ± 0.001 | 0.067 ± 0.001 |
| 0.0153 | 0.084 ± 0.002 | 0.076 ± 0.002 | 0.0160 | 0.071 ± 0.001 | |
| 0.0158 | 0.086 ± 0.001 | | 0.0200 | 0.069 ± 0.001 | |
| 0.0184 | 0.080 ± 0.001 | | 0.0252 | 0.059 ± 0.001 | 0.063 ± 0.002 |
| 0.0214 | 0.0774 ± 0.0005 | | 0.0265 | 0.067 ± 0.001 | |
| 0.0218 | 0.078 ± 0.001 | 0.070 ± 0.005 | 0.0384 | 0.063 ± 0.001 | |
| 0.025 | 0.069 ± 0.001 | | 0.0574 | 0.061 ± 0.001 | |
| 0.0280 | 0.071 ± 0.001 | | 0.0790 | 0.0557 ± 0.0003 | |
| 0.042 | 0.061 ± 0.001 | | 0.0967 | 0.056 ± 0.001 | |
| 0.052 | 0.061 ± 0.001 | | 0.102 | 0.0505 ± 0.0005 | |
| 0.0750 | 0.058 ± 0.001 | 0.062 ± 0.003 | 0.102 | 0.053 ± 0.001 | |
| 0.077 | 0.058 ± 0.001 | | 0.122 | 0.054 ± 0.001 | |
| 0.090 | 0.054 ± 0.001 | | 0.132 | 0.050 ± 0.001 | |
| 0.0923 | 0.054 ± 0.001 | 0.052 ± 0.002 | 0.148 | 0.049 ± 0.001 | 0.051 ± 0.001 |
| 0.093 | 0.054 ± 0.001 | | 0.148 | 0.0505 ± 0.0002 | |
| 0.117 | 0.054 ± 0.001 | | 0.186 | 0.0480 ± 0.0001 | |
| 0.121 | 0.055 ± 0.001 | | 0.217 | 0.042 ± 0.001 | 0.042 ± 0.001 |
| 0.130 | 0.050 ± 0.001 | | 0.226 | 0.041 ± 0.001 | |
| 0.174 | 0.048 ± 0.001 | | 0.242 | 0.040 ± 0.001 | |
| 0.202 | 0.045 ± 0.001 | | 0.275 | 0.025 ± 0.002 | |
| 0.226 | 0.043 ± 0.001 | 0.043 ± 0.001 | 0.297 | 0.0345 ± 0.0005 | 0.035 ± 0.001 |
| 0.237 | 0.046 ± 0.001 | | 0.316 | 0.019 ± 0.001 | |
| 0.268 | 0.043 ± 0.001 | | 0.344 | 0.021 ± 0.001 | |
| 0.323 | 0.041 ± 0.001 | 0.041 ± 0.001 | 0.372 | $0.016^{+0.007}_{-0.003}$ | |
| 0.352 | 0.037 ± 0.001 | | 0.389 | 0.013 ± 0.001 | |
| 0.504 | 0.031 ± 0.001 | | 0.425 | 0.007 ± 0.001 | |

[a] All sef-diffusion coefficients given in units of $10^{-9}$ $m^2$ $s^{-1}$. $D^a$, $D^s$, and $D^c$ are diffusion coefficients of surfactant ion, of solubilized isooctane, and of counterion, respectively. [b] Error limits correspond to 80% statistical confidence intervals, regarding random errors only.

concentration but rather $m_f^a$ stays approximately constant (0.014 ± 0.004 $m$) in a wide concentration range. Secondly, counterion binding is strongly dependent on concentration and shows no ion condensation type behavior; $\beta$ is low at low concentrations but increases to values typical of normal surfactant micelles at higher concentrations. Thirdly, there is a considerably more extensive (and concentration-independent) hydration of cholate aggregates than of simple surfactant micelles. Although one must have some reservation in applying this type of analysis to the small cholate aggregates, these qualitative differences are clear. A low cooperative association and a progressively increasing aggregation number with increasing concentration, which explain our observed effects, are well documented in previous work on bile salt systems (such as ref 29–32).

*Summarizing Remarks on Ionic Surfactant Micellization.* The present study in combination with our previous work[7-9] provides information on ionic surfactant self-association under a wide range of conditions, inter alia widely different cmc's, cationic and anionic amphiphiles, and different monovalent counterions, and permits some general conclusions on micellar solutions. It is immediately clear that, with the exception that association starts at different concentrations (depending essentially on the alkyl chain length), the different surfactants show closely the same behavior in all respects covered by the self-diffusion work.

