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Microscopic Viscosity of the Interior Water Pool in Dodecylammonium Propionate Reversed Micelles

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^{13}C-Chemical shifts and spin lattice relaxation times have been determined for dodecylammonium propionate/water/benzene or CCl_4 reversed micelles and for [^{13}C]glycine cosolubilized therein. Data obtained have been discussed in terms of the mobility of glycine molecules being effectively isolated from the surfactant headgroups by water molecules. The determined relaxation times of [^{13}C]glycine in glycerol-water mixtures correlated well with the macroscopic and microscopic viscosities of the reversed micellar solution. In a relatively small water pool, the apparent viscosity of water surrounding glycine in the micelle (microviscosity) was corresponding to that of 78% aqueous glycerol solution. Increasing the size of water pool resulted in decrased microviscosities.

Equilibria, rates, and pathways of inorganic and organic reactions are dramatically and specifically controlled by surfactant–water aggregates in apolar solvents, termed revesed micelles.[1] The reacting substrates are localized in a specific and restricted field provided by reversed micelles. In many respects, this water pool represents a unique and versatile reaction field. Depending on its water content, the microscopic polarity,[2,3] and viscosity[3–5] of the field and reactivity of water[6,7] can vary markedly, by which one can control chemical reactions as required. Therefore, detailed understanding of the nature of specific reaction field is not only inherently interesting, but is essential for the meaningful interpretation of the observed effects in controlling rate, equilibrium, and pathway.

As part of our overall program on the interactions and reactions in reversed micelles, we have investigated the microscopic viscosity of the water pool in the micelles using ^{13}C-NMR technique. The major advantage of this technique is that the use of probes which may perturb the system is avoided.[8] Additionally, ^{13}C-relaxation time measurements provide information on factors which determine molecular motions.[9] ^{13}C-NMR techniques have been applied to the investigations of aqueous micelles so far.[10] The present work reports data on ^{13}C-chemical shifts and spin lattice relaxation times for dodecylammonium propionate (DAP) aggregates in benzene or carbon tetrachloride and ^{13}C-labeled glycine cosolubilized therein. Glycine was chosen as the probe since it completely partitions into the water pool and the substantial rate enhancements have been observed in its ligand exchange reactions with vitamin B_{12}.[6a] The obtained data allows the elucidation of the apparent microscopic viscosity around glycine encapsulated in the restricted field provided by reversed micelles.

Experimental

DAP was prepared and purified by the established procedures.[11] Samples of [1-^{13}C]glycine and [2-^{13}C]glycine (90% enriched) were used as received from Merck, Sharp, and Dohm Co. Inc., N. J. Reagent grade benzene and carbon tetrachloride were distilled and stored over Linde 5A molecular sieve.

Special care was taken to eliminate paramagnetic impurities in sample preparations. The recommendations of Drs. Roberts[12a] and Smith[12b] were followed. Specifically, all glassware and NMR sample tubes were washed by caustic methanol (NaOH : MeOH : H_2O=1 : 4 : 1, w/w), soaked overnight in 0.35% EDTA (pH 8) and rinsed extensively by deionized and doubly distilled water. All NMR tubes were additionally steamed for 10—15 min prior to placing the sample solutions. Subsequent to introducing the sample into the NMR tubes, gaseous hydrogen sulfide was bubbled through them for approximately 10 min. Although any precipitate of metal sulfides was not discernible, the sample tubes were centrifuged just prior to commencing the measurements. Using these precautions, the observed spin lattice relaxation times for the carboxyl carbon of glycine agreed well with those reported.[12]

^{13}C-NMR chemical shifts and relaxation times (T_1) were determined at 25.0 MHz on a JEOL PFT-100 pulse-Fourier transform spectrometer connected to a Nicolet 1080 computer system. Wilmad coaxial NMR tubes were employed. First, a mixture of TMS and acetone-d_6 (1 : 1, by vol) in the coaxial tube was used to obtain the external standard and the NMR lock signal for 1.0 M (M=mol dm^{-1}) aqueous ammonium propionate as well as for the initial experiment in reversed micellar systems. Subsequently, solvent benzene was used as the second internal standard using external D_2O placed in a coaxial tube to obtain the lock signal. All the chemical shifts were given in ppm measured downfield form TMS. The inversion-recovery method was utilized for T_1-measurements under conditions of complete proton noise decoupling. FID signals for each spectrum were accumulated 8—32 times, depending on the glycine concentration. T_1-Values were computationally calculated employing either peak heights or areas. Differences between the two methods were less than the experimental error, ±10%. Viscosities of benzene solutions containing DAP–water aggregates, so-called macroscopic viscosities, were determined with use of an Ostwald viscometer at 27.0 °C (the temperature of the NMR probe). The viscometer was frequently calibrated with pure water.

