

pected stability changes are observed for these anions. For 2-norbornanone the stability lies between that for five- and six-membered cyclic enolate anions. The enolate anion of 2,5-dimethylcyclopentanone shows a decrease in stability over cyclopentanone which is of the magnitude expected in going from a secondary to a tertiary system.⁵ These observations give no indication that through space internal solvation interactions are significant for these anions, although it is not clear that these two systems have the size or molecular flexibility to exhibit such interactions. The entire problem of internal solvation in negative ions remains to be explored more thoroughly.

Conclusions

Electron affinities for cyclic enolate radicals determined from photodetachment threshold measurements prove to be extremely sensitive to the interactions accompanying the imposition of geometrical constraint on the molecular system. From the observed electron affinity trend we conclude that angle strain is the major factor which determines the relative stabilities for the smaller cyclic enolate anions.

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The Water Content of a Micelle Interior. The Fjord vs. Reef Models

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Abstract: Water penetrates micelles up to at least the first seven carbons beyond which there exists a nonpolar core. Neither the recently proposed "fjord model" nor the "reef model" satisfactorily explains our data.

Forty years have passed since Hess reported the first X-ray diffraction patterns of soap micelles.¹ Yet micellar structure remains poorly understood even on the elementary level. Consider the uncertainty in the water concentration inside a micelle (i.e., the depth to which water penetrates into the hydrocarbon portion of the aggregates). Svens and Rosenholm in 1973 presented evidence that water permeates nearly to the center of the micelles.² At the other extreme, Stigter in 1974 stated that water at the micelle surface meets a nonaqueous core at an abrupt interface; the surfactant methylenes α to the ionic head groups lie within this core.³ We designate these two descriptions the "fjord" and the "reef" models (Figure 1). In an effort to differentiate the two hydration schemes, we have studied the ¹³C NMR of carbonyl groups inserted into micelles. Carbonyls were selected for the purpose because: (a) it is known that ¹³C chemical shifts of carbonyls are solvent sensitive⁴ and (b) carbonyls should perturb the micelle structure much less than fluorescent compounds,⁵ spin labels,⁶ and other environmental probes commonly used with micelles.

There are two ways to incorporate a carbonyl into a micelle. The carbonyl can be attached to an additive adsorbed inside a micelle (e.g., octanal in hexadecyltrimethylammonium bromide) or the surfactant itself can bear the carbonyl (e.g., 8-ketohexadecyltrimethylammonium bromide). Both approaches were exploited in the present work.

Experimental Section

¹³C NMR spectra were obtained with a Varian CFT-20 spectrometer. Typically, 100 000 transients were collected using 8-mm sample tubes bearing a coaxial inner cell with 10% dioxane in D₂O. The latter served for external referencing and locking purposes. Solvents were either reagent grade (methanol, 2-propanol), Spectro grade (acetonitrile, *n*-heptane), or distilled immediately prior to use (dioxane). 8-Ketohexadecyltrimethylammonium bromide (7-KHTAB), generously given to us by Professor R. Hautala, possessed satisfactory spectral and analytical properties. Hexadecyltrimethylammonium bromide was commercial material recrystallized from aqueous acetone. Specific sample concentrations and conditions are listed in Table I.

Chemical shifts of the dioxane reference (measured over a few days at constant transmitter offset) showed little variation with the solvent surrounding the inner cell: water (63.16), methanol (63.11), ethanol (63.11), acetonitrile (63.10), dioxane (62.96), and heptane (63.12).

Results and Discussion

In Table I we list ¹³C chemical shifts δ (relative to external dioxane) for several aldehyde and ketone carbonyls as a function of a solvent polarity parameter, E_T .⁷ Chemical shift values for acetaldehyde (column 3) increase by a sizable 12.6 ppm as the solvent changes from heptane to water. Figure 2A, based on the data in column 3, shows that δ vs. E_T is linear for

Table I. ^{13}C NMR Chemical Shifts of Carbonyl Carbons in Micelles, Water, and Organic Solvents^{a,k}

solvent	E_T	CH_3CHO^b	$\text{CH}_3(\text{CH}_2)_6\text{CHO}^b$	$\text{C}_{10}\text{H}_7\text{CHO}^b$	$(\text{C}_6\text{H}_{13})_2\text{CO}^c$	8-KHTAB ^d
aqueous HTAB ^e			<i>138.1^f</i>	<i>128.3^g</i>	<i>142.4^h</i>	<i>147.2ⁱ</i>
water	63.1	140.3	(143.3) ^j	(134.0) ^j	(147.8) ^j	146.6
methanol	55.5				145.8	145.7
ethanol	51.9				144.6	144.7
2-propanol	48.6	136.5	138.9	130.1		
acetonitrile	46.0	133.3	135.8		143.9	144.0
Me_2SO	45.0	134.8	136.7	127.8		
dioxane	36.0	131.9	134.4	126.1	142.0	
benzene	34.5	130.1	133.1	125.3	141.0	
CCl_4	32.5	129.6				
heptane	30.9	127.7	131.1		138.7	

