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of the metal is bare again and the oxidation process can go on until the whole metal has been destroyed. Once again the oxidative dissolution of metal particles by treatment with NO points out the powerful ability of NO for "desintering" supported metals.

The oxidation by O_2 is more difficult. For sample reduced at 200 °C a very long time in O_2 at 200 °C is needed for recovering the previously ionic state of nickel. But for the sample treated at 500 °C under H_2 , reoxidation is limited. Even heated at 500 °C the metal cannot be completely converted into ions. This probably occurs because at elevated temperature nickel cannot be prevented from sintering and large particles are formed as shown by magnetic measurements. Moreover it cannot be excluded that oxygen reacts with metal particles forming nonvolatile surface oxide deposited onto the metallic phase. So oxidation would be inhibited.

Conclusion

The present study reveals that the zeolite support is of first importance for ion properties. It is known that when we deal with transition-metal ions, the coordination state is very important for obtaining complexes having catalytic properties.

Mordenite is a noncubic zeolite with cationic sites of low symmetry. In these sites the nickel ions are not well coordinated and consequently very reactive. They can add

CO or NO to form cationic complexes stable at room temperature. The carbonyl complex destabilizes the ions which are partially reduced by hydrogen at room temperature. The nitrosyl complex is more inert toward hydrogen because of a stronger bonding between nickel and nitrogen atoms.

The low crystal field stabilization energy of Ni(II) in cationic sites make the ions reactive toward H_2 . A good deal of reduction is obtained at relatively low temperature for NiNa-Z, while for NiH-Z reduction is more difficult.

Therefore we can consider the whole zeolite as a rigid macrochelate. This concept in zeolite chemistry may be of consequence. Suppose a rigid matrix which coordinates the ion on every side, so it is protected against reactants. On the other hand, if we have a matrix which can coordinate the ion on one side only, the other one will be accessible and will be a reactive zone. The electric potential will be very heterogeneous, i.e., with a strong field gradient near the zeolite wall. New complexes may be formed or grafted with perhaps new intriguing properties (like Ni-CO mordenite). We feel that with unusual zeolites (those with zig-zag channels or with highly asymmetrical cationic sites) some new interactions between ion and support may result. Unexpected chemical properties might then be obtained.

Registry No. CO, 630-08-0; NO, 10102-43-9; mordenite, 12173-98-7.

Static and Dynamic Light Scattering Studies of Micellar Growth and Interactions in Bile Salt Solutions

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From static and dynamic light scattering measurements we have deduced the apparent mean aggregation number (\bar{n}_{app}) and mean hydrodynamic radius (\bar{R}_H)_{app} for sodium taurodeoxycholate (TDC) micelles as a function of TDC concentration (0.25–10 g/dL) in 0.8 M NaCl at 20 °C. A nonmonotonic behavior is found for \bar{n}_{app} , whereas (\bar{R}_H)_{app} increases steadily from ~15 Å at the critical micelle concentration (cmc) to greater than 90 Å at 10 g/dL. The data are analyzed in terms of a general theoretical framework incorporating the possible influences of micellar growth and micellar interactions. Using the quantitative model of primary-secondary bile salt aggregation proposed by Mazer et al. in conjunction with the theory of excluded-volume interactions for rodlike particles, we obtain a quantitative explanation for the concentration dependence of both \bar{n}_{app} and (\bar{R}_H)_{app}. These studies provide strong support for the view that TDC micelles grow into elongated structures above the cmc in the presence of high NaCl concentration.

Introduction

Static and dynamic light scattering experiments provide information on the distribution of molecular weights and translational diffusion coefficients of macromolecules in solution.^{1,2} In recent years these techniques have been applied to the study of the aggregation of amphiphilic molecules^{3,4} and in particular to examine the influence of amphiphile concentration on the aggregation behavior.⁵⁻⁸ In the case of aqueous solutions of ionic detergents there is a present controversy as to whether the concentration

dependence of the apparent mean molecular weight \bar{M}_{app} and mean diffusion coefficient \bar{D} reflects a real change of

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the micelle size distribution or whether these quantities are mainly influenced by intermicellar interactions.^{5,7,9,10}

For the systems sodium dodecyl sulfate (SDS) and bile salt the addition of NaCl has been found to have a strong influence on the observed concentration dependence of \bar{M}_{app} and \bar{D} .^{5-7,11,12} At low NaCl concentrations (0–0.3 M) repulsive electrostatic interactions^{5,12} appear to dominate the concentration dependence whereas at high NaCl concentrations (≥ 0.5 M) the data for both systems strongly suggest the growth of micelles from globular to rodlike structures.^{3,6,7,13} Nevertheless, there have been attempts to interpret data from the high-salt regime on the basis of excluded-volume and attractive van der Waals intermicellar interactions with little or no micellar growth.⁵

In order to gain more insight into the influence of micellar growth and interactions on the light scattering data in the high-salt regime, we have investigated the aggregative behavior of the dihydroxy bile salt sodium taurodeoxycholate (NaTDC) in aqueous solutions containing 0.8 M NaCl by means of static and dynamic light scattering methods. This system was chosen because previous investigations in 0.6 M NaCl had shown a strong concentration dependence of \bar{D} and had further led to a quantitative thermodynamic model for rodlike micellar growth in the TDC system.⁶ On the basis of this work an even stronger concentration dependence of \bar{D} and \bar{M}_{app} was expected in 0.8 M NaCl and could be used to compare the predictions of the micellar growth model with an interpretation of the data based solely on micellar interactions. In the following sections we present a general theoretical framework for interpreting static and dynamic light scattering data in micellar systems, in which both models are contained. We then compare and contrast interpretations of the present TDC data based on the two approaches.

Experimental Section

Materials and Solutions. The TDC was obtained from Calbiochem (A grade), recrystallized twice by the method of Pope,¹⁴ and found to have a purity of approximately 98% by reversed-phase high-performance liquid chromatography.¹⁵ The NaCl was obtained from Merck (analysis grade). Toluene (Merck, spectroscopic grade) was used as a reference standard for static light scattering.

