Solvation and Segmental Motions of *n*-Alkylammonium Ions. A Carbon-13 Spin–Lattice Relaxation Study

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Abstract: Carbon-13 spin–lattice relaxation times of individual carbons were used to monitor segmental motions in several *n*-alkylamines and the corresponding *n*-alkylammonium ions (trifluoroacetate salts) in D_2O and various organic solvents. The relaxation behavior in the amines is similar to that observed previously for *n*-alkanes, where a moderate increase in motion is observed near the chain ends. Motional restriction of the ionized amino function can result in the observation of a large degree of segmental motion along these chains. In D_2O solutions, increasing concentration of ammonium ion results in increasing restriction of the polar end, with a reduced effect as one moves toward the terminal methyl. At relatively high dilution in polar solvents such as D_2O, solvent-ion motional restrictions are markedly lessened for the shorter chain ammonium ions (especially butyl and hexyl). For the longer chains the motion of the aliphatic chain terminus is essentially "decoupled" from that of the polar head group, and also from macroscopic viscosity. A self-consistent analysis yielded the rate of terminal methyl spinning, which in the butylammonium case was found to decrease as ion concentration increased. The relaxation behavior for micellar structures indicated considerable fluidity in the hydrophobic interior. For the longer chains T_1 changed gradually along the first six carbons, with much larger increases for the last 2–3 carbons.

Carbon-13 spin–lattice relaxation measurements on small organic molecules and ions can be used to study generalized and specific solvation effects and aggregation in a wide variety of solvent systems.[2–5] Observed ^{13}C spin–lattice relaxation times (T_1's) can yield information on the rate and anisotropy of overall molecular tumbling of a rigid carbon framework in solution.[3,6] They also effectively probe detailed internal motions along aliphatic chains[2,4] (which in turn monitor the anchoring of ionic or polar sites in the solvent "lattice"). The ^{13}C spin–lattice relaxation of protonated carbons in large and intermediate sized molecules is in general overwhelmingly dominated by ^{13}C–^1H dipolar interactions with the attached hydrogens,[6,7] and T_1 is given by

$$1/T_1 = N\hbar^2\gamma_C^2\gamma_H^2 r_{CH}^{-6}\tau_{eff} \qquad (1)$$

where N is the number of directly attached hydrogens, γ_C and γ_H are the magnetogyric ratios for ^{13}C and ^1H, r_{CH} is the C–H bond length (1.09×10^{-8} cm), and τ_{eff} is an effective rotational correlation time of the C–H vector. For a rigid molecule rotating isotropically, τ_{eff} is equal to the correlation time for overall molecular reorientation in the extreme narrowing limit. If internal motions are present or if the overall reorientation is anisotropic, τ_{eff} is an average correlation time. In such a case one can write[4]

$$1/\tau_{eff} = 1/\tau_c \text{ and } 1/\tau_i \qquad (2)$$

where τ_i is an *effective* correlation time for internal rotation of the group, and τ_c is the correlation time for overall reorientation. It is apparent from eq 2 that for molecules with relatively fast overall reorientation compared with the rates of segmental motion, $1/\tau_c$ will dominate $1/\tau_{eff}$. As the overall reorientation becomes slower, the effect of $1/\tau_i$ becomes more pronounced and eventually dominates τ_{eff}.

The present study examines the ^{13}C T_1 behavior of several *n*-alkylamines and corresponding ammonium ions as a function of the concentration and solvent system. The alkylammonium ions are particularly interesting since they can form micellar structures in solution. The results yield considerable information concerning the detailed motional behavior of straight-chain organic ions in isotropic and micellar phases.

Experimental Section

Neat *n*-alkylamines were obtained from commercial sources. The trifluoroacetate salts were prepared by mixing the appropriate amounts of trifluoroacetic acid and *n*-alkylamine, washing with hexane, and drying overnight under vacuum. All viscosities were measured at 38° using Cannon-Manning semimicro viscometers.

