poly(ethylene glycols)[16]), the similarity of general ion structures and the intensity changes resulting from air oxidation of the sample prepared from $Cr(TFA)_3$ suggest that spectra provide at least semiquantitative measures of the relative abundances of ions in the solutions. Extensive studies are currently under way, with an aim of better quantitation through a more detailed understanding of the EH ionization process.

Conclusions

The results of this study suggest that EHMS can provide a simple and direct probe for characterization of the solution chemistry of transition metal complexes. The spectra accurately reflect the relative lability of the metal complexes sampled; that is, the labile chromium(II) complex undergoes ligand exchange reactions whereas the inert ruthenium(II) complex does not. Furthermore, because of the sensitivity of mass spectrometry, impurities in solution can also be detected and identified.

The need for low volatility and high electrical conductivity for solutions sampled with existing EH instrumentation enforce some constraints on the range of systems which can be sampled. While the latter condition (conductivity) is readily met in solutions of transition metal complexes, the former (volatility) precludes the use of many important solvents (most notably, water). Design refinements presently under consideration may relieve volatility restrictions. However, even in its present form, EHMS appears to be a valuable probe of these (and related) systems.

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Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $Cr(bpy)_3^{2+}$, 17632-84-7; $Cr(bpy)_2Cl^+$, 82621-23-6; $Cr(bpy)_2Cl_2^+$, 21748-31-2; $Cr(bpy)_2(G\text{-}2H)^+$, 82621-24-7; $Cr(bpy)_2Cl(G\text{-}H)^+$, 82621-25-8.

Rotation about the Carbonyl Carbon–Nitrogen Bond in Micelles of *N*-(Dodecyloxycarbonyl)sarcosinate

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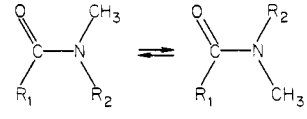
Abstract: The sodium salt of the title compound forms micelles readily, exhibiting a critical micelle concentration of 6×10^{-4} M at 25 °C. Quasi-elastic light scattering shows that most of the micelles are approximately 6.0 nm in diameter, although indications of larger aggregates (~170 nm diameter) were also observed. These diameters do not change beyond experimental error over the temperature range 25–50 °C. Proton NMR experiments were used to determine the kinetics of rotation about the carbonyl carbon–nitrogen bond of the detergent both in micelles and in the monomer. While $\Delta G^{\ddagger}$ for rotation was found to be independent of aggregation state, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the process are substantially larger in the micelle. Variations in the activation parameters as the identity of the counterion is changed suggest that disruption of ionic interactions at the surface of the micelle is a part of the rotational process.

The nature of the micellar structures formed when amphiphilic molecules are placed in water has generated interest and controversy for many years.[1-3] At this point it seems to be generally accepted that these structures include a hydrophobic core region from which water is largely absent; outside this nucleus some fraction of the remaining hydrocarbon and the polar head group of each detergent are in contact with water to some degree. Many experiments point to decreased fluidity inside the micelle,[3,4] and carbon-13 NMR data suggest that molecular motion in the head-group region of these structures is significantly reduced in the micelle relative to that observed in nonmicellized states.[5] A fluidity gradient is observed as one progresses from the head-group region to the hydrophobic core with motion becoming freer as the core is approached. These conclusions are similar to observations made with lipid bilayers and biological membranes—in these systems the polar surface is highly ordered, and molecular motion increases in rate and amplitude as the more hydrophobic interior of the structure is approached.[6]

Many micelles formed by ionic amphiphiles in water appear to be approximately spherical structures coated with electrical charges, first those of the ionic groups of the detergent and then a layer containing a large fraction of the counterions that accompanied the detergent into solution. A highly heterogeneous electrical environment is thus present at the "surface" of a micelle that is not unlike that which exists on the surface of a cell membrane.

There is evidence that the relative conformational energies of the two forms of the amide functional group (Ia, Ib) are altered



Ia Ib

when this group is present at the surface of a micelle,[7] and when surfactant molecules incorporating this structural element form micelles, the population of the trans isomer (Ib) relative to the

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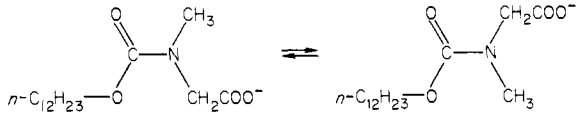
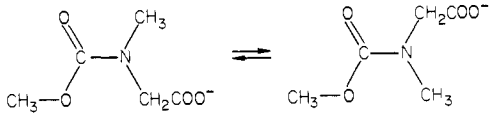
cis form (Ia) is found to increase substantially. Because of the biological relevance of this functional group and the analogies between micelle and membrane structure, we became interested in determining the kinetics of the process that interconverts these conformational isomers in a micelle. The structural ordering present could possibly have an effect, and both theory[8] and experiment[9] indicate that electrical environment, as represented by cation complexation, can alter amide rotation rates.