Results and Discussion

Chemical shifts for the magnetically discrete carbon atoms of 1.0 M DAP in benzene with and without glycine ([1-^{13}C]glycine and [2-^{13}C]glycine) as a function

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Table 1. ^{13}C-Chemical shifts of surfactant molecule and glycine in DAP/H_2O/benzene reversed micelles[a)]

$[H_2O]$ M	10^3[Glycine] M	δ DAP Carbons[b)] 1	2	3	4–5	6–9	10	11	12	1′	2′	3′	α-Carbon[c)] of glycine	Carboxyl carbon[d)] of glycine
<6 ppm	0.0	40.1	28.8	27.5	30.2	30.6	32.7	23.5	14.8	181.6	31.8	11.6		
1.3	0.0	40.5	28.8	27.8	30.3	30.6	32.8	23.6	14.8	182.3	31.9	11.7		
1.3	10.0	40.5	28.7	27.7	30.3	30.6	32.7	23.5	14.7	182.1	31.8	11.6	43.0	173.8
2.5	10.0	40.6	28.7	27.8	30.3	30.6	32.8	23.5	14.8	182.5	31.8	11.6	43.0	
2.5	50.0	40.5	28.7	27.8	30.4	30.7	32.9	23.6	14.8	182.6	31.9	11.7	43.1	
6.0	10.0	40.6	28.6	27.8	30.4	30.7	32.8	23.5	14.8	183.1	31.8	11.5	42.9	
9.0	10.0	40.6	28.6	27.8	30.4	30.7	32.8	23.6	14.8	183.4	31.8	11.6	42.9	

a) In ppm, relative to TMS, at 27.0 °C (probe temperature). b) DAP carbon are designated as $^{12}_{C}$-$^{11}_{C}$-$^{10}_{C}$-$^{9}_{C}$-$^{8}_{C}$-$^{7}_{C}$-$^{6}_{C}$-$^{5}_{C}$-$^{4}_{C}$-$^{3}_{C}$-$^{2}_{C}$-$^{1}_{C}$-$^{+}_{NH_3}$ $^{-}_{O_2C}$-$^{1'}_{C}$-$^{2'}_{C}$-$^{3'}_{C}$. c) In water, δ= 43.0. d) In water, δ= 173.7.

of water content are given in Table 1. Table 1 also contains values of the glycine carbon atoms cosolubilized in the micelles. The assignment for DAP carbon atoms was based on the known chemical shifts of alkyl amines and ammonium ions.[13,14)] The chemical shifts of C-1, C-2, and C-3 carbon atoms of DAP in benzene, 40.1, 28.8, and 27.5 ppm (Table 1), respectively, agree well with those of the corresponding carbon atoms of octylammonium trifluoroacetate in D_2O (40.2, 28.3, and 27.7 ppm). Although DAP is known to undergo polydispersion type association such as monomer$\rightleftharpoons$ dimer $\rightleftharpoons$ trimer$\cdots\rightleftharpoons n$-mer,[15)] there were no observable distinct chemical shifts for monomers and aggregates. This implies, of course, that the equilibration between monomers and aggregates are rapid on the NMR time scale. Similar observations have been made for a variety of normal aqueous micelles.[10a)]