The free-surfactant concentration in all cases shows a broad maximum around the cmc and decreases to values much below the cmc in a wide concentration range. We have previously demonstrated that by treating the electrostatic interactions by the Poisson–Boltzmann (PB) equation, as elaborated by Jönsson and Wennerström,[34-36] one can quantitatively account for these effects.[8,9] Phenomenologically, we may understand this behavior as follows: The ionic surfactant micelle has a high charge number and charge density which creates an uneven counterion distribution in the system, the counterion concentration being much higher close to the micelle than in the bulk solution. This uneven counterion distribution corresponds to a negative entropy contribution to the micelle formation process and thus conteracts micellization. As the surfactant concentration is increased above the cmc, the counterion concentration close to the micelles stays rather constant (cf. below) while the concentration in the bulk

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increases due to a partial counterion dissociation. Therefore, the uneven counterion distribution becomes successively evened out and the negative entropy contribution is reduced. The effect is to stabilize the micelles relative to the free surfactant ions and the micelles at higher concentrations coexist with monomer concentrations well below the cmc. It should also be noted that a decreased surfactant ion activity above the cmc has been obtained in work using ion-specific electrodes[5,37,38] and that a decreased monomer concentration above the cmc has been inferred from kinetic work.[39]

Although the micelle hydration numbers are obtained with a relatively low precision, a definite conclusion can be drawn from their low values: The alkyl chain–water contact is almost completely eliminated when a surfactant molecule is transferred from the free monomeric to the micellar state. Since the surfactant head groups and the bound counterions are hydrated,[4] the low number of water molecules diffusing with the micelles allows for some water contact of the $\alpha$-$CH_2$ groups but essentially no water contact further away from the head group. Considering the micelle interior as essentially a water-free oil droplet was done in the pioneering work of Hartley[40] and this has since formed the basis of models used in theoretical work which has successfully accounted for many aspects of surfactant–water systems. There has been much interest in the sharpness of the water–oil interface in micelles and other surfactant systems, and work using a broad spectrum of methods (neutron scattering,[41] different types of NMR relaxation,[42-44] etc.) seems to demonstrate unambiguously that this interface is quite sharp. One could also note that permitting even a relatively small water contact along the alkyl chains in surfactant aggregates would invalidate our accepted views on phase structures and phase behavior with water-continuous and oil-discontinuous phases occurring at quite high surfactant concentrations.[9,45] Important studies on the problem of water penetration into micelles have recently been presented by Balasubramanian and co-workers.[46-48] It was inter alia shown that a large number of partly polar or polarizable probes used in previous work are located in the head-group region and cannot, therefore, as anticipated in earlier work, report on the conditions in the micelle interior.

The invariance of counterion binding to changes in micelle concentration by orders of magnitude is now well established for several systems and counterion binding is also insensitive to added salt and to other parameters.[4,49-56] This type of behavior has been noted for linear polyions and in this field the term counterion condensation was introduced.[57,58] In recent years, theoretical work[34-36,59-61] on the basis of the Poisson–Boltzmann equation has given a rationalization of these observations and also demonstrated that an ion condensation behavior is expected also for polycharged systems of other geometries, inter alia for spheres. Our observations on counterion binding for micellar systems are throughout in excellent qualitative agreement with the PB theoretical work. Quantitative theoretical rationalization cannot be attempted with the crude description of counterion binding in terms of a single parameter, $\beta$. In fact, the counterion concentration decays progressively as one moves away from the micelles, making a simple two-site model unrealistic. A counterion condensation behavior of ionic surfactant–water systems has now been observed for a large numer of systems (different surfactants and counterions, different micelle shapes, and different phases) by a large number of experimental techniques (inter alia electrical conductance, counterion NMR chemical shifts, fluorescence quenching, counterion NMR quadrupole splittings, counterion activity, and counterion self-diffusion; for a review see ref 3) and seems to be a quite general characteristic at least of systems with monovalent inorganic counterions.

As regards the details of the counterion binding, as observed in the present study, the following may be noted: Excepting the very short chain surfactants (such as sodium octanoate), we observe in general a weak but significant decrease in $\beta$ as the concentration is increased. This is also in perfect agreement with the PB calculations[8,34] and is attributed to an increased total concentration of free ions (due to counterion dissociaiton) which screens the electrostatic potential from the charged micelle. The range of the decreased electrostatic potential is as a result reduced and thus also the distance at which counterions are affected enough to be immobilized (in their long-range motions) by the micelles. Under the conditions investigated, hexadecyltrimethylammonium bromide is the only surfactant showing any significant change in micellar shape;[62] the increase in $\beta$ at higher concentrations observed in this case is attributed to the transition from spherical to rodlike micelles,[13] which have higher charge numbers as well as higher charge densities.

A small but significant counterion specificity was observed in the pair $Li^+/Na^+$ for dodecyl sulfate and in the pair $Cl^-/Br^-$ for hexadecyltrimethylammonium, the $Na^+$ and $Br^-$ ions having the higher $\beta$ values. The slightly lower cmc values for these counterions also point to a higher degree of charge neutralization in these cases. The information provided in this work on counterion specificity is certainly too limited to warrant any lengthy discussion of this point. We merely note that cmc and $\beta$ values are generally observed to be very little affected by counterion substitution (inorganic counterions) while other parameters, like counterion competition and micellar growth, may be strongly counterion dependent.[4] In fact, growth of dodecyl sulfate and hexadecyltrimethylammonium micelles is more pronounced in the presence of the ions ($Na^+,Br^-$) with the higher $\beta$ values[62,63] and ion competition experiments also demonstrate that the larger the (nonhydrated) ion the more preferred is the interaction.[8,13] (This is different for different head groups, however.)