Initial experiments with detergents similar in structure to those examined by Takahashi et al. indicated that the barrier to rotation in these compounds was so large that it was not possible to determine the rotation kinetics by common NMR methods.[10] The carbamate *N*-(dodecyloxycarbonyl)sarcosine (II) was synthesized



IIa IIb

to provide a system with a reduced barrier; this compound was found to have a barrier to rotation of the carbamate group that makes the kinetics of this process accessible to NMR methods. In this paper we describe (1) the preparation of II, (2) the nature of the micelles formed by II, and (3) the effect of micellization on conformational isomerism about the carbonyl carbon–nitrogen bond. The model compound III was also examined to provide



IIIa IIIb

a reference point for our observations; this structure presumably will not aggregate appreciably under our experimental conditions of low solute concentration in aqueous solution.

Experimental Section

Sodium *N*-(Dodecyloxycarbonyl)sarcosinate. The synthesis was adapted from the procedure of Haas et al.[11] Phosgene (Linde) was slowly passed into 50 mL of toluene maintained at −10 °C until the volume of the solution was about 75 mL. 1-Dodecanol (Aldrich, 15 g, 0.08 mol) was added to the solution slowly; the solution was stirred magnetically and kept at 0–5 °C. When addition of the alcohol was complete, the mixture was stirred an additional 0.5 h at the same temperature and then allowed to warm to room temperature. After standing 2 h the reaction mixture was poured onto 100 g of crushed ice. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated in vacuo to about 40 mL. Sarcosine (Aldrich, 4 g, 0.045 mol) was dissolved in 30 mL of 20% dioxane in water, and the solution pH was adjusted to 10 with solid NaOH. The crude dodecyl chloroformate mixture (6 g) was added to this solution dropwise; 2 M NaOH was added concurrently to keep the solution pH between 9 and 12. The mixture was stirred 3 h, acidified to pH 2 with concentrated HCl, and extracted 4 times with a total of 100 mL of chloroform. After the organic phase was dried over Na_2SO_4, the chloroform was removed on a rotary evaporator. The residue was dissolved in hot cyclohexane, and the solution was filtered through paper and then cooled to afford a white, waxy solid (mp 54–55 °C). The solid was mixed with 50 mL of water and titrated to pH 7.9 with 0.1 N NaOH; at this point all solid was in solution. The aqueous solution was filtered through paper and lyophilized to obtain 5.5 g (36%) of a white powder, which was recrystallized 3 times from 95% ethanol. ^{1}H NMR spectra showed that at least this number of recrystallizations was needed to remove impurities. The sample melted at 83.5–85 °C. Anal. Calcd for $C_{16}H_{30}NO_4 \cdot H_2O$: C, 56.29; H, 9.45. Found: C, 56.60; H, 9.30.

Lithium *N*-(Dodecyloxycarbonyl)sarcosinate. The lithium salt of the detergent is much less soluble in water at room temperature than the sodium salt. To 1 mL of water was added 0.1 g of the sodium salt described above, and the mixture was warmed over a steam bath until dissolution was complete. Solid LiCl was added until the concentration of LiCl was 0.3 M. The solution was allowed to cool, and the white precipitate that formed was removed by filtration and dried at 110 °C under vacuum. The ^{1}H NMR spectrum of the material (mp 212 °C) was identical with that of the sodium salt.

Potassium *N*-(Dodecyloxycarbonyl)sarcosinate. Recrystallized sodium salt of the detergent (0.25 g) was dissolved in water (10 mL), and the solution pH was adjusted to 1.9 with concentrated HCl. The mixture was extracted 4 times with a total volume of 30 mL of ether. The combined extracts were washed with water (3 × 10 mL), dried over Linde 4-A molecular sieves, and evaporated to dryness in vacuo. The residue was suspended in 15 mL of water, and the sample pH was adjusted to 8.5 with 0.5 M KOH. After filtration the solution was lyophilized to yield 0.16 g (61%) of a white powder, mp 125–130 °C, with premelting at 88–93 °C. The ^{1}H NMR spectrum was identical with that of the sodium salt.

Sodium *N*-(Methyloxycarbonyl)sarcosinate. Sarcosine (8.9 g, 0.1 mol) was stirred into 50 mL of H_2O, and 18.9 g of methyl chloroformate (Aldrich, 97%, 0.2 mol) was added. This system was stirred for 1 h, during which time the pH was maintained near 10 by the addition of 1 M NaOH. After the pH was adjusted to 6.8, the solvent and excess methyl chloroformate were removed by rotary evaporation in vacuo. About 40 mL of methanol saturated with hydrogen chloride was added, and the solution was filtered through a sintered glass funnel. Removal of the methanol in vacuo left a residue, which was dissolved in 20 mL of H_2O with warming and titrated to pH 8 with 1 N NaOH. After filtration through paper the solution was lyophilized to give 12 g (83%) of product, mp 152–155 °C. ^{1}H NMR spectrum of this material was consistent with that of the expected product.