Addition of water alters the chemical shifts of only the carboxyl carbon (C-1′) and the carbon atom nearest to the cationic headgroup (C-1) of the surfactant. However, the magnitude of the change was modest (Table 1). This is not unexpected since the shielding of carbon nucleus is known to be less sensitive to medium change than that of hydrogen nucleus.[8b)] Even when propylammonium dodecanoate was employed instead of DAP, the effect of water content on the chemical shift of the C-1′ atom was larger than that of the C-1 atom. This may be explicable in terms of the difference in the type and strength of hydrogen bonding between the two headgroups and water: namely, $-\overset{O}{\overset{\|}{C}}-O^-\cdots H-OH$ and $-\overset{+}{N}H_2-H\cdots OH_2$.[16)] As expected, chemical shifts of the inner methylene carbon atoms (C-2 to C-12) of DAP are unaffected by solubilized water. These observations substantiate our proposal[1,3,16)] that water is solubilized upon interacting with the ionic headgroups of DAP and is isolated from the bulk apolar solvent by surfactant aggregates. Chemical shift of the C-1′ carbon atom of 1.0 M DAP shifts downfield from 181.6 ppm in the least amount (<6 ppm) of water to 183.4 ppm in the presence of 9.0 M water (Table 1). Chemical shifts of the methyl, methylene, and carboxyl carbon atoms of 1.0 M ammonium propionate in water at pH 7 were determined to be 11.7, 32.1, and 186.2 ppm, respectively. Chemical shifts of the methyl and methylene carbon atoms of propionate ion in the DAP/benzene reversed micellar system agreed well (Table 1) with those of ammonium propionate in water. Conversely, the chemical shift of the carboxyl carbon atom of 1.0 M ammonium propionate differs substantially from that of C-1′ of 1.0 M DAP in benzene. These results preclude the possibility of an experimental artifact in the observed chemical shift differences. Apparently, even at R=9.0 (R=[H_2O]/[DAP]), the environment of the surfactant headgroups is significantly different from that in bulk water. Chemical shifts of the surfactant carbon atoms are not altered by adding glycine. Magnetic resonances of the glycine carbon atoms in bulk water and reversed micellar core were found to be identical, implying that the amino acid, at least in the present series of experiments, is free enough from the direct interaction with headgroups of DAP.

^{13}C-Spin lattice relaxation times, T_1, of the carbon atoms of DAP are in Table 2. Since the exchange of DAP molecules between monomeric and aggregated environments is rapid with respect to $1/T_1$, the observed spin lattice relaxation times represent weighted averages of relaxation times in these environments:

$$1/T_1 = X_m/T_{1m} + X_d/T_{1d} + X_t/T_{1t} + \cdots X_i/T_{1i},$$

where suffixes, m, d, t, and i, stand for monomeric, dimeric, trimeric, and i-meric environments in the mole fraction, X, and relaxation time, T_1, respectively. Lack of information of the distribution of different sized aggregates in the 1.0 M DAP/benzene micelle precludes the dissection of T_1-values. Since ^{13}C-spin lattice relaxation times of micellar alkylammonium ions are considerably shorter than those of their monomers,[13)] the reported T_1-values are considered to represent upper limits in the environment of the aggregates. The relaxation times for the resolved carbon atoms of dodecylammonium ion in benzene (Tabel 2) are even longer than those reported for hexyl- and decylammonium ions in the same solvent,[13)] indicating further overall restriction in the motion of the ions.

T_1-Values for carbon atoms of the dodecylammonium ion increase along with the carbon chain on going from C-1 to C-12 (Table 2), indicating an increase in the segmental motion of methylene units.[13)] The segmental motion of a molecule can be expressed in terms of its ω/α-value, defined as the ratio of the spin lattice relaxa-

Table 2. ^{13}C-Spin-lattice relaxation times of dodecylammonium propionate in 1.0 M DAP/H_2O/glycine/benzene reversed micelles

$[H_2O]$/M	10^3[Glycine]/M	T_1/s[a]											ω/α[b]
		1	2	3	4–5	6–9	10	11	12	1′	2′	3′	
<6 ppm	0.0	0.15	0.36	0.54	0.82	0.79	1.8	2.5	3.0	4.1	0.83	2.7	20.0
1.3	0.0	0.15	0.35	0.34	0.78	0.64	1.7	2.6	3.4	5.5	0.83	2.8	22.7
1.3	10.0	0.15	0.31	0.25	0.79	0.61	1.6	2.0	2.8	5.5	0.80	3.1	18.7
2.5	10.0		0.28	0.30	0.59	0.51	1.3	2.1	2.8	7.2	0.70	2.9	
2.5	50.0	0.14	0.37	0.36	0.77	0.60	1.4	2.2		5.1	1.1	3.3	
6.0	10.0		0.33	0.33	0.56	0.48	1.3	1.8	2.3	10	1.3	2.6	
9.0	10.0	0.24	0.35	0.73	0.69	0.51	1.4	1.9	3.1	10	1.4	2.9	12.9

a) See footnote b in Table 1 for designation of the carbon atoms of DAP. b) Segmental motion, see text.