^a In ppm relative to 10% dioxane in D_2O as external reference. ^b 1.0 M aldehyde except in micellar solutions. ^c 0.30 M ketone. ^d 0.10 M 8-ketohexadecyltrimethylammonium bromide. ^e Hexadecyltrimethylammonium bromide in water. ^f 0.10 M octanal in 0.50 M HTAB. ^g 0.045 M 1-naphthaldehyde in 0.50 M HTAB. ^h 0.13 M di-*n*-hexyl ketone in 0.27 M HTAB. ⁱ 0.046 M 8-KHTAB + 0.20 M HTAB. ^j Extrapolated from least-squares plots of chemical shift vs. E_T (± 0.8 ppm). ^k Micellar data are italic.

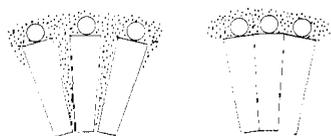


Figure 1. The fjord and reef models of micellar hydration. "Models are to be used, not believed" (paraphrased from Henri Theil in "Principles of Econometrics").

the entire polarity range (heptane to water). This is a useful result because it permits our extrapolating chemical shifts for water-insoluble aldehydes into the water region (see below).

Column 4 presents chemical shifts for a hydrophobic aldehyde, octanal, in various organic solvents. Extending a linear plot of δ vs. E_T (Figure 2B) leads to $\delta_{\text{H}_2\text{O}}$ 143.3 ppm. This value exceeds by 5 ppm the 138.1 shift for 0.1 M octanal adsorbed within micelles of 0.50 M hexadecyltrimethylammonium bromide ($\text{cmc} = 1 \times 10^{-3}$ M).⁸ Comparing the micellar shift of 138.1 with others in column 4 indicates that micellar octanal experiences an environment whose average polarity resembles that of 2-propanol. Similarly, chemical shifts of micellar 1-naphthaldehyde and di-*n*-hexyl ketone (columns 5 and 6) correspond roughly to the polarities of dimethyl sulfoxide and dioxane, respectively.

Note that the micelle-solubilized substrates must be almost entirely adsorbed within the micelles because their concentrations in the aqueous HTAB vastly exceed their solubility in pure water.⁹ Di-*n*-hexyl ketone did not generate a ^{13}C NMR spectrum in pure water even after prolonged sonication. This proves that ketone in the surfactant solutions but outside the micelles, if present at all, does not contribute to the observed micellar δ values.

The data in Table I show that the apparent micellar polarity (ranging from 2-propanol to dioxane) depends on the structure of the external probe. Octanal can align itself with the surfactant molecules so as to place the carbonyl near the water. Di-*n*-hexyl ketone, on the other hand, has a carbonyl flanked by two long alkyl groups which drag it closer to a nonpolar inner core. It is simpler and more reasonable to postulate two micellar environments (water and hydrocarbon) rather than a continuum of environments. The polarity observed with a particular probe would thus depend on the fractional residence times at the two polarity extremes. Since di-*n*-hexyl ketone manifests a micellar polarity of dioxane, the ketone must reside a greater percentage of its time within the inner core than does octanal. In any event, we can definitely rule out a "fjord model" in which bulk water penetrates to the very center of the micelle.

The depth of water penetration into a micelle can be determined only by using a probe of known location. For this reason,

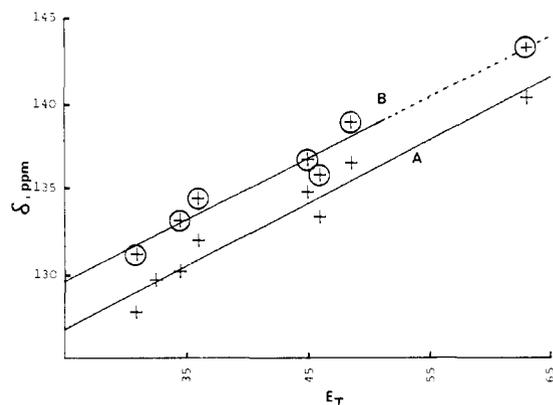
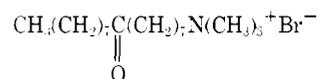


Figure 2. Least-squares plots of ^{13}C NMR shifts of (A) acetaldehyde and (B) octanal as a function of solvent polarity E_T . Data are taken from Table I.

we studied a surfactant which has a carbonyl positioned in the center of the hydrocarbon chain, 8-ketohexadecyltrimethylammonium bromide (8-KHTAB, column 7). Since the δ values for nonmicellar solutions of this compound in organic