The solutions were made on a weight/volume basis, and no attempt was made to adjust the pH which approximated 6–7.⁶

In view of the tendency of TDC–NaCl solutions to form gels at 4 °C,^{6,16} the present samples were prepared at 20 °C and equilibrated for 24 h at this temperature prior to investigation. Under these conditions there was no detectable gelation and the light scattering parameters showed no variation over a 4-day period. After further equilibration at 20 °C for 1 week gelation was observed.

Apparatus and Methods. Our light scattering apparatus for both static and dynamic measurements consists of an argon ion laser (Spectra Physics, $\lambda = 5145$ Å), a temper-

ature-controlled scattering cell holder, a variable-angle light detection system, a digital Malvern autocorrelator (96 channels), and an "on-line" data analysis with a Nova 3 computer. Details are provided elsewhere.¹⁷

Bile salt solutions (0.5 mL) were pipetted into acid-washed cylindrical quartz scattering cells (inner diameter, 8 mm) that were sealed and centrifuged at 15000g for 10 min to sediment dust from the solution. Measurements were performed at 90° scattering angle at a temperature of 20 °C.

Measurements of the Scattered Intensity. The time-averaged intensity \bar{I} scattered from the micellar solutions was compared to the scattered intensity of a pure toluene standard sample by taking the ratio \bar{I}/\bar{I}_{Tol} . In order to obtain the scattering due to the micelles alone, we subtracted the thus normalized scattered intensity of a 0.8 M NaCl solvent from \bar{I}/\bar{I}_{Tol} .¹⁸ The difference $\Delta\bar{I} = \bar{I}/\bar{I}_{Tol} - \bar{I}_0/\bar{I}_{Tol}$ was analyzed in accordance with classical light scattering theory to give the apparent mean micellar weight \bar{M}_{app} using the formula¹⁹⁻²¹

$$\bar{M}_{app} = \Delta\bar{I} R_{90,Tol}^u \frac{2}{(1 + \rho_u)} \left(\frac{n}{n_{Tol}} \right)^2 \frac{\lambda_0^4 N_A}{4\pi^2 n^2 (\partial n / \partial C)^2} \frac{1}{(C - cmc)} \quad (1)$$

where $R_{90,Tol}^u$ is the Rayleigh ratio and ρ_u the depolarization ratio for toluene,^{19,22} n and n_{Tol} are the refractive indices of the solution and of toluene, respectively, λ_0 is the laser wavelength in vacuo, and $\partial n / \partial C$ is the refractive index increment for TDC (extrapolated to 0.8 M NaCl from ref 23). The third and fourth factor take into account the use of a polarized light source and the difference between the refractive indices of the micellar solution and the standard.²⁰ The apparent mean aggregation number \bar{n}_{app} was obtained by dividing \bar{M}_{app} by the molecular weight of the TDC ion (499).

Dynamic Light Scattering. The autocorrelation function of the scattered light intensity $C(\tau)$ was measured at 48 channels equally spaced in time and the remaining 48 channels were delayed to provide a direct measurement of the base line B . The B values agreed within experimental error with the base line computed from the monitor channels. This indicates the absence of dust or other sources of long decay times. A cumulant analysis²⁴ of $C(\tau) - B$ was used to deduce the mean diffusion coefficient \bar{D} and the micellar polydispersity V (as defined in ref 3). In nearly all cases a second-order cumulant analysis was sufficient to fit the measured correlation functions with a precision of better than 1 part in 10^3 ; however, in a few highly polydisperse systems a third-order function was used.

From \bar{D} an apparent mean hydrodynamic radius $(\bar{R}_H)_{app}$ as defined in eq 2 was calculated by analogy with the Stokes–Einstein relation

$$(\bar{R}_H)_{app} = kT / (6\pi\eta\bar{D}) \quad (2)$$

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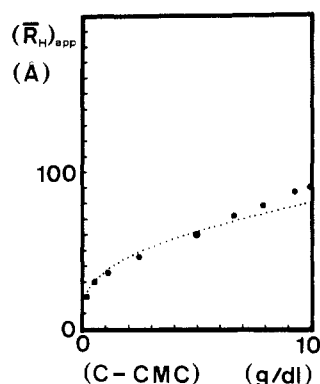


Figure 1. Mean hydrodynamic radii $(\bar{R}_H)_{app}$ as a function of the TDC concentration. The dotted curve shows the theoretical dependence of \bar{R}_H on $C - cmc$ based on the model of primary-secondary micelle formation.

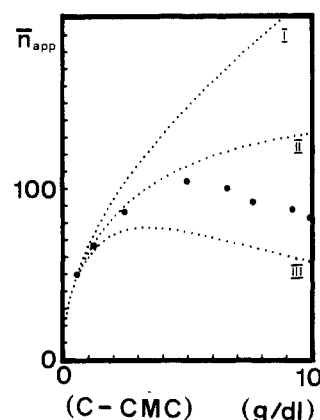


Figure 2. Apparent mean aggregation numbers \bar{n}_{app} as a function of the TDC concentration. Curve I shows the theoretical dependence of \bar{n}_w on $C - cmc$ based on the model of primary-secondary micelle formation. Curve II takes into account the excluded-volume interactions between spherical particles ($\bar{n}_{app} = \bar{n}_w / (1 + 8\bar{v}C)$), and curve III includes in addition the corrections for the nonspherical shape of the secondary micelles ($\bar{n}_{app} = \bar{n}_w / (1 + 8\bar{v}C)$).

where kT is the thermal energy and η the viscosity of the solvent. The theoretical basis for this equation is given elsewhere^{3,9} and will be discussed later.