Table 3. ^{13}C-Spin lattice relaxation times of glycine in DAP reversed micelles[a]

Solvent	[DAP]/M	$[H_2O]$/M	10^3[Glycine]/M	T_1/s	
				α-Carbon of glycine	Carboxyl carbon of glycine
H_2O				3.7, 3.9	40 (44)[b]
C_6H_6	1.0	1.3	10	0.14	2.9
	1.0	2.5	10	0.29	
	1.0	2.5	50	0.35	
	1.0	6.0	10	0.96	
	1.0	9.0	10	1.3	
	0.20	1.3	10		13
	0.20	1.3	50		13
CCl_4	0.20	2.0	10		22
	0.20	2.0	20		21
	0.20	2.0	30		20
	0.20	2.0	40		19
	0.20	2.0	50	1.3	22

a) Using 90% enriched [1-^{13}C]glycine and [2-^{13}C]glycine. b) Ref. 12.

Table 4. Macroscopic and microscopic viscosities in DAP reversed micellar solutions

Solvent	[DAP]/M	$[H_2O]$/M	10^3[Glycine]/M	Viscosity/cP	
				Macroscopic[a]	Microscopic[b]
C_6H_6	1.0	1.3	10	2.70	32[c]
	1.0	2.5	10	3.89	13[c]
	1.0	2.5	50		11[c]
	1.0	6.0	10	6.90	3.5[c]
	1.0	9.0	10	8.48	2.6[c]
	0.2	1.3	10		3.1[d]
	0.2	1.3	50		3.1[d]
	1.0	0	0	1.64	
CCl_4	0.2	2.0	10		1.7[d]
	0.2	2.0	20		1.8[d]
	0.2	2.0	30		1.8[d]
	0.2	2.0	40		2.0[d]
	0.2	2.0	50		1.7[d]

a) Determined by the Ostwald viscosimeter at 27.0 °C in the absence of glycine. b) Estimated using Fig. 1. c) Using T_1-values of α-carbon atom. d) Using T_1-values of carbonyl carbon atom.

tion time of the terminal methyl carbon (ω) to that on or the nearest one to the ionic headgroup (α).[13] The higher the ω/α-value is, the more the segmental motion is pronounced. In the absence of glycine, ω/α for 1.0 M dodecylammonium ion in DAP/benzene micelle was 20.0. This value should be compared to 19.5 which was determined for 1.2 M decylammonium ion in benzene-d_6.[13] Solubilizing 0.01 M glycine in 1.3 and 9.0 M water/DAP/benzene micellar systems results in ω/α-values of 18.7 and 12.9 respectively. It should be pointed out that changes in ω/α-values is predominantly the consequence of changes in the relaxation times of the

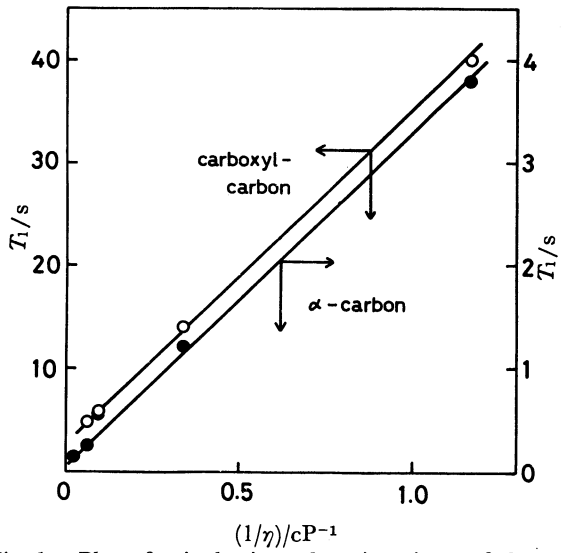

Fig. 1. Plot of spin lattice relaxation times of the carboxyl and α-carbon atoms of glycine in aqueous glycerol against the reciprocal viscosity of the solvent.