Critical micelle concentration (cmc) determinations for sodium *N*-(dodecyloxycarbonyl)sarcosinate were carried out by measuring the surface tension of aqueous solutions of this material as a function of concentration. A Cenco-Du Nouy tensiometer was employed, and the procedure of Daniels et al.[12] was followed. All measurements were performed at pH 7 (25 ± 2 °C) and were corrected by a calibration factor obtained with the surface tension of water at 25 °C.[13] A plot of surface tension vs. the logarithm of the concentration showed a pronounced discontinuity, and the concentration at this point was presumed to be the cmc. In pure water the cmc observed in this way was 0.6 mM while in a solution containing 0.3 M NaCl the cmc was 0.1 mM. We estimate that these values are accurate to within ±15% as judged by possible variation in the position of the break in the surface tension plots.

Quasi-elastic (photon correlation) light scattering spectroscopy was used to determine the mean translational diffusion coefficient D and associated Stokes–Einstein hydrodynamic radius R_h, given by $R_h = kT/6\pi\eta D$, of the surfactant micelles in aqueous solution.[14] A Spectra-Physics Model 164 argon ion laser operating at a wavelength of 488.0 nm at a power level of 100–200 mW was used as the exciting coherent source.

The scattering cell consisted of a 6-mm diameter borosilicate glass culture tube located at the center of a standard 1-cm glass fluorimeter cuvette, filled with toluene for refractive index matching to reduce the level of stray reflected light. Tubes containing the surfactant solutions were sealed with Parafilm and centrifuged for 10–15 min at 5000*g* to sediment dirt and undissolved surfactant aggregates. The resulting solutions were found to scatter light quite uniformly and exhibited no large fluctuations due to suspended impurities or gas bubbles. The glass cuvette was in turn housed in a rectangular black anodized aluminum cell block, the temperature of which was regulated to ±0.1 °C by a Peltier thermoelectric regulator.

Scattered light was collected from approximately one coherence area at a scattering angle of 90° and imaged onto the slit of an EMI type 9789 PMT (1-cm photocathode). A 64-channel, 4-bit, 10-MHz computing autocorrelator (Nicomp Model 6864) was used to obtain rapid least-squares (cumulants) analysis of the digital autocorrelation function.

Proton NMR spectroscopy was carried at 100, 360, or 500 MHz with a Varian XL-100, Nicolet NT-360, or Bruker WM-500 spectrometer, respectively, and 5-mm samples. Sample temperatures were maintained with the manufacturers' controllers. At 100 MHz sample temperatures were determined with a 5-mm o.d. mercury thermometer (Wilmad). At 360 MHz the readout of a thermocouple directly below the sample was calibrated via the ^{1}H NMR spectrum of methanol,[15] and a similar pro-

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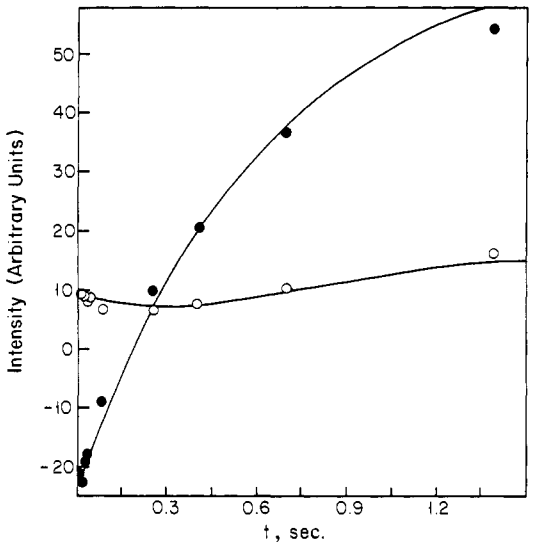

Figure 1. Representative determination of the rate of interchange of conformers by selective inversion-recovery ("soft-pulse") experiments. In this experiment with sodium *N*-(dodecyloxycarbonyl)sarcosinate (0.02 M) at 25 °C, the low-field *N*-methyl resonance was inverted and the behavior of both this resonance and the upfield signal with time followed. The experimental data (points) are fit by T_1 = 0.4 s for both resonances and τ_A = 0.72 (solid curve generated by eq 1 and 2). The sample contained 0.3 M NaCl, and the data were collected on the 360-MHz spectrometer.

cedure employing ethylene glycol was used at 500 MHz. Sample temperatures are believed to be accurate to ±1 °C. Series of spectra with a given sample at different temperatures were recorded with the temperatures set in random order. Spectra at ambient temperature were obtained before and after a series of experiments at other temperatures to check for sample decomposition (hydrolysis). No evidence for this was ever found.