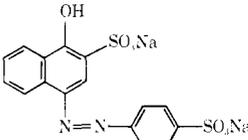
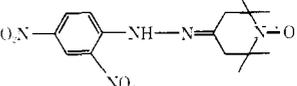
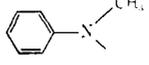
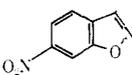


solvents are identical with those of di-*n*-hexyl ketone, the quaternary nitrogen is not affecting the chemical shift of the distant carbonyl. When 0.10 M 8-KHTAB is dissolved in water, it forms micelles ($\text{cmc} = 0.003$ M) with δ 146.6. Judging from other δ values in columns 6 and 7 of Table I, the surfactant carbonyl is bathed in a highly aqueous medium (the polarity falls between that of methanol and water). The aqueous environment persists in a mixed micelle of 0.046 M 8-KHTAB and 0.20 M "normal" surfactant HTAB (δ 147.2). We conclude that water penetration into the micelle reaches at least the first seven carbons of the chains, thereby invalidating the "reef model".

Muller and Birkhahn have investigated micellar 10,10,10-trifluorocaproate by fluorine NMR.¹⁰ Their work also suggests a considerable penetration of water into the micelles.

The possibility exists that the carbonyl of micellized 8-KHTAB is locally hydrated but that water is absent from "normal" micelles lacking carbonyls. In other words, the carbonyl group could conceivably modify the environment it is intended to probe. This is a type of problem that must be considered in any probe work (although the issue is often ignored). In Table II we assemble a few structures of probes that have been used in elucidating micellar and membrane struc-

Table II. Probe Molecules Used in the Study of Micelles

Probe	Method	Ref
	UV-visible	a
	ESR	b
	fluor.	c
	NMR	d
	kinetics	e

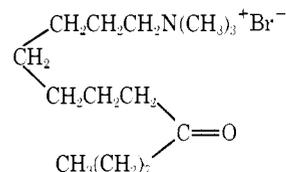
^a R. L. Reeves, R. S. Kaiser, and H. W. Mark, *J. Colloid Interface Sci.*, **45**, 396 (1973). ^b A. S. Waggoner, O. H. Griffith, and C. R. Christensen, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 1198 (1967). ^c M. Gratzel, K. Kalyanasundaram, and J. K. Thomas, *J. Am. Chem. Soc.*, **96**, 7869 (1974). ^d J. C. Eriksson and G. Gillberg, *Acta Chem. Scand.*, **20**, 2019 (1966). ^e C. A. Bunton, A. Kamego, and M. J. Minch, *J. Org. Chem.*, **37**, 1388 (1972).

ture. Our carbonyl group seems considerably less harmful than any of these probes. Hence, one can only dismiss the 8-KHTAB data by doing likewise to a large quantity of chemistry and biochemistry. This is not to deny the value of caution here and wherever else a system is perturbed.

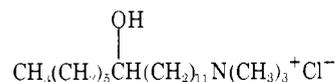
Our defense of the carbonyl probe need not be confined to favorable comparisons with the even more disruptive functionalities in Table II. We have carried out referencing experiments which firmly support our interpretations. If the carbonyl of 8-KHTAB "pulls" water into a normally aprotic micellar interior, then *other* micelle-solubilized carbonyls should behave similarly. But we have shown that this is not necessarily the case (Table I, columns 4-6). For example, micellar di-*n*-hexyl ketone is surrounded by an environment equivalent to dioxane (dielectric constant 2.2). In contrast to di-*n*-hexyl ketone, 8-KHTAB has a carbonyl which is strongly hydrated. The most likely and certainly the simplest explanation is that water penetrates micelles until at least the first seven carbons. Di-*n*-hexyl ketone adsorbs deeper into the micelle interior where the water levels are appreciably reduced.

There exists another intriguing explanation for the hydration of the 8-KHTAB carbonyl. The surfactant chain might fold back on itself so as to place the carbonyl at the aqueous micelle surface.¹⁰ Several arguments, taken collectively, eliminate this

possibility from serious consideration. (a) Folding reduces the "effective" surfactant chain length to a few atoms:



Since short-chain salts fail to aggregate in water, one could hardly expect the folded conformation to form micelles in the usual sense of the word. Importantly, 8-KHTAB has a cmc only three times larger than surfactant of the same chain length but lacking a carbonyl. This small difference could easily be attributed to the trigonal geometry at the ketone site of 8-KHTAB. A carbon-carbon double bond in the hydrocarbon chain *also* raises the cmc by a factor of 2-3.¹¹ Thus, the ketone group has not caused a drastic change in micellization properties as would be expected from a folded configuration. (b) It has been demonstrated unquestionably by ¹³C NMR relaxation methods that a surfactant hydroxylated in the center does *not* fold to expose the hydroxy group to external water.¹² Our carbonyl analogue should be even less prone to fold.



(c) We have shown previously that favorably looping of chains separating two polar functionalities at an air-water interface requires chain lengths greater than eight.¹³ If these results can be extrapolated to a micelle-water interface, then folding as pictured above is sterically unlikely.

In summary, neither the "fjord model" nor the "reef model" fits our data. Although micelles have a nonpolar core, water penetrates deeply into the structure.

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