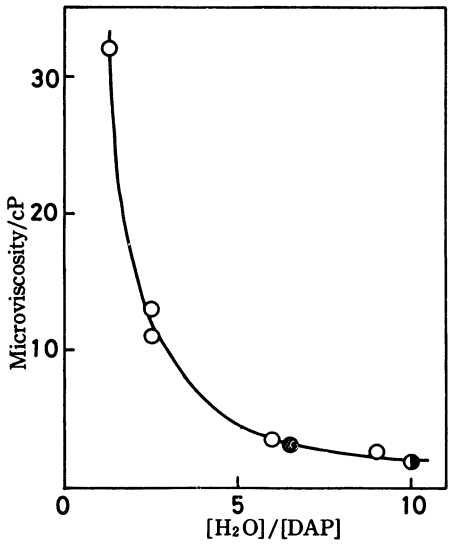

Fig. 2. Microscopic viscosity of the water pool estimated from T_1-values of glycine solubilized in DAP reversed micells as a function of R (=[H_2O]/[DAP])-value: ○, 1.0 M DAP/benzene micelle; ●, 0.2 M DAP/benzene micelle, and ◑, 0.2 M DAP/CCl_4 micelle, respectively.

C-1 carbon atoms (Table 2). A decrease in the segmental motion is brought about by an increase in the hydration at the site of the ionic headgroups. Increased hydration reduces the dipole-dipole interactions between surfactant headgroups and increases in the overall molecular motion.

Using ^{13}C-enriched glycine allowed the determination of spin lattice relaxation times of the carboxyl and α-carbon atoms of glycine (Table 3). Taking appropriate precautions, the determined T_1-values for the carboxyl carbon atom agree well with those cited.[12] The most significant fact emerged from Table 3 is the dramatic reduction in the relaxation times of both α and carboxyl carbon atoms in the water pool of DAP reversed micelles compared with those in bulk water. Evidently, the molecular motion of glycine is considerablly restricted in the micellar core. Macroscopic viscosities of the DAP/benzene reversed micellar system, the viscosity of the whole solution, were determined as a function of water content (Table 4). Increasing the water content results in an increase in the macroscopic viscosity of the whole system, which is ascribed to an increase in the size of water pool and the aggregation number. Consideration of the microenvironment of glycine in the DAP reversed micelle is more meaningful. Microscopic viscosities of the water pool of micelles have been assesed from the ruler obtained by the determined viscosities and ^{13}C-spin lattice relaxation times of glycine in aqueous glycerol solutions. A linear relationship has been obtained between the T_1-values of both the carboxyl and α-carbon atoms of glycine in glycerol–water mixtures and the reciprocal viscosities of the corresponding solution (Fig. 1). Using this correlation as a ruler, microviscosities of the water pool of DAP micelles have been read off (Table 4). Surprisingly, the apparent viscosity of the water pool of 1.0 M DAP/1.3 M water/benzene micelle containing 1.0×10^{-2} M glycine resembles that of approximately 78% aqueous glycerol solution. Conversely to the observed trend in the macroscopic viscosity, increasing the size of water pool resulted in a decreased microviscosity (Fig. 2). Figure 2 shows that the microscopic viscosity is determined predominantly by the R-value irrespective of the bulk organic solvent and the surfactant concentration, and that the microviscosity drastically decreases at the lower R-value region. Similar trends are seen in the relaxation time of water proton in ^{1}H-NMR[5b] and in the fluorescence polarization of pyranine[3] as a function of R-value. It is of interest to observe that changes of glycine concentration in a given DAP reversed micelle do not alter the microviscosity (Table 4). This is in accord with the above postulate that glycine may be appreciably isolated from the surfactant headgroup by water in the present systems. This means also that glycine must be localized in the "type II phase"[3] of water pool of reversed micelles.