Samples for ^{1}H NMR spectroscopy were made up in "100%" deuterium oxide (Aldrich) in order to minimize the magnitude of the HOD resonance.

Line shapes were analyzed for the rate of exchange between conformations by comparing visually line shapes computed for two-site exchange.[16] The soft-pulse experiment has been discussed by others.[17,18] In a system involving interchange of nuclei between sites A and B, the time dependences of the magnetizations for each site in the direction of the applied field ($M_z(t)$) are given by

$$M_z^A(t) = c_1 e^{\lambda_+ t} + c_2 e^{\lambda_- t} + M_\infty^A \quad (1)$$

$$M_z^B(t) = c_1 \tau_B\left(\lambda_+ + \frac{1}{\tau_{1A}}\right)e^{\lambda_+ t} + c_2 \tau_B\left(\lambda_- + \frac{1}{\tau_{1A}}\right)e^{\lambda_- t} + M_\infty^B \quad (2)$$

where

$$\frac{1}{\tau_{1A(B)}} = \frac{1}{T_{1A(B)}} + \frac{1}{\tau_{A(B)}} \quad (3)$$

$$\lambda_\pm = \frac{1}{2}\left(-\left(\frac{1}{\tau_{1A}} + \frac{1}{\tau_{1B}}\right) \pm \left[\left(\frac{1}{\tau_{1A}} + \frac{1}{\tau_{1B}}\right)^2 - 4\left(\frac{1}{\tau_{1A}\tau_B} + \frac{1}{\tau_A\tau_B}\right)\right]^{1/2}\right) \quad (4)$$

$$c_1 = M_0^A - M_\infty^A - c_2 \quad (5)$$

$$c_2 = [1/(\tau_B(\lambda_+ - \lambda_-))]\left(\tau_B\left(\lambda_+ + \frac{1}{\tau_{1A}}\right)(M_0^A - M_\infty^A) + (M_0^B - M_\infty^B)\right) \quad (6)$$

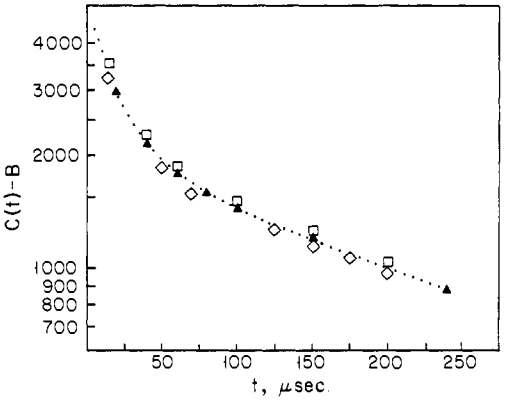

Figure 2. Typical photon correlation light scattering spectroscopic data for sodium *N*-(dodecyloxycarbonyl)sarcosinate (0.018 M, 25 °C). The experimental autocorrelation function $C(t)$ is plotted vs. t (small points) and exhibits the strongly bimodal character described in the text. The larger symbols indicate the sensitivity of curves calculated by eq 7 to the input parameters; the triangles correspond to R_f (small species) = 3.1 nm, R_s (large species) = 80 nm, while the squares are calculated if R_f is the same but R_s = 77 nm. With R_f = 3.1 nm and R_s = 83 nm, data represented by the diamonds are calculated. For all calculations the ratio of large to small species was fixed (Table I).

$M_0^{A(B)}$ are the initial values of the magnetization following a selective ("soft-pulse") perturbation of one of them and $M_\infty^{A(B)}$ are the values of the sample magnetizations at equilibrium; these latter magnetizations are proportional to the concentration of nuclei in sites A and B. All soft-pulse data were obtained at 360 MHz. For analysis of the data, the spin-lattice relaxation times (T_1) were estimated by an inversion-recovery sequence and eq 1-6 were used to compute recovery curves until, by adjusting the value for τ_A, the half-life of the system in site A, a good fit of the experimental variation of the A and B magnetizations with time was observed. Figure 1 indicates the nature of the agreement between observed and fitted data in the soft-pulse experiments.

Activation parameters ($\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$) for rotation were obtained by fitting the Eyring equation[19] by a nonlinear least-squares method.[20] The error estimates given below are based on standard deviations produced by this program.