Results

From the static and dynamic light scattering measurements we have deduced the apparent mean aggregation number \bar{n}_{app} and mean hydrodynamic radius $(\bar{R}_H)_{app}$ as functions of the TDC concentration in 0.8 M NaCl at 20 °C (Figure 1 and 2). Both quantities vary significantly with bile salt concentration over the range from 0.25 to 10 g/dL (approximately 5–200 times the cmc). The apparent hydrodynamic radius $(\bar{R}_H)_{app}$ increases monotonically from 21 to 90 Å over this range, whereas \bar{n}_{app} increases at low concentrations, passes through a maximum of approximately 100 at 5 g/dL, and decreases at higher concentrations. By plotting the data at low concentration vs. $(C - cmc)^{1/2}$, one can linearly extrapolate the micellar properties to the cmc (see Figure 3, A and B). In this way we obtain a mean hydrodynamic radius of 15 ± 1 Å and a mean aggregation number of 12 ± 3 for the TDC micelle at the cmc. From the autocorrelation function measurements it was also possible to obtain some estimates of the polydispersity index V for the TDC micelles. In the majority of measurements the second-order cumulant analysis gave V values that were typically $25 \pm 5\%$. At high concentrations (5–10 g/dL), the third-order cumulant analysis was of comparable statistical significance as the second-order analysis and gave larger V values of $50 \pm 5\%$.

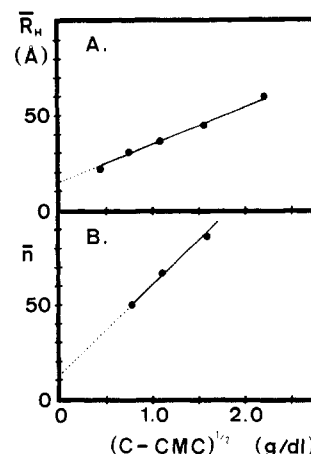


Figure 3. Extrapolations of $(\bar{R}_H)_{app}$ and \bar{n}_{app} to the critical micellar concentration cmc.

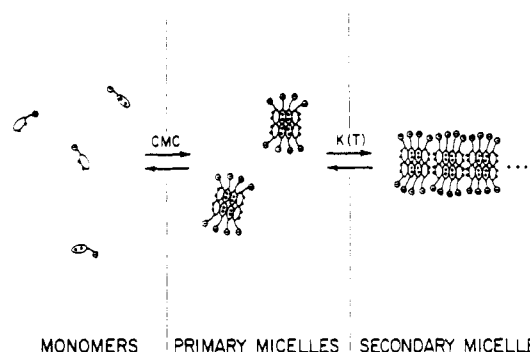


Figure 4. Schematic diagram of bile salt aggregation based on the primary-secondary micelle hypothesis. (See text for details.)

Discussion

Comparison with Previous Studies. The monotonic increase of $(\bar{R}_H)_{app}$ with TDC concentration (Figure 1) found in the present work is similar to that reported previously for TDC micelles in 0.6 M NaCl but, as expected, results in even larger apparent micellar sizes at high concentrations.⁶ On the other hand, the mean hydrodynamic radius extrapolated to the cmc in 0.8 M NaCl is in good agreement with that obtained for TDC micelles of lower NaCl concentrations⁶ and falls in the range of values (11–16 Å) found by dynamic light scattering for other bile salt micelles near the cmc.^{6,25} This size range is consistent with the view that the initial stage of bile salt aggregation involves the formation of small globular primary micellar aggregates with aggregation numbers of approximately 10 or less (shown schematically in Figure 4). The second stage of bile salt aggregation has been hypothesized to result from the concentration-dependent polymerization of primary micelles to form rodlike secondary micelles.⁶ Such micellar growth is suggested by the observed growth of $(\bar{R}_H)_{app}$ with increasing concentration (Figure 1).

With regard to the primary-secondary micelle hypothesis, the mean aggregation number extrapolated to the cmc (12 ± 3) agrees with that expected for primary micelles.²⁶ Moreover, the increase of \bar{n}_{app} seen at low concentrations is consistent with micellar growth. However, the finding that \bar{n}_{app} increases to a maximum and then decreases at higher concentrations is a new observation for the TDC system and is not immediately reconcilable with the primary-secondary micelle hypothesis.

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It is noteworthy that the concentration dependence of $(\bar{R}_H)_{app}$ and \bar{n}_{app} for TDC micelles in 0.8 M NaCl is quite similar to the behavior of SDS micelles studied by static and dynamic light scattering at high NaCl concentration.^{7,11} In the latter system, where a sphere-to-rod transition is believed to occur, \bar{R}_H increases monotonically with concentration while \bar{n}_{app} increases above the cmc and then passes through a maximum.

In view of the strikingly different behavior exhibited by $(\bar{R}_H)_{app}$ and \bar{n}_{app} in these micellar systems, it remains to be shown whether a quantitative explanation of the data is provided by a model of micellar growth, by a model based solely on micellar interactions, or eventually by a suitable combination of both models.

Theoretical Issues Concerning the Interpretation of Static and Dynamic Light Scattering Data in Micellar Systems. Micellar systems are inherently polydisperse and can be represented by a set of mole fractions, $\{X_n\}$, corresponding to the concentrations of micelles with aggregation number n .²⁷ Recent theories²⁸⁻³⁰ suggest that this distribution of aggregation numbers can be markedly influenced by the total amphiphile concentration, C , which provides a constraint on the set $\{X_n\}$ and on the equilibrium monomer concentration X_1 that results from material conservation

$$C = X_1 + \sum_n nX_n \quad (3)$$

In particular it has been shown that for rodlike micellar structures the mean aggregation number can increase approximately as $C^{1/2}$ at concentrations above the cmc.^{6,7,28,29}

In the case of bile salt aggregation the model of primary-secondary micelle formation implies that primary micelles with aggregation numbers n_0 polymerize in a stepwise fashion to form rodlike secondary micelles with aggregation numbers $2n_0, 3n_0, 4n_0, \dots$ (see Figure 4).⁶ The polymerization constant K is assumed to be the same in each step. It is a function of bile salt species, temperature, and NaCl concentration. According to the model the set $\{X_{in_0}; i = 1, 2, 3, \dots\}$ is determined by the product $K(C - \text{cmc})/n_0$. A monotonic increase in mean aggregation number is predicted as this product exceeds unity, consistent with the general behavior of rodlike micelles.