This work had been carried out mostly in Texas A & M University when Janos H. Fendler was Professor of Chemistry in Department of Chemistry, Texas A & M University.

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References

1) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York (1975); J. H. Fendler, *Acc. Chem. Res.*, **9**, 153 (1976); J. H. Fendler, "Membrane Mimetic Chemistry," John Wiley and Sons, New York (1982); J. Sunamoto and H. Kondo, *Yukagaku*, **26**, 389 (1977); J. Sunamoto, "Kagaku Sosetzu," ed by the Chemical Society of Japan, Japan Scientific Societies Press,

Tokyo (1983), No. 40, p. 105.

2) F. M. Menger and G. Saito, *J. Am. Chem. Soc.*, **100**, 4376 (1978).

3) H. Kondo, I. Miwa, and J. Sunamoto, *J. Phys. Chem.*, **86**, 4826 (1982).

4) J. Sunamoto, K. Iwamoto, M. Akutagawa, M. Nagase, and H. Kondo, *J. Am. Chem. Soc.*, **104**, 4904 (1982); J. Sunamoto, H. Kondo, J. Kikuchi, H. Yoshinaga, and S. Takei, *J. Org. Chem.*, **48**, 2423 (1983).

5) a) M. Wong, J. K. Thomas, and M. Grätzel, *J. Am. Chem. Soc.*, **98**, 2391 (1976); b) M. Wong, J. K. Thomas, and T. Nowak, *ibid.*, **99**, 4730 (1977); c) F. M. Menger, G. Saito, G. V. Sanzero, and J. R. Dodd, *ibid.*, **97**, 909 (1975).

6) a) C. J. O'Connor, E. J. Fendler, and J. H. Fendler, *J. Am. Chem. Soc.*, **95**, 600 (1973); b) C. J. O'Connor, E. J, Fendler, and J. H. Fendler, *J. Chem. Soc., Dalton Trans. 1*, **1974**, 625; c) J. H. Fendler, F. Nome, and H. C. vanWoert, *J. Am. Chem. Soc.*, **96**, 6745 (1974).

7) J. Sunamoto, H. Kondo, and K. Akimaru, *Chem.Lett.*, **1978**, 821 ; J. Sunamoto and T. Hamada, "Fundamental Research in Homogeneous Catalysis," ed by M. Tsutsui, Plenum Press, New York (1978), Vol. 3, p. 809.

8) a) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley Interscience, New York (1972); b) J. B. Stothers, "Carbon-13 NMR Spectroscopy," Academic Press, New York (1972).

9) G. C. Levy, *Acc. Chem. Res.*, **6**, 161 (1973); E. Breitmaier, K.-H. Spohn, and S. Berger, *Argew. Chem., Int. Ed. Engl.*, **14**, 144 (1975).

10) a) T. Nakagawa and F. Tokiwa, *Surface and Colloid Sci.*, **9**, 69 (1976); b) K. Kalyanasundaran, M. Grätzel, and J. K. Thomas, *J. Am. Chem. Soc.*, **97**, 3915 (1975).

11) A. Kitahara, *Bull. Chem. Soc. Jpn.*, **28**, 234 (1955); **30**, 586 (1957).

12) a) H. Pearson, D. Gust, I. M. Armitage, H. Huber, J. D. Roberts, R. E. Stark, R. R. Vold, and R. L. Vold, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 1599 (1975); b) I. C. P. Smith, private communication.

13) G. C. Levy, R. A. Kamoroski, and J. A. Halstead, *J. Am. Chem. Soc.*, **96**, 5456 (1974).

14) H. Eggert and C. Djerassi, *J. Am. Chem. Soc.*, **95**, 3710 (1973).

15) F. Y.-F. Lo, B. M. Escott, E. J. Fendler, E. T. Adams, Jr., R. D. Larsen, and P. W. Smith, *J. Phys. Chem.*, **79**, 2609, (1975); K. Tsujii, J. Sunamoto, F. Nome, and J. H. Fendler, *ibid.*, **82**, 423 (1978).

16) J. Sunamoto, T. Seto, and S. Yamamoto, *Bull. Chem. Soc. Jpn.*, **53**, 583 (1980).