Results

Light Scattering. The technique of quasi-elastic (photon correlation) homodyne light scattering spectroscopy was used to determine the hydrodynamic size of the micelles formed by II; this method yields the autocorrelation function $C(t) = \langle I(t')I(t' + t)\rangle$ where $I(t')$ is the intensity of light scattered at an arbitrary time t' and $I(t' + t)$ is the same quantity at a latter time $(t' + t)$.[21] For particles of uniform size $C(t)$ is a simple exponential function, which decays to a base-line value B, the square of the mean scattered intensity. In the present work solutions containing the detergent at two concentrations (~0.01 M and ~0.02 M) well above the cmc were examined with various amounts of added NaCl present. Unlike solutions of sodium dodecyl sulfate (SDS) with added NaCl,[22] these solutions exhibited correlation functions that deviated from a single exponential function. Rather than deviating in a smooth way from a single exponential decay, a behavior that is characteristic of the polydispersity observed for SDS and other ionic surfactants,[22,23] these correlation functions all exhibited a distinct break point. That is, they possessed a fast initial decay superimposed on a curve of much longer time constant (Figure 2), an observation that suggested a bimodal distribution of aggregate sizes. In analyzing the data we, therefore, avoided the cumulants approach, which is more appropriate for smooth, Gaussian size distributions,[23] and instead performed a simple two-component analysis. We assumed the existence of fast (f)

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and slow (s) diffusing components, such that[21,24]

$$C(t) = \langle I(t')I(t'+t)\rangle = [I_f \exp(-D_f\mathbf{K}^2t) + I_s \exp(-D_s\mathbf{K}^2t)]^2 + B \quad (7)$$

Constant $\mathbf{K}$ in eq 7 is the scattering wave vector,

$$\mathbf{K} = (2\pi n/\lambda) \sin(\theta/2) \quad (8)$$

where n is the solvent index of refraction, λ the laser wavelength, and θ the scattering angle. The diffusivities D_f and D_s are related to particle hydrodynamic radii R_f and R_s by the Stokes–Einstein relation:

$$D_{f,s} = kT/(6\pi\eta R_{f,s}) \quad (9)$$

where k is Boltzmann's constant, T the absolute temperature, and η the solvent (water) viscosity. In this simplified analysis we have neglected the effect of interparticle interactions on the measured diffusivities.

The preexponential weighting factors I_f and I_s in eq 7 are simply the relative scattering intensities of the two species, obtained from classical light scattering.[25] If the effects of interparticle interactions (i.e., virial coefficients) on the particle scattering intensities and diffusivities are ignored, coefficient I_i (due to the ith species) is proportional to the product of the number concentration N_i, the square of the particle volume V_i, and an integral expression due to the interference form factor for the particle, averaged over all orientations. We possess no understanding of the nature of the large micellar aggregates or surfactant structures that are responsible for the long delay component in the correlation function $C(t)$. Hence, for the purposes of obtaining an approximate two-component fit, it is reasonable to assume a spherical particle shape (radius R_i) for both the fast and slow diffusing species. In this case, the intensity weighting factor I_i becomes

$$I_i \propto N_iR_i^6\left[\frac{\sin \mathbf{K}R_i - \mathbf{K}R_i \cos \mathbf{K}R_i}{(\mathbf{K}R_i)^3}\right]^2 \quad (10)$$

Using an iterative computer fitting procedure, we obtained estimates of R_f and R_s and relative concentrations N_f and N_s. Accurate determination of the long decay time and the corresponding particle radius, R_s, was straightforward. A summary of the two-component fits to our correlation function data is given in Table I. An illustration of the sensitivity of the resulting computer simulations of $C(t)$ to parameters R_f and N_f is shown in Figure 2.

The strongly bimodal nature of $C(t)$ is an unusual feature of this surfactant system. However, the results of the fitting procedure show that the slowly relaxing component of $C(t)$ is caused by a relatively *small* number of large micelles or aggregate structures (i.e., only one part in 10^8, or less). Given our simplified picture of spherical particles, we obtain a radius for the larger species of about 90 nm. The predominant species is the smaller, faster diffusing species, which possesses an apparent radius of 3 nm. This dimension is entirely consistent with results of molecular modeling, which suggest that the fully extended detergent (II) molecule is approximately 2.4 nm long. Most of the detergent molecules in these systems therefore appear to be contained in approximately spherical micelles of radius about 3 nm. The experimental results indicate that the size and, presumably, structures of these aggregates do not depend significantly on temperature, detergent concentration, or the presence of sodium chloride and, thus, are in sharp contrast to observations made with SDS.[25]

It was observed that solutions of II containing NaCl over a period of weeks gradually lost the slowly relaxing component of $C(t)$ observed with freshly prepared solutions, and after this time the system was well characterized by the single value $R_h \sim 3.0$ nm. Presumably the very large but minor component equilibrates to the smaller micellar structures. This change was not observed when NaCl was absent, and in this case the ratio of large to small structures seemed to be constant.

Table I. Sizes of Micelles of II[a]

[surfactant], M	[NaCl], M	25 °C R_f, nm	25 °C R_s, nm	25 °C N^b	50 °C R_f, nm	50 °C R_s, nm	50 °C N^b
0.020	0.	3.0	85.	4×10^{-8}	3.0	85.	5×10^{-9}
0.019	0.33	3.0	95.	2×10^{-9}	3.1	90.	6×10^{-9}
0.018	0.63	3.1	80.	1×10^{-8}	3.0	85.	9×10^{-9}
0.010	0.	2.8	95.	3×10^{-8}	3.0	90.	8×10^{-9}
0.0094	0.33	3.0	95.	4×10^{-9}	2.8	65.	1×10^{-9}
0.0087	0.63	2.6	65.	6×10^{-9}	3.0	80.	2×10^{-9}

[a] Data obtained by fitting eq 10. The uncertainty in R_f and R_s by this procedure is estimated to be ±0.2 nm and ±10 nm, respectively, while the values for N are uncertain by approximately 50%. [b] N is the ratio of the number of large particles (of radius R_s) to the number of small particles.