Interpretation of \bar{n}_{app} . For a polydisperse system of noninteracting micelles \bar{n}_{app} will be related to the set $\{X_n\}$ by⁷

$$\bar{n}_{app} = \frac{\sum_n n^2 X_n P_n(\theta)}{\sum_n n X_n} \quad (4)$$

where $P_n(\theta)$ is the light scattering form factor corresponding to an n -mer at the scattering angle θ . In the limit where $P_n(\theta)$ approximates unity, eq 4 implies that \bar{n}_{app} corresponds to the weight-average aggregation number $\bar{n}_w(C)$, which in general will be a function of the amphiphile concentration. In this limit the influence of micellar interactions on \bar{n}_{app} can be expressed to first order as⁵

$$\bar{n}_{app} = \bar{n}_w(C) / [1 + k_I(C - \text{cmc})] \quad (5)$$

where k_I depends on the pair interaction potential between micelles in solution. In ionic micellar systems repulsive electrostatic interactions, excluded-volume effects, and attractive interactions can contribute to k_I .⁵ At high NaCl

concentrations such as 0.8 M, however, the electrostatic interactions are effectively screened and the excluded-volume effects would be expected to dominate. For polydisperse systems the excluded-volume contribution to k_I can be formally expressed as³¹

$$k_I^{EV} = \left(\frac{\sum_i \sum_j (iX_i/C)(jX_j/C)\mu_{ij}}{\sum_i (iX_i/C)V_i} \right) \bar{v} \quad (6)$$

where μ_{ij} is the excluded volume associated with the interaction of i -mer and j -mer aggregates, V_i is the actual volume of the i -mer, and \bar{v} is the partial molar volume of the micelles which is assumed to be the same for all aggregates. In the case of monodisperse spherical particles, eq 6 reduces to $8\bar{v}$. For polydisperse and/or nonspherical particles it is therefore convenient to express k_I^{EV} as²⁸

$$k_I^{EV} = 8f\bar{v} \quad (7)$$

where the parameter f incorporates the influences of shape and polydispersity on the excluded-volume interaction and might therefore vary as a function of C . A detailed calculation of f for polydisperse rodlike systems is given in the Appendix.

When eq 7 is substituted into eq 5, it is appreciated that \bar{n}_{app} will not increase with concentration as rapidly as $\bar{n}_w(C)$ and as shown by Mukerjee²⁸ can even begin to decrease at high concentration in rodlike micellar systems.³² Conversely if one assumes that $\bar{n}_w(C)$ remains constant, then such nonmonotonic behavior of \bar{n}_{app} must be due to the parameter k_I , whose sign would have to be negative and whose magnitude would vary as a function of concentration. Such behavior could not be accounted for by excluded-volume interactions (eq 7) alone.

Interpretation of $(\bar{R}_H)_{app}$. For a polydisperse system of noninteracting micelles the mean diffusion coefficient \bar{D} measured by dynamic light scattering is related to the micelle size distribution by⁶

$$\bar{D} = \frac{\sum_n n^2 X_n P_n(\theta) D_n}{\sum_n n^2 X_n P_n(\theta)} \quad (8)$$

where D_n is the translational diffusion coefficient of a micelle of aggregation number n . This value can be related to a hydrodynamic radius $(R_H)_n$ of the micelle by means of the Stokes-Einstein relation³

$$D_n = kT / [6\pi\eta(R_H)_n] \quad (9)$$

where η is the solvent viscosity. From the definition of $(\bar{R}_H)_{app}$ (eq 2) and from eq 8 and 9 it follows that in a noninteracting system $(\bar{R}_H)_{app}$ is given by

$$(\bar{R}_H)_{app} = \frac{\sum_n n^2 X_n P_n(\theta)}{\sum_n n^2 X_n P_n(\theta) \left(\frac{1}{(R_H)_n} \right)} = \bar{R}_H(C) \quad (10)$$

which we shall denote as $\bar{R}_H(C)$, emphasizing the possible concentration dependence of the micelle size distribution.³⁴

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TABLE I: Experimental Values of $(\bar{R}_H)_{app}$ and \bar{n}_{app} of TDC Micelles in 0.8 M NaCl as a Function of Concentration and a Comparison of the Interaction Parameters Obtained from the Two Different Analyses^a

$C - \text{cmc}$, g/dL	experiment			analysis 1		analysis 2				
	$(\bar{R}_H)_{app}$, Å	\bar{n}_{app}	$(\bar{R}_H)_{app}/\bar{n}_{app}$, Å	k_I/\bar{v} , no growth	k_f/\bar{v} , no growth	$\bar{R}_H(C)$, Å	$\bar{n}_w(C)$	$\bar{R}_H(C)/\bar{n}_w(C)$	k_I/\bar{v} , growth	k_f/\bar{v} , growth
9.95	90	83	1.084	-11.1	-1.62	79.5	212	0.375	20.6	21.6
9.25	88	88	1	-12.0	-2.64	77.3	203	0.380	18.6	20.1
7.64	79	92	0.86	-14.7	-4.72	72	183	0.392	17.1	17.9
6.62	72	100	0.72	-17.1	-8.0	68.3	170	0.401	14.0	13.7
4.95	60	104	0.57	-23.0	-14.5	61.8	147	0.419	11.1	8.43
2.45	45	86	0.523	-45.3	-30.7	48.5	102	0.475	9.99	4.24
1.20	36	67	0.537	-88.2	-62.0	38.9	72	0.540	8.18	
0.57	30	50	0.6	-170.3	-119.5	31.5	51	0.62		
0.20	21			-416.9	-332.7	24.0	31	0.769		
(0)	(15)	(12)	(1.25)			15.0	12	1.25		

^a Analysis 1 is based on the assumption of no micellar growth, whereas in analysis 2 the calculations are based on the model of primary-secondary micelle formation. The parameters used in the calculation of the size distribution were a polymerization constant $K = 2.7 \times 10^5$, an aggregation number $n_0 = 12$, and a mean hydrodynamic radius $R_H = 15$ Å for the primary micelles (according to the extrapolated values for $(\bar{R}_H)_{app}$ and \bar{n}_{app}).