Except as noted below, ^{13}C spectra and spin–lattice relaxation times were obtained with complete proton decoupling at 25.16 MHz and 38 ± 2° on a Varian XL 100 Fourier transform nmr spectrometer. T_1's at 25.16 MHz were obtained using the Freeman–Hill modification[8] of the inversion–recovery method.[9] The pulse sequence is $(T\text{–}90_\infty{}^\circ\text{–}T\text{–}180^\circ\text{–}t\text{–}90_t{}^\circ)_n$. For carbons 8, 9, and 10 of the *n*-decylammonium ion (15% in D_2O), T_1's were determined at 67.9 MHz using the unmodified inversion–recovery pulse sequence[9] $(T\text{–}180^\circ\text{–}t\text{–}90^\circ)_n$. T_1's obtained at 67.9 MHz were still within the region of extreme narrowing and thus were not frequency dependent[10] (note: T_1's of less than *ca*. 250 msec at 67.9 MHz cannot be directly compared with T_1's obtained at 25.2 MHz).

Figure 1 gives a typical set of ^{13}C PRFT spectra obtained using the Freeman–Hill modification. The data from Figure 1 are plotted semilogarithmically in Figure 2, yielding ^{13}C T_1 values. The accuracies of T_1 measurements in this study generally range from ±5 to ±15%, depending on S/N and the number of t values. For

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[1] (a) Florida State University; (b) General Electric undergraduate researcher.

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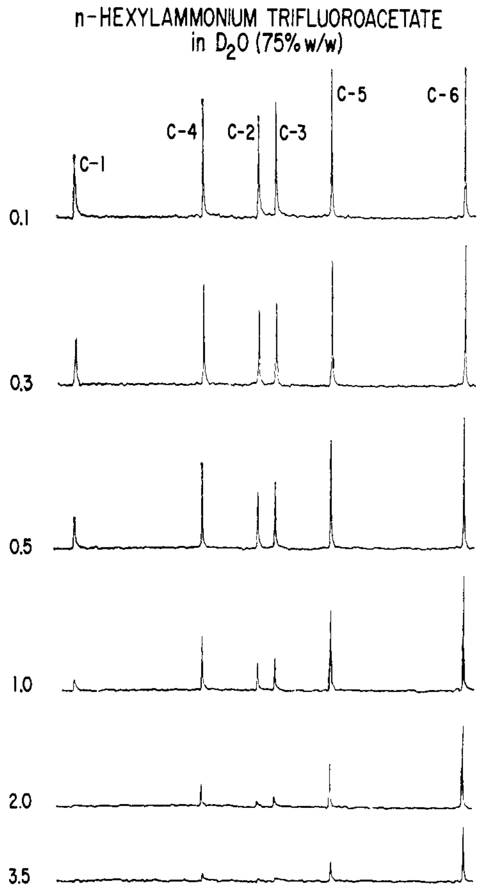

Figure 1. Set of PRFT spectra using the Freeman-Hill modification[9] of the inversion-recovery sequence.[10] Number to the left of each spectrum is the t value in seconds (25 scans, 1250-Hz spectral width).

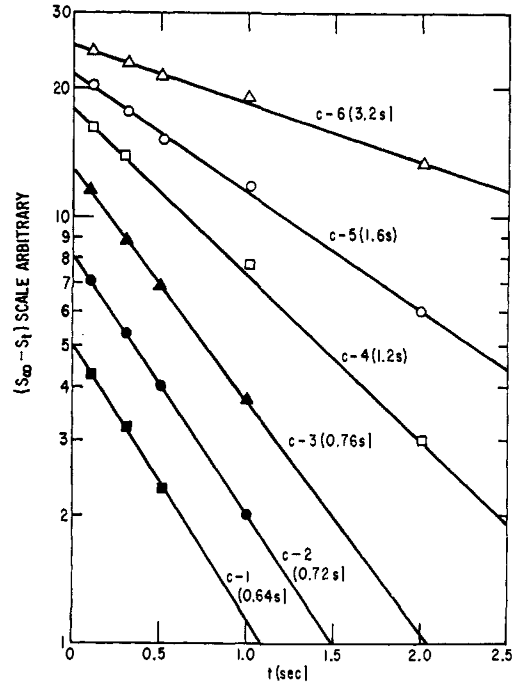

Figure 2. Semilogarithmic plots of $S_\infty - S_t$ (taken from spectra in Figure 1) *vs.* t (sec) for all carbons of the *n*-hexylammonium ion ($CF_3CO_2^-$ salt, 75% w/w in D_2O).