In conclusion, it is demonstrated that a polyelectrolyte behavior governs the basic aspects of the self-association of simple ionic surfactants with monovalent counterion and that system-specific

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effects (different head groups and counterions) are small but definitely significant. With a bulkier and more rigid hydrophobic part and with a less distinct separation of hydrophobic and hydrophilic parts the behavior is markedly different as demonstrated for the case of sodium cholate.

# Computer Modeling of Data from Pulse Radiolysis Studies of Aqueous Solutions Containing Scavengers of Spur Intermediates

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With the calculations reported here, all of the data from a comprehensive study of the kinetics of hydrated-electron decay in the 14-MeV-electron pulse radiolysis of pure water and aqueous solutions have been modeled within experimental error. The overlapping-spur model utilized employs a constant-energy fraction (0.2) of high, constant spur density regions (representing blobs/short tracks) and another constant-energy fraction (0.8) of a low, variable spur density region (representing isolated spurs) whose spur density is proportional to the pulse dose. The model also contains a new hydrated-electron probability density distribution function with the maximum in the probability density displaced from the center of the spur. Adjustments made to fit experimental data from different aqueous-solution pulse radiolysis studies have been minor. In this paper, hydrated-electron decay kinetics have been modeled within experimental error for a variety of scavengers of transient reactive intermediates originating in the spur. Thus, this new spur model has been successfully tested against experimental data for 14-MeV electrons over a wide range of pulse doses (0.5–80 Gy), time regimes ($10^{-11}$–$10^{-5}$ s), and types of scavengers of the major spur transients ($e_{aq}^-$, $\cdot OH$, and $H^+$).

## Introduction

The kinetics and yields in the radiolysis of water and aqueous solutions have been explained on the basis of energy deposition by ionizing radiation resulting in localized, nonhomogeneous regions of relatively high concentrations of reactive intermediates called spurs.[1] The deposition of energy along energetic electron tracks in condensed media has been further modeled in terms of isolated-spur, "blob", and "short-track" regions.[2] The latter are regions of increased spur density at track ends or where relatively large amounts of energy are deposited in a small region along the electron track.

The introduction, at the center of the spur, of a minimum in the hydrated-electron ($e_{aq}^-$) probability distribution function in our computer modeling program[3] has produced excellent fits between calculations and experimental data for hydrated-electron and OH radical decay for pure water in the nanosecond time regime following the pulse under a variety of pulse radiolysis conditions.[4] The use of a spur model with two different spur density regions has enabled us to model qualitatively the anomalous decay kinetics of the hydrated electron following low radiation pulse doses in pure water.[5] The two spur density regions are introduced in our calculations as first-order approximations of (1) the isolated spurs (<100-eV energy deposited)[1] along the electron track (low spur density) and (2) the higher LET (linear energy transfer) blob and short-track regions[2] near track ends and in regions along the electron track in which larger amounts of energy (>100 eV) are deposited in a nonhomogeneous fashion. The average energy per spur (60 eV) used to attain the desired fit between our computer calculations and experimental data is

more in accordance with that assumed by Magee and Chatterjee (40 eV)[6] than that suggested by Kuppermann (273 eV).[7]

Our modeling efforts thus far have concentrated primarily on pure-water pulse radiolysis results. We now wish to report further results in modeling the remainder of the pulse radiolysis hydrated-electron decay data of Fanning[8] taken with 14-MeV electrons from the Argonne linac and employing a series of scavengers of the reactive intermediates ($e_{aq}^-$, $\cdot OH$, and $H^+$). These data were taken by using 14-MeV pulsed electrons under conditions where the average distance between isolated spurs is equal to or greater than the average distance between electron tracks. This allows the assumption of a random distribution of isolated spurs, blobs, and short tracks.

Our hydrated-electron calculations are within experimental error of nearly all the data tested over a wide range of pulse dose and concentrations of scavengers of the predominant reactive intermediates produced in water by ionizing radiation.

## Computations and Experiments

Computer simulations were performed in the same manner as previously reported.[5] Pulse radiolysis experiments on the Argonne linac were generously performed by W. Mulac in essentially the same manner as that reported by Fanning et al.[9] We have found that in almost all cases the fits between computations and experimental data are much better in the $10^{-6}$–$10^{-5}$-s region if we include in the program a contribution for hydrated-electron scavenging by small amounts (2 $\mu$m) of dissolved oxygen. Since Fanning reports[8] that the 2-$\mu$m value is the upper limit of oxygen concentration found in his spot-checks of oxygen concentration

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