Table II. Exchange Parameters for Model Systems

concn, M	[NaCl] added, M	δ_{AB},[a] ppm	P_A/P_B[b]	$\Delta G^{\ddagger}$, kcal/mol[b]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
			II			
8×10^{-5} [c]	0	0.0247	49/51	16.9	15.6	−4
8×10^{-5} [c]	0.3	0.0247	49/51	17.0	16.0	−3
8×10^{-5} [d]	0	0.0229	49/53	16.7	13.2	−11
			III[c]			
8×10^{-5}	0	0.0375	48/52	16.9	14.4	−8
8×10^{-5}	0.3	0.0375	48/52	16.8	13.5	−10
2×10^{-2}	0	0.0375	49/51	16.9	14.9	−7
2×10^{-2}	0.3	0.0375	49/51	16.9	14.0	−9

[a] Chemical shift difference for the N-CH_3 signals. [b] Computed at 40 °C. [c] Sodium salt. [d] Lithium salt.

Table III. Exchange Parameters for Micellar Systems[a]

counterion	[NaCl] added, M	δ_{AB},[b] ppm	P_A/P_B[c]	$\Delta G^{\ddagger}$, kcal/mol[c]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
Li^+	0	0.0420	66/34	17.3	23.7	20
Na^+	0	0.0478	72/28	17.2	19.9	9
Na^+	0.3	0.0478	72/28	17.1	18.6	5
K^+	0	0.0440	62/38	16.8	17.1	−1
Na^+ (SDS)[d]	0	0.0420	78/22	16.9	20.0	10

[a] Except as noted the concentration of II was 0.02 M. [b] Chemical shift difference of the NCH_3 signals. [c] Computed at 40 °C. [d] Compound II (3×10^{-4} M) was present in micelles of sodium dodecylsulfate (0.02 M).

Rotation in Model Systems. The ^{1}H NMR spectrum of II at room temperature and a concentration below the cmc are shown in Figure 3. The signals for the N-methyl group (2.8 ppm) and, less clearly, for the sarcosine methylene (3.6 ppm) appear as sets of two unequal lines, since rotation about the carbonyl carbon–nitrogen bond is slow at this temperature. The ^{1}H NMR spectrum of model compound III was similar in these regions. The low-field N-CH_3 signal, designated A, is tentatively assigned to the trans conformer (IIa or IIIb) on the basis of the anisotropy of the carbonyl group[10] and agrees with similar assignments made by Takahashi et al.[7] Line shapes for nonmicellar II and III were obtained over a range of temperatures up to 60 °C and analyzed for the rate constant for interchange of conformers; selective inversion (soft-pulse) experiments[17,18] were used to provide additional rate data at lower temperatures where there were no discernible effects of exchange on the line shape. The temperature dependence of the rate constants led to an estimate of the activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for the rotation in each case, and Table II records these results, as well as the observed chemical shift differences for the N-methyl signals and the relative amounts of conformational isomers A and B.

Rotation in Micelles of II. ^{1}H NMR spectra of micellar II were generally less well resolved than those of the model systems (Figure

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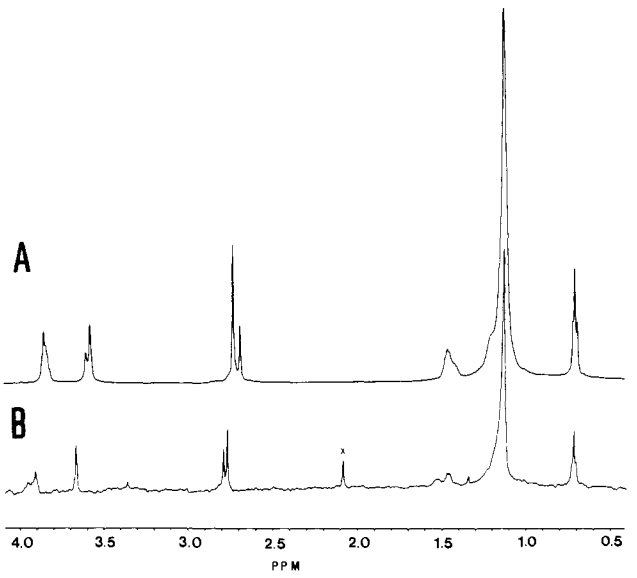

Figure 3. ^{1}H NMR spectra of *N*-(dodecyloxycarbonyl)sarcosinate at 500 MHz (25 °C). In trace B the detergent concentration is 8×10^{-5} M (Li^+ salt) while in trace A the concentration is 2×10^{-2} (K^+ salt). The latter concentration is well above the cmc (6×10^{-4} M). On the chemical shift axis each division represents 0.1 ppm and the scale is set relative to Me_4Si by assuming that the HOD resonance appears at 4.8 ppm.