concentrated solutions (*n*-butyl and *n*-hexyl $\gtrsim$ 15%; *n*-octyl and *n*-decyl $\gtrsim$ 30%) the accuracies were highest. For a few dilute solutions ($\lesssim$10% ion concentration) T_1's should be considered accurate to ±15–20%. Reproducibility was in general better than 10%; however, preliminary experiments on several nonylammonium ion solutions obtained in the two laboratories showed significant differences.

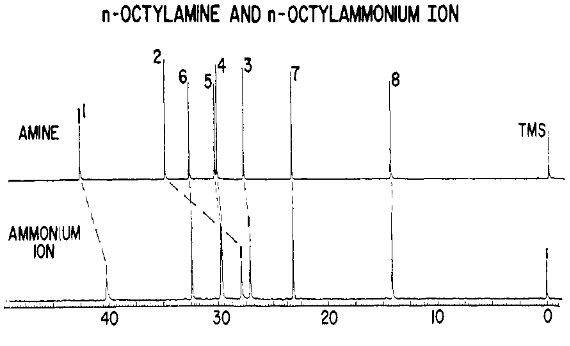

Figure 3. Proton-decoupled carbon-13 Fourier transform nmr spectra of neat *n*-octylamine and *n*-octylammonium ion ($CF_3CO_2^-$ salt).

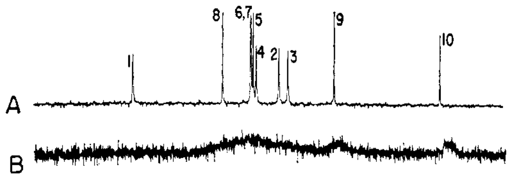

Figure 4. ^{13}C FT nmr spectra of *n*-decylammonium ion ($CF_3CO_2^-$ salt, 70% in D_2O) at (a) 39° and (b) 36°.

Results and Discussion

Assignments for the *n*-alkylamines have been given previously.[11] Assignments for the *n*-alkylammonium ions were made on the basis of the amines and known shift effects upon protonation of the amino group.[11,12] In some cases ambiguous assignments[11] were confirmed by T_1 measurements. The changes for the ^{13}C chemical shifts of *n*-octylamine resulting from protonation are shown in Figure 3.

Large effects are seen for C-1 and C-2 (2.3 and 6.8 ppm, respectively) with smaller effects for carbons 3 to 5. The larger shift for C-2 than for C-1 is generally seen for aliphatic amines.[12,13] The resonances of C-1 and C-2 in the ammonium ion are broadened by unresolved scalar coupling to cationic nitrogen. This behavior has recently been observed in the *n*-alkyltrimethylammonium bromides.[14] It was found that the *n*-decylammonium trifluoroacetate aqueous solutions underwent a "phase change" between 36 and 39°, resulting in spectra with extremely broad resonances at the lower temperature. It is probable that a liquid crystal phase is formed below 39°. This transition is shown in Figure 4. Similar spectral behavior has been oberved for synthetic lecithins.[15]

In Tables I–IV the spin-lattice relaxation times are given for all resolved carbons in a number of *n*-alkyl-

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Table I. ^{13}C Relaxation Behavior of *n*-Butylamines and Ammonium Ions