For a monodisperse system of particles the influence of macromolecular interactions on the diffusion coefficient D measured by dynamic light scattering can be described by a generalized Stokes-Einstein relation, which to first order is given by^{35,36}

$$D = \frac{kT}{6\pi\eta\bar{R}_H} \left[\frac{(1 + k_I C)}{(1 + k_f C)} (1 - \bar{v}C) \right] \quad (11)$$

where k_I is the same thermodynamic interaction factor that appears in eq 5, k_f describes the concentration dependence of the particle friction factor, and $1 - \bar{v}C$ is a reference frame correction factor. For a polydisperse micellar system the influence of macromolecular interactions on \bar{D} remains an unsolved theoretical problem. We will treat this problem in an approximation using the theory for monodisperse systems (eq 11), but with \bar{D} and $\bar{R}_H(C)$ substituted for D and R_H and $C - \text{cmc}$ for C . $(\bar{R}_H)_{app}$ will then be given by

$$(\bar{R}_H)_{app} \approx \bar{R}_H(C) \left[\frac{1 + k_f(C - \text{cmc})}{(1 + k_I(C - \text{cmc}))(1 - \bar{v}(C - \text{cmc}))} \right] \quad (12)$$

From this equation we see that the concentration dependence of $(\bar{R}_H)_{app}$ will in general be influenced by micellar growth $(\bar{R}_H(C))$ as well as by intermicellar interactions (given by the expression in brackets). However, in the case of nongrowing micelles interacting only as hard spheres, it has been pointed out that an appreciable cancellation should take place between the thermodynamic and frictional terms so that only a weak concentration dependence of $(\bar{R}_H)_{app}$ results as has been observed in other macromolecular systems.^{35,36} For this reason it has been argued that for ionic micellar systems in the presence of high NaCl concentration, where electrostatic interactions are screened, the concentration dependence of $(\bar{R}_H)_{app}$ should largely reflect changes in the micelle size distribution.³ On the other hand, if one assumes that $\bar{R}_H(C)$ is a constant even in the high-salt regime, then it follows that the observed concentration dependence of $(\bar{R}_H)_{app}$ reflects the lack of cancellation between the thermodynamic and frictional terms. It is interesting to point out that the concentration dependence of the ratio $(\bar{R}_H)_{app}/\bar{n}_{app}$ provides additional insight into the contributions of micellar growth

and micellar interactions. Equations 5 and 12 imply that the thermodynamic term $1 + k_I(C - \text{cmc})$ cancels in this ratio, leaving

$$\frac{(\bar{R}_H)_{app}}{\bar{n}_{app}} = \frac{\bar{R}_H(C)}{\bar{n}_w(C)} \frac{[1 + k_f(C - \text{cmc})]}{[1 - \bar{v}(C - \text{cmc})]} \quad (13)$$

and that it depends in general on the concentration dependence of the micellar size distribution and on the frictional term $1 + k_f(C - \text{cmc})$. With the assumption of no micellar growth the first term will be a constant which can be estimated from the extrapolation of $(\bar{R}_H)_{app}$ and \bar{n}_{app} to the cmc. The concentration dependence of $(\bar{R}_H)_{app}/\bar{n}_{app}$ thus permits a deduction of the parameter k_f .

Quantitative Analysis of Static and Dynamic Light Scattering Data in TDC Systems. Using the theoretical framework outlined in the previous section, we offer two analyses of our data on TDC micelles in 0.8 M NaCl. In the first one we assume that there is no micellar growth, and in the second one that micellar growth does occur in accordance with the primary-secondary micelle model.

Analysis 1. No Micellar Growth. In this analysis we shall assume that at all concentrations the TDC micelles are globular aggregates with a mean hydrodynamic radius of 15 Å and a mean aggregation number of 12 consistent with our extrapolations to the cmc. The observed concentration dependence of \bar{n}_{app} and $(\bar{R}_H)_{app}$ will be attributed solely to micellar interactions.

Using eq 5 we deduce the thermodynamic factor k_I from the concentration dependence of \bar{n}_{app} and find that it varies markedly with concentration from -417 Å close to the cmc to -11.1 Å at 10 g/dL (see Table I). These negative k_I values would imply a strong attractive interaction between the TDC micelles rather than the repulsive excluded-volume interaction expected for the high-NaCl regime. Corti and Degiorgio⁵ have presented a theory of micellar interactions in SDS systems which allows for van der Waals attraction between spherical micelles. Such a theory cannot explain the strong concentration dependence of k_I observed here. Moreover, it is impossible to account for our value of k_I close to the cmc using a Hamaker constant comparable to that used by Corti and Degiorgio ($A \approx 4.5 \times 10^{-20}$). The same authors have noted a similar problem in accounting for the magnitude and concentration dependence of k_I in SDS systems at high NaCl concentrations (≥ 0.5 M), conditions at which there is considerable experimental and theoretical evidence for micellar growth from spheres to rods.^{7,11}

Under the present assumption of no micellar growth it is more illuminating to analyze the concentration depen-

(35) G. D. J. Phillies, G. B. Benedek, and N. A. Mazer, *J. Chem. Phys.*, **65**, 1883 (1976).

(36) P. N. Pusey in "Photon Correlation and Light Beating Spectroscopy", M. Z. Cummins and E. R. Pike, Eds., Plenum Press, New York, 1975, p 387.