3). While the chemical shift difference between the *N*-methyl signals of the detergent increases slightly in the micelles (Table III), this change is not sufficient to compensate for the additional line broadening, and acceptable data for line-shape analysis could only be obtained at high magnetic fields. While there was no evidence for temperature dependence of the chemical shift difference between the *N*-methyl signals of the rotamers, it was apparent in some cases that the nonexchange (natural) line width was temperature dependent, and in order to fit the high-temperature fast-exchange data, we had to assume that the nonexchange line width decreased with temperature. Typically the change involved was from ~2.5 Hz at 15 °C to 0.9 Hz at 60 °C, and we assumed that the alteration of line width was linear with temperature over this range. Soft-pulse experiments at temperatures near 25 °C gave rate constants in good agreement with the line-shape analysis, but we cannot rule out a systematic error in these analyses because of the variability of the nonexchange line width.

Table II records the activation parameters found for II in its micellar form. We find that while the free energy of activation for rotation is essentially the same as those observed for the model systems, there appears to be a significant increase in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for rotation in the micelles. Moreover, the activation parameters depend on the nature of the counterion accompanying the detergent into solution.

It was of interest to know if the changes in chemical shift difference, rotamer populations, and the activation parameters observed were general attributes of the micellar state or would only arise in micelles of II. A small quantity of II was doped into micelles of sodium dodecyl sulfate and the NMR analysis repeated. The chemical shift difference for the *N*-methyl resonance, the ratio of the populations of the two rotamers, and the activation parameters for rotation were scarcely altered (Table III) when II was present as a guest in dodecyl sulfate micelles. Thus, the differences observed relative to the model systems (Table I) must be a reflection of general influences of the micellar state.

Discussion

It is clear from both surface tension measurements and light scattering data that sodium *N*-(dodecyloxycarbonyl)sarcosinate (II) forms micelles. If we ignore the identity of the atoms in the chain attached to the carboxyl group and presume that this structure will behave as a normal alkyl chain, we predict that the cmc should be $\sim 1 \times 10^{-3}$ at 25 °C[26] and should decrease in the presence of added electrolyte. The observed cmc (0.6×10^{-3} M) is about that expected, and it does decrease substantially when the detergent is present in 0.3 M NaCl solution. The actual atoms in the chain of II should make the head-group region more polar than a simple aliphatic chain, and this might be expected to increase the cmc; there is no indication this is a large effect.

A fully extended molecule of II will be about 2.4 nm long depending upon the rotational isomer at the carbonyl carbon–nitrogen bond that is present; rotamer IIa is about 0.1 nm shorter than IIb. If the aggregates of II in solution are approximated as spheres, the light scattering results suggest that the radius of these spheres is somewhat larger than the length of a fully extended detergent molecule. However, the presence of a polar functional group in addition to the ionized carboxyl function possibly causes the head-group region of these micelles to be more hydrated than, say, the same region in an SDS micelle, thereby increasing the steric requirements of each headpiece. Moreover, the conformational interchange (IIa $\rightleftarrows$ IIb) alters the shape of the detergent molecule as it takes place such that a slightly larger volume is required to contain these (equilibrating) conformers than would be occupied if all molecules existed only as IIa or IIb. If we accept the hypothesis that the volume requirements per head group of II in the micelles are slightly larger than normal, then the only way these requirements can be met in a spherical structure is by a slight expansion of the radius.

The effect of micellization on the relative amounts of each conformer present that we have observed is similar to results obtained by Takahashi et al. with sodium salts of *N*-acylsarcosinates.[7] In their systems the trans conformation analogous to IIb represented about 46% of the molecules when the detergent concentration was below the cmc. Above the cmc, the trans isomer was present to the extent of 76%. These authors suggested that the more fully extented trans conformation could be incorporated more easily into the micelle because of the smaller cross section of the polar region.[7] Although the structure of our detergent is similar to the amides used by Takahashi et al., the effects of micelle formation on the rotamer chemical shift differences for both the *N*-methyl and *N*-methylene signals are not similar; we note at all concentrations the $N\text{-}CH_3$ chemical shift difference is much smaller than observed with the *N*-acylsarcosinates and that micelle formation increases this shift difference. Those factors responsible for the chemical shifts of each rotational isomer in the micellar state must therefore be only loosely coupled to structural features of the micelle that affect relative conformational energies.