Solution	η, cP	T_1, sec[a]				τ(4,3)
		C-1	C-2	C-3	C-4	
n-$BuNH_2$, neat		13.4	13.4	15.0	12.1	
n-$BuNH_2$ in D_2O (10%)[b]		9.0	10	10	10	
Tri-*n*-$BuNH_2$, neat		2.2	2.8	3.6	4.6	
n-$BuNH_3{}^+CF_3CO_2{}^-$						
in D_2O, 5%	0.67	5.0	5.2	5.8	6.3	6.2
10%	0.77	4.6	4.7	6.2	6.0	8.3
20%	0.95	3.8	4.3	5.0	5.0	9.1
35%	1.3	2.7	3.6	4.3	4.6	9.1
50%	1.8	1.8	2.4	2.9	4.1	7.1
75%	3.3	1.2	1.8	2.4	3.8	7.1
80%	4.5	0.88	1.2	1.6	3.0	8.3
85%	5.9	0.60	0.95	1.3	2.5	9.1
90%	9.1	0.44	0.67	0.95	2.1	11
95%	~67	0.25	0.43	0.74	1.8	12
in DMF-d_7, 20%		1.8	2.7	3.5	4.3	8.3
in dioxane, 20%	1.7	0.88	1.5	2.0	3.4	7.1
in CD_3OD, 20%	1.2	3.1	4.5	5.4	5.6	7.7
in acetone-d_6, 20%		2.4	3.7	4.8	5.0	8.3
in 2:1 v/v CD_2Cl_2–acetone, 24%	0.66	0.91	1.7	2.4	3.9	6.7
in CF_3CO_2H, 15.4%	1.3	1.5	2.3	3.1	4.0	7.7
in CF_3CO_2H, 28.4%	3.0	0.97	1.5	2.1	3.5	7.7
(*n*-Bu)$_3NH^+CF_3CO_2{}^-$ 20% in CF_3CO_2H		0.60	1.3	2.0	3.0	9.1

[a] Estimated accuracies ±5–15% (see text). [b] At 44°.

Table II. ^{13}C Relaxation Behavior of *n*-Hexylamine and Ammonium Ion

Solution	η, cP	T_1, sec[a]						τ(6,5)
		C-1	C-2	C-3	C-4	C-5	C-6	
n-Hexylamine, neat[b]		8.4	7.5	8.5	7.9	8.9	8.0	
n-Hexylammonium ion								
($CF_3CO_2{}^-$) in D_2O, 7%	1.0	3.0	3.6	3.8	4.1	5.0	6.3	5.3
12%	1.2	2.6	2.8	3.0	3.4	4.0	5.3	6.2
22% (1.1 *M*)	1.6	1.5	1.6	1.8	2.4	3.3	4.7	6.7
40%[c]	2.9	0.95	1.2	1.3	1.7	2.3	4.3	5.6
60%[c]	5.3	0.82	0.96	1.1	1.5	2.2	3.7	7.1
75%	8.1	0.64	0.72	0.76	1.2	1.6	3.2	7.7
90%[c]	24.1	0.28	0.39	0.46	0.70	1.0	2.6	7.7
in CD_3OD, 1 *M*	0.89	2.5	3.2	3.6	4.5	4.9	5.0	9.1
in CD_2Cl_2, 1 *M*	1.3	0.36	0.80	1.4	1.8	2.5	4.0	6.7
in benzene-d_6 1 *M*	1.4	0.26	0.70	0.77	1.4	2.0	3.6	6.7
in $CDCl_3$, 1.1 *M*	2.5	0.35	0.55	0.85	1.5	2.1	3.5	7.7

[a] Estimated accuracies ±10–15% (see text). [b] Average of three independent runs. [c] Average of two independent runs.

amines and the corresponding ammonium ions in D_2O and various organic solvents. A portion of this work has been reported previously.[2,3]

The T_1 results for the neat amines reveal a number of trends. As expected, T_1 generally decreases all along the chain as the size of the chain increases. This behavior arises from the slower overall reorientation accompanying increased size and molecular weight. For a given amine there is very little change in T_1 along the chain, indicating that $1/\tau_c$ dominates $1/\tau_{eff}$ in this case. This is not surprising since in this case the NH_2 group acts essentially like a methyl and does not serve to "anchor" the chain as for the ammonium ions (see below). For the larger aliphatic chains a slight but reproducible decrease in correlation time is observed as one proceeds from the center to the ends of the chain. This behavior has been seen in a number of *n*-alkanes[16,17] to about the same extent and becomes more pronounced as the chain length increases. For these large aliphatic chains the central bulk of the chain restricts motion of the CH_2 units with the observed effect of segmental motion increasing toward the ends.