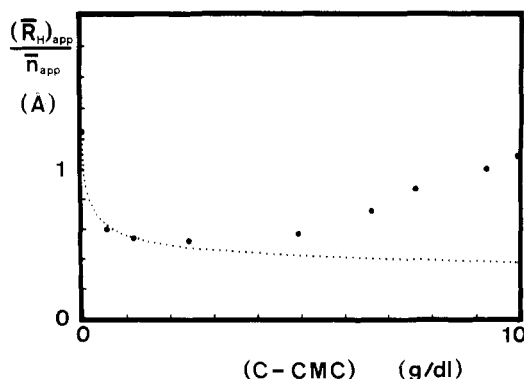


Figure 5. Ratios $(\bar{R}_H)_{app}/\bar{n}_{app}$ as a function of the TDC concentration. The first point is obtained from the extrapolations to the cmc (Figure 3, A and B). The dotted curve represents the calculated ratios $\bar{R}_H(C)/\bar{n}_w(C)$ on the basis of the model of primary-secondary micelle formation. The difference between the measured ratios and the calculated curve can be related to the influence of interactions on the frictional coefficient.

dence of the ratio $(\bar{R}_H)_{app}/\bar{n}_{app}$ rather than $(\bar{R}_H)_{app}$ itself (see Figure 5). From an initial value of ~ 1.25 Å deduced from the extrapolations of $(\bar{R}_H)_{app}$ and \bar{n}_{app} to the cmc this ratio decreases sharply at low concentrations, reaches a broad minimum of ~ 0.52 Å, and then increases linearly at concentrations above 4 g/dL. From eq 13 we deduce the frictional interaction parameter k_f and find that it varies strongly with concentration from $-333\bar{v}$ close to the cmc to $-1.6\bar{v}$ at 10 g/dL (see Table I). These values differ markedly from the theoretical estimates of k_f based on hard-sphere repulsion which fall in the range of $\sim 7\bar{v}$.^{37,38} While suggesting some form of attractive interactions between micelles the observed magnitude and concentration dependence of k_f cannot be accounted for by van der Waals attraction using the model outlined by Corti and Degiorgio.⁵

Summarizing we can say that the assumption of no micellar growth leads us to values of the interaction parameters k_1 and k_f that cannot be adequately explained by either hard-sphere repulsion or attractive van der Waals interactions between TDC micelles in the high-salt regime.

Analysis 2. Primary-Secondary Micelle Formation. As mentioned previously the quantitative model of primary-secondary micelle formation predicts that the size distribution of bile salt micelles will depend on bile salt concentration through the product $K(C - cmc)/n_0$,¹⁶ where K is the polymerization constant and n_0 is the aggregation number of the primary micelles. After fixing the value of n_0 (which will be taken as 12 from our extrapolation of \bar{n}_{app} to the cmc), this model in essence requires the knowledge of one single parameter K to predict the concentration dependence of the quantities $\bar{n}_w(C)$ and $\bar{R}_H(C)$ which are related to the measured quantities \bar{n}_{app} and $(\bar{R}_H)_{app}$ according to eq 5 and 12, respectively.³⁹

On the assumption that the interaction term in eq 12 has a negligible influence, Mazer et al.⁶ were able to fit their experimental data in TDC systems at 0.6 M NaCl with the theoretical concentration dependence $\bar{R}_H(C)$ using the single parameter K . In a similar manner we have compared the theory with our $(\bar{R}_H)_{app}$ values in 0.8 M NaCl and find that with a value of K ⁴⁰ equal to 2.7×10^5 there

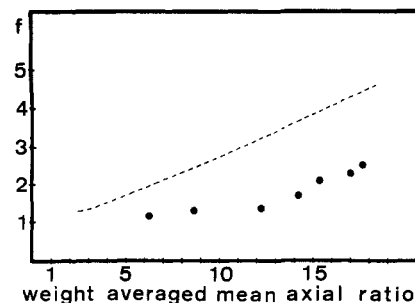


Figure 6. Parameter f as a function of the axial ratio. The broken line represents the theoretical values for monodisperse prolate ellipsoids.¹¹ The experimental values of f are deduced from the difference between the measured mean aggregation numbers \bar{n}_{app} and the calculated $\bar{n}_{app} = \bar{n}_w(C)/(1 + 8\bar{v}C)$ (curve II in Figure 2). For each f the weight-averaged mean axial ratio was calculated from the ratio $\bar{n}_w(C)/n_0$.

is excellent agreement between theory and experiment except for a small deviation at high concentrations (Figure 1). The polydispersity parameter V can also be calculated from the theory and is predicted to increase with concentration to a value of 50% at 10 g/dL, consistent with the experimental V values obtained from the third-order cumulant analyses.

Using the above value of K we proceed to analyze the concentration dependence of \bar{n}_{app} . As seen in Figure 2 the predicted behavior of $\bar{n}_w(C)$ is close to \bar{n}_{app} at low concentrations but deviates progressively from the data above 2 g/dL. From eq 5 this deviation can be attributed to the thermodynamic interaction parameter k_1 whose estimated magnitude is given in Table I as a function of concentration. At low concentrations k_1 is close to $8\bar{v}$, the theoretical value expected for excluded-volume interactions between monodisperse spherical particles. At higher concentrations k_1 increases monotonically and reaches $20.6\bar{v}$ at 10 g/dL. This increase is still consistent with excluded-volume interactions if one takes account of the shape dependence of k_1^{EV} given by the parameter f in eq 7. To show this we have deduced the parameter f from the k_1 values and have plotted it in Figure 6 vs. the corresponding weight-averaged axial ratio of the TDC micelles (which is equivalent to the ratio $\bar{n}_w(C)/n_0$). The resulting values are between unity, corresponding to monodisperse spheres, and the theoretical values for monodisperse prolate ellipsoids calculated with the same axial ratio.⁴¹ As discussed in the Appendix polydispersity⁴² cannot explain the deviation between the theoretical curve and the experimental values. In view of the amount of data reduction involved in deducing f and the possibility of micellar flexibility (which would decrease f), such a discrepancy is not unexpected. Nevertheless, it can be shown that the excluded-volume interaction for growing rodlike micelles is of the right order of magnitude to account for the unusual nonmonotonic behavior of \bar{n}_{app} . This is shown in Figure 2, where we have plotted a theoretical curve for \bar{n}_{app} obtained from eq 5 and 7 using the theoretical f values for prolate ellipsoids given in Figure 6. Although the calculated \bar{n}_{app} curve falls below the experimental values, it exhibits a similar shape and reaches a maximum at approximately the same concentration. If one uses a constant value of $8\bar{v}$ for k_1 (i.e., neglecting the influence of shape on the excluded volume), the resulting \bar{n}_{app} curve falls above the data and does not display a

(37) C. W. Pyun and M. Fixman, *J. Chem. Phys.*, **41**, 937 (1964).