The mechanism for interconversion of IIa and IIb likely does not involve a sequence in which the detergent dissociates from the micelle, rotates, and then returns to the micelle. The overall free-energy change for such a process would include the free-energy difference between micellar and nonmicellar detergent (about 4.4 kcal/mol in the present case[27]) plus the barrier for rotation, known to be about 17 kcal/mol (Table I). The observed free-energy barriers are substantially below the barrier calculated for this mechanism (~21 kcal/mol). Whatever the exact rotation itinerary is, it must include an aspect that is influenced by the nature of the counterion present. In a crude sense we can regard the surface of the micelle as an array of interacting positive and negative charges. In monolayers of stearic acid salts, the surface area required per acid molecule decreases in the order $Li^+ < Na^+ < K^+$;[28] ionic interactions in the lithium salt produce a more compact network than does the potassium salt. (This trend does not follow the radius of the *hydrated* cation and is not observed with alkyl sulfates.)[29] Rotation of the carboxylate end of the detergent must involve a temporary disruption of this ordered situation, and the larger values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ observed for

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the lithium salt of II, compared to the potassium salt, are consistent with the behavior of the stearic acid salts.

The near constancy of $\Delta G^{\ddagger}$ for rotation in all of our systems implies the existence of a compensation mechanism and, indeed, plotting $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ using the data in Tables II and III gives an excellent line with a slope corresponding to a compensation temperature of 325 K. This value is close to those observed for conformational changes in proteins.[30] Although the light scattering data indicate no temperature dependence of the micelle shape, the partial molar volumes for carboxylate salts are usually slightly temperature dependent.[31] We have observed an apparent change in transverse relaxation time with temperature, consistent with a "loosening" of molecular motion at higher temperatures, and its is possible that variations of the chemical shifts with temperature occur in a temperature range where we could not detect them. If improperly controlled, either of these factors could lead to systematic errors in our activation parameters, and it has already been noted that such errors can contribute to an apparent linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.[32] Thus, the question of compensation behavior in our micellar system should be approached cautiously.

There appears to be little effect on the kinetics of rotation about the carbonyl carbon–nitrogen bond of sodium *N*-(dodecyloxycarbonyl)sarcosinate when this molecule is incorporated into a micelle. A rather loose structure for the micelle is indicated, and the major effect observed, in agreement with earlier work,[7] is a biasing of the conformational equilibrium to favor the most extended form of the detergent.

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Registry No. I ($R^1 = C_{12}H_{23}$, $R^2 = CH_2CO_2Na$), 82639-79-0; I ($R^1 = C_{12}H_{23}$, $R^2 = CH_2CO_2Li$), 82639-80-3; I ($R^1 = C_{12}H_{23}$, $R^2 = CH_2CO_2K$), 82639-81-4; I ($R^1 = MeO_2C$, $R^2 = CH_2CO_2Na$), 82639-82-5; phosgene, 75-44-5; 1-dodecanol, 112-53-8; sarcosine, 53998-08-6; dodecyl chloroformate, 24460-74-0; methyl chloroformate, 79-22-1.

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Self-Consistent Molecular Orbital Methods. 24. Supplemented Small Split-Valence Basis Sets for Second-Row Elements

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Abstract: The recently introduced 3-21G split-valence basis sets for second-row elements have been supplemented with functions of d-type symmetry. The resulting basis sets, termed 3-21G(*), are for use in conjuction with unsupplemented 3-21G representations for first-row elements. Equilibrium structures calculated by using 3-21G(*) are generally in good accord with available experimental data and are markedly improved over the corresponding 3-21G level geometries, especially for hypervalent compounds and for molecules incorporating bonds between two second-row elements. 3-21G(*) level normal-mode vibration frequencies, hydrogenation energies, and electric dipole moments are also generally but not always in better agreement with their respective experimental quantities than are those obtained by using the unsupplemented 3-21G basis set. Overall, the 3-21G(*) basis set yields molecular properties that are uniformly close to those obtained with the much larger 6-31G* representation. The 3-21G(*) basis set is still relatively compact and as such is generally applicable to molecules of moderate size.

Introduction

The classical octet rule is frequently violated in compounds incorporating second-row elements. Lewis structures drawn for such "hypervalent" species as PF_5 and SF_6 depict valence manifolds comprising 10 and 12 electrons, respectively, more than the 8 electrons normally associated with a completely filled s and p shell. That such compounds exist and often exhibit high thermochemical stability is due to the availability for bonding of unfilled but low-lying d-type atomic orbitals on the second-row element. The concept of d-orbital participation in the bonding of hypervalent compounds has been repeatedly confirmed by quantitative molecular orbital calculations.[2]

The simplest levels of molecular orbital theory developed for compounds comprising second-row elements generally do not incorporate functions of d-type symmetry in the atomic basis set. It is not surprising, therefore, that such methods are apt to perform poorly in their description of the bonding in molecules containing a second-row element with an expanded valence shell. For example, while both the widely used minimal STO-3G[3] and split-

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