For the *n*-alkylammonium ions (trifluoroacetate salts) the T_1's are greatly reduced relative to the parent amines indicating much slower overall reorientation of the ions in solution. This restricted motion arises from electrostatic solute ordering effects, as well as intermolecular interactions between the ammonium ion, its counterion, and the solvent shell. The end result is that the ionic site is fixed relative to the free amine, allowing increasing segmental motion to be observed for methylene units as a function of distance from the ionic site. For the most part, a steady increase in T_1 is found along the aliphatic chain when proceeding from C-α to C-ω. Of course, the details of the segmental motion depend on the ammonium ion concentration, the solvent, and the chain length.

It is interesting to investigate in more detail the segmental motion of the ions in D_2O. On the average, as the length of the aliphatic chain increases, the ω/α

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Table III. ^{13}C Relaxation Behavior of *n*-Octylamines and Ammonium Ions

Solution	η, cP	T_1, sec[a]								$\tau(8,7)$
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	
n-Octylamine, 90% in benzene-d_6[b]		5.0	4.9	4.6	4.3	4.4	4.8	6.0	5.8	
Tri-*n*-octylamine, 90% in benzene-d_6		0.24	0.35	0.42	0.63	0.95	1.4	2.0	3.0	9.1
n-Octylammonium ion ($CF_3CO_2^-$)										
in D_2O 15%	2.1	0.60	0.62	0.61	0.70	0.78	1.1	1.5	3.5	6.2
60%	8.7	0.41	0.47	0.46	0.68	0.73	1.2	1.6	3.5	6.7
82%	16.3	0.27	0.35	0.42	0.39	0.61	0.66	1.2	2.9	7.1
90%	28.1	0.19	0.26	0.27	0.44[c]	0.44[c]	0.56	1.1	2.6	8.3
15% in CF_3CO_2H										
Tri-*n*-octylammonium ion 30% in CD_2Cl_2		0.36	0.45	0.68	1.3[c]	1.3[c]	2.5	2.7	3.4	9.1
Tri-*n*-octylammonium ion (Cl^-)[d]		0.27	0.32	0.43	1.1[c]	1.1[c]	1.8	2.6	3.1	11

[a] Estimated accuracies ±10–15% (see text). [b] Average of two independent runs, N_2 degassed. [c] Determined from two-carbon resonance. [d] N_2 degassed.

Table IV. ^{13}C Relaxation Behavior of *n*-Decylamine and Ammonium Ion

Solution	T_1, sec[a]										$\tau(10,9)$
	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	
n-Decylamine, neat	4.4	3.9	3.9	2.9[b]	2.9[b]	2.9[b]	3.1	3.2	4.7	5.5	
20% v/v *n*-decylamine in benzene-d_6	6.2	5.5	5.9	4.7[b]	4.7[b]	4.5[b]	4.9	4.7	6.7	6.3	
n-Decylammonium ion ($CF_3CO_2^-$) in D_2O, 8%	0.44[e]	0.55[e]	0.56[e]	0.52[e]	0.64[e]	0.64[e,c]	0.70[e]	1.2	2.0	3.8	6.2
15%	0.34	0.46	0.53	0.53	0.51[c]	0.51[c]	0.62	1.5[d]	2.0[d]	3.6[d]	6.7
70%[f]	0.33	0.39	0.39	0.43	0.49[c]	0.49[c]	0.63	1.2	1.8	3.6	6.7
90%[f]	0.24	0.34	0.34	0.42	0.49	0.50	0.66	1.2	1.8	3.5	7.1
in benzene-d_6, 1.2 *M*	0.21	0.48	0.42	0.64	0.62	0.82	0.86	2.3	3.2	4.1	8.3