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

(39) The dependence of $\bar{R}_H(C)$ on $K(C - cmc)/n_0$ also requires specifying the set $(\bar{R}_H)_n$ and the form factors $P_n(\theta)$ (eq 10). In the present calculations the micelles are modeled identically as in ref 6, with a minimum size of 15 Å for the primary micelles and the $P_n(\theta)$ are taken to be unity.

(40) K is expressed here in dimensionless units corresponding to the use of mole fraction units for the concentration $(C - cmc)$; see ref 6.

(41) A. Ishihara and T. Hayashida, *J. Phys. Soc. Jpn.*, **6**, 46 (1950).

(42) It can be shown that for systems of rodlike micelles this theoretical curve properly takes into account the influence of both shape and polydispersity on the parameter f if one replaces the axial ratio by its weight average (see the Appendix).

maximum over the concentration range studied (Figure 2). The feasibility of explaining the concentration dependence of \bar{n}_{app} for TDC micelles on the basis of micellar growth and excluded-volume interactions has also been shown by Missel et al.⁷ in the SDS system at high NaCl concentrations using a quantitative model of the sphere-to-rod transition.

Finally, it is interesting to examine the concentration dependence of $(\bar{R}_H)_{app}/\bar{n}_{app}$ in the context of the micellar growth model used in the present analysis. From eq 13 this dependence should, in part, reflect the behavior of $\bar{R}_H(C)/\bar{n}_w(C)$ which we have plotted in Figure 5. The initial decrease observed experimentally at low concentrations is consistent with the behavior of the theoretical curve; however, at higher concentrations the data deviate linearly from $\bar{R}_H(C)/\bar{n}_w(C)$ as would be expected from the contribution of the frictional interaction term. From this deviation we have calculated the values of k_f given in Table I. They are positive in sign and increase from 4.2 \bar{v} at low concentration to 21.6 \bar{v} at 10 g/dL. These values are of the same order of magnitude as expected for the hard-sphere contribution to k_f . Their variation with concentration is presumably a reflection of the influence of micellar shape on k_f , by analogy with the behavior of k_t . The finding that k_f and k_t are comparable in magnitude and vary similarly with TDC concentration is a consequence of our earlier observation that $(\bar{R}_H)_{app} \approx \bar{R}_H(C)$.

In summary we have shown in this analysis that a one-parameter model of primary-secondary micellar growth accounts for the concentration dependence of $(\bar{R}_H)_{app}$ and, when combined with the theory of excluded-volume interactions for rodlike particles, provides a quantitatively consistent explanation of the nonmonotonic behavior of \bar{n}_{app} . In view of the finding that excluded-volume interactions do occur in these solutions, one can ask whether the underlying model of primary-secondary micelle equilibrium would be affected by such interactions. This question has very recently been explored by Ben-Shaul and Gelbart⁴³ for both rodlike and disklike micellar systems. They have shown that, to lowest order, excluded-volume interactions between rodlike micelles have no effect on the micelle size distribution, whereas for disklike systems interactions can enhance micellar growth. In the present study of bile salt micelles, where rodlike growth has previously been deduced,⁶ the treatment of micellar interactions influencing only the parameters k_t and k_f , and not the quantities $\bar{n}_w(C)$ and $\bar{R}_H(C)$, is justified.

Conclusions

We have presented new experimental data for the concentration dependence of the apparent mean aggregation number (\bar{n}_{app}) and mean hydrodynamic radius $(\bar{R}_H)_{app}$ as deduced from static and dynamic light scattering measurements on aqueous sodium taurodeoxycholate solutions in 0.8 M NaCl. In addition, we have presented a general theoretical framework for interpreting these data, which incorporates the possible influences of micellar growth as well as micellar interactions. Using the quantitative model of primary-secondary bile salt aggregation proposed by Mazer et al.⁶ in conjunction with the theory of excluded-volume interactions for rodlike particles, we obtain a quantitative explanation for the concentration dependence of both \bar{n}_{app} and $(\bar{R}_H)_{app}$. Conversely, if one assumes that no micellar growth takes place above the cmc, the values for the thermodynamic (k_t) and frictional (k_f) interaction parameters deduced from the experimental data imply a strong attractive interaction between micelles that varies

markedly with concentration. Such behavior cannot be accounted for in a simple way by the assumption of van der Waals attraction between globular micellar aggregates. The present findings support the view⁶ that TDC micelles undergo a concentration-dependent growth from globular to elongated structures in the presence of high NaCl concentration that is similar to the sphere-to-rod transition reported for SDS and other ionic chain detergents under similar conditions.^{3,7,8,27} The present study further supports the view that excluded-volume interactions do not markedly influence the concentration dependence of $(\bar{R}_H)_{app}$ in ionic micellar systems at high salt concentrations. The appreciable cancellation between the thermodynamic and frictional interaction parameter which is apparently taking place in these polydisperse rodlike systems remains to be explored in further theoretical and experimental investigations.