[a] Estimated accuracies ±10–15% (see text). [b] Assignments for C-4, -5, and -6 are ambiguous. T_1's determined from one two-carbon and one single-carbon resonance. [c] Determined from two-carbon resonance. [d] At 67.9 MHz. [e] Average of two independent runs. [f] 40 ± 2°.

ratio (here defined as the ratio of the T_1 of the terminal methyl carbon to that of the methylene α to the ionic site) increases as a result of the additional degrees of freedom present in the longer chains.[18] The change in T_1 between adjacent carbons decreases as chain length increases, especially when closer to the ionic site. In many cases it is within the experimental error of the T_1 measurements. For the octyl- and decylammonium ions, the change in T_1 is relatively small for about the first six to eight carbons. Then large changes in T_1 occur at the last three carbons. This breakoff point probably reflects the micellar structures formed by these ions (see below).

For a given chain length, the ω/α ratio increases as the concentration of that ion increases. For the *n*-butylammonium ion, for example, the ω/α ratio is about 2 at 5% and increases to 11 at 95%. Similar changes were observed for the other ammonium ions. This change arises chiefly from the large decrease in T_1 of the α carbon with increase in concentration.[18] Significant changes in both viscosity and *effective solvent polarity* occur as the concentration is raised from 5–10 to 90–95%. Although the overall rotational motion is slowed considerably, the T_1's at the chain termini are little affected, especially for the larger chains (see below).

It is informative to compare the segmental motion in the *n*-butyl- and *n*-hexylammonium ions as a function of the solvent system. In the nonpolar media (*e.g.*, benzene, dioxane, $CDCl_3$) the overall motion is restricted relative to the same concentration in D_2O, and segmental motion is present to a considerable extent. However, in the polar solvents (CD_3OD, acetone, D_2O), overall reorientation is much faster as indicated by the higher T_1's all along the chain, and segmental motion is less pronounced than in the nonplar solvents. In fact, the ω/α ratio roughly correlates with the solvent dielectric constant. Somewhat similar behavior has been observed for lecithins in $CDCl_3$ and CD_3OD.[15] Presumably the ion is more easily stabilized electrostatically in polar media, reducing ion–counterion interactions. In nonpolar media the ionic moieties interact strongly, resulting in restriction of motion at the ionic site.

The data for two tri-*n*-alkylamines and the corresponding ammonium ions indicate that the junction point can perform the function of a "molecular anchor" for a short aliphatic chain,[4,19a] reflecting the bulk of the remainder of the molecule, and with evidence of considerable segmental motion. Similar behavior has also been observed for dipalmitoyllecithin and egg yolk lecithin in sonicated aqueous suspensions.[15,19b] Further restriction of the overall motion accompanies formation of the tri-*n*-butylammonium ion, and the effect of segmental motion increases (the ω/α T_1 ratio goes from 3.2 to 7.6). For the octyl case, formation of the ammonium ion produces little change in either the overall rotation or segmental motion. The longer eight-carbon chains already are effectively anchored at the chain junction; ionization and solvent effects do not significantly increase motional restriction.

It is appropriate to compare our results with a recent study[14] of molecular motions in nonmicellar and

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(18) Although this effect is limited by apparent near independence for T_1's at carbons ω to $\omega - 2$, for limiting cases of segmental motion, the α carbon T_1 still varies as a function of chain length.

(19) (a) G. C. Levy and G. L. Nelson, *J. Amer. Chem. Soc.*, **94**, 4897 (1972); (b) J. C. Metcalfe, N. J. M. Birdsall, J. Feeney, A. G. Lee, Y. K. Levine, and P. Partington, *Nature (London)*, **233**, 199 (1971).