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Appendix

Excluded-Volume Interactions for a Polydisperse Rodlike System. In order to evaluate the thermodynamic parameter k_I^{EV} for a polydisperse system of rodlike macromolecules, we use eq 6 and Onsager's⁴⁴ result for the orientationally averaged excluded volume μ_{ij} of two prolate spherocylinders with diameter d and lengths l_i and l_j :

$$\mu_{ij} = \frac{4\pi}{3}d^3 + \Delta d^2(l_i + l_j) + \frac{\pi}{2}l_i l_j d \quad (A-1)$$

Substitution of eq A-1 into eq 6 along with the expression for $V_i = \frac{4}{3}\pi(d/2)^3 + \pi(d/2)^2 l_i$ gives

$$k_I^{EV} = \frac{\sum_{i,j} w_i w_j \left[\frac{4\pi d^3}{3} + \pi d^2(l_i + l_j) + \frac{\pi}{2} l_i l_j d \right]}{\sum_i w_i \left[\frac{4\pi}{3} \left(\frac{d}{2} \right)^3 + \pi \left(\frac{d}{2} \right)^2 l_i \right]} \bar{v} \quad (A-2)$$

where the variable w_i has been introduced in place of iX_i/C to indicate the weight fraction⁴⁵ of macromolecular species i . Performing the weight averages we obtain

$$k_I^{EV} = \frac{\left(\frac{4\pi}{3}d^3 + 2\pi d^2 \bar{l}_w + \frac{\pi}{2}(\bar{l}_w)^2 d \right)}{\frac{4}{3}\pi \left(\frac{d}{2} \right)^3 + \pi \left(\frac{d}{2} \right)^2 \bar{l}_w} \bar{v} \quad (A-3)$$

where \bar{l}_w is the weight-averaged length of the distribution. This can be rewritten as

$$k_I^{EV} = 8 \left[1 + \frac{\frac{1}{4} \frac{\bar{l}_w}{d}}{1 + \frac{2}{3} \left(\frac{\bar{l}_w}{d} \right)^{-1}} \right] \bar{v} \quad (A-4)$$

which identifies the shape factor f of eq 7 with the ex-

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(44) L. Onsager, *Ann. N. Y. Acad. Sci.*, **51**, 627 (1949).

(45) Flory and Krigbaum have shown that, in computing the excluded-volume coefficient measured by osmotic pressure one must use the number fraction $X_i/\sum_i X_i$ for polydisperse systems.

pression in brackets. This result shows that f is a function of the weight-averaged axial ratio⁴⁶ only and is identical in form with the shape factor for monodisperse systems, f_i , which is given by

$$f_i = \frac{\mu_{ii}}{8V_i} = 1 + \frac{\frac{1}{4} \frac{l_i}{d}}{1 + \frac{2}{3} \left(\frac{l_i}{d} \right)^{-1}} \quad (\text{A-5})$$

(46) For prolate spherocylinders this axial ratio is given by $l_w/d + 1$.

Thus, for polydisperse rodlike systems f simply corresponds to the value that one would obtain for monodisperse systems having the weight-average axial ratio and is insensitive to the precise form of the particle size distribution. This result would not be true for polydisperse spherical particles (f would be <1), but it should be approximately correct for elongated structures in general, such as the prolate ellipsoids used for calculating the theoretical curve in Figure 5.

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Mechanism of the Catalytic Reduction of Nitric Oxide by Ammonia over Cobalt–Amine Complexes in Na–Y Zeolite

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The mechanism of the NO–NH₃ reaction over Co(en)₂(NO₂)₃ complex (en = ethylenediamine), ion exchanged into Na–Y zeolite, was studied extensively and compared with that by the same complex in an aqueous solution, which has been reported previously. At room temperature, the catalytically active species are similar in both media, exhibiting similar reaction mechanisms. Ammonia treatment of the catalyst at 363 K caused the reduction of cobalt cation to Co^{II} with the removal of NO₂ groups. The catalytic behavior of this Co^{II}(en)–Y zeolite was compared to that of Co^{II}(NH₃)–Y zeolite, prepared by a conventional cation-exchange method. During the NO–NH₃ reaction, mononitrosyl and dinitrosyl intermediate species were much more stable in Co(NH₃) zeolite than Co(en)–Y zeolite, resulting in different reaction orders and kinetic isotope effects. It is demonstrated that a zeolite cavity can be a microreactor, where residual water acts as a solvent to assist the stabilization of the catalytically active species.

I. Introduction

The catalytic reduction of nitric oxide by ammonia has been studied over transition-metal ions in zeolites, such as Cu–Y^{1,2} and Co–Y zeolites.³ In these systems, the catalysts were prepared by a cation-exchange method, and [Cu(NH₃)₄]²⁺ or [Co(NH₃)₆]³⁺ (ref 4) is postulated to be a catalytically active species in the zeolite cavity. Recently Lunsford et al.⁵ compared the catalytic behavior of [Cu^{II}(NH₃)₄]²⁺ in zeolite to that in an aqueous solution and concluded that cavities of the zeolite could be microreactors for the NO–NH₃ reaction, where residual water is a solvent and the zeolite framework is an anion.

We have also found a similar phenomenon in the case of the NO–NH₃ reaction catalyzed by Co^{III}(en)₂(NO₂)₃ complex (en = ethylenediamine), exchanged in Y-type zeolite,⁶ which exhibited catalytic behavior quite similar to that in an aqueous solution.^{7,8} The interesting point of this system is that the NO–NH₃ reaction proceeds only very slowly when these complexes are supported on silica, alumina, or silica–alumina, indicating that an important role of the zeolite cavity is to stabilize catalytically active

species similar to that in the solution. There exists a large solvent effect in the solution reaction, and the kinetics in DMF are quite different from those in aqueous solution, which may be explained by the shift of the rate-determining step. The kinetics of the reaction over the zeolite-supported complex are similar to those in the aqueous solution, but the real structure of the complex in the cavities of zeolites and the reaction mechanism have not been clarified yet.

In this report, infrared and X-ray photoelectron spectroscopic techniques are applied to investigate the working state of the catalyst during the reaction. Detailed kinetic experiments and tracer studies using ¹⁵NO and ¹⁵NH₃ are carried out to elucidate the reaction mechanism of the NO–NH₃ reaction, and the correlation between two different media, in zeolite and in solution, is discussed in depth.

II. Experimental Section

(1) *Catalyst Preparation.* Complexes employed in this study were prepared with a method similar to that reported by Holtzclaw, Jr., et al.⁹ An aqueous solution of the complex was mixed with powdered Na–Y zeolite (Linde) and stirred at 350 K for a few hours. After filtration the catalyst was washed thoroughly with water and dried at room temperature. The amount of the complex ion exchanged was determined spectroscopically from the amount of the complex left in the solution. In the case

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