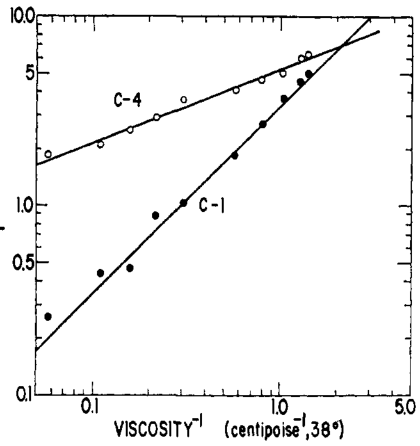

Figure 5. Log-log plot of ^{13}C T_1's *vs.* viscosity^{-1} for *n*-butylammonium ion ($CF_3CO_2^-$) in D_2O at 38° and 25 MHz.

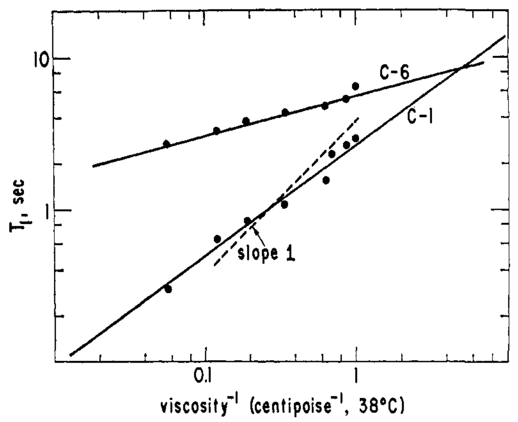

Figure 6. Log-log plot of ^{13}C T_1's *vs.* viscosity^{-1} for *n*-hexylammonium ion ($CF_3CO_2^-$) in D_2O at 38° and 25 MHz.

micellar aqueous solutions of several *n*-alkyltrimethylammonium bromides. For solutions of unaggregated molecules it was found that overall reorientation was rapid with a slight degree of segmental motion present as one moves away from the polar terminus. We observe similar behavior at low concentrations of *n*-butyl- and *n*-hexylammonium ion. For the micellar *n*-alkyltrimethylammonium bromides, the polar end was considerably more restricted, with more pronounced segmental motion along the chain. Much the same has recently been observed for aqueous micellar solutions of sodium lauryl sulfate.[20b] Such behavior is the case for all observed concentrations of the longer *n*-alkylammonium ions and for the higher concentration of *n*-butyl- and *n*-hexylammonium ions.

It is known that a number of *n*-alkylammonium salts form micellar structures in aqueous[21,14] and organic[20a] solutions. The critical micelle concentrations[21] (cmc's) for aqueous octylammonium chloride and decylammonium chloride and acetate (0.175 and 0.03–0.06 *M*, respectively) indicate that all of our solutions were predominantly micellar for these chain lengths. This assumes no dramatic changes in cmc's upon change of counterion. A cmc of 0.9 *M* for hexylamine hydrochloride[21] is consistent with our relaxation results for the aqueous trifluoroacetate salt, where the restriction becomes pronounced at a concentration of about 1 *M* (~20% w/w). The cmc of hexylammonium propionate in benzene (0.02–0.03 *M*)[20a] indicates that the T_1's of the CF_3CO^- salt at 1 *M* reflect a micellar environment. It is fair to assume that the similar patterns of segmental motion observed in solvents of low dielectric constant (Tables II and IV) result from micellar structures, probably of the inverted type, where the charged hydrophilic groups occupy the interior of the micelle. The somewhat anomalous T_1's for C-8, C-9, and C-10 of decylammonium trifluoroacetate in benzene-d_6 may result from the inverted micelle structure. Here the chain ends are extended outward, possibly increasing their motional freedom (see Table IV).[15]

Since exchange of a molecule between nonmicellar and micellar environments is rapid with respect to $1/T_1$,[22] the observed T_1 is the weighted average of the relaxation times in the two environments.

$$1/T_1 = x_f/T_{1f} + x_m/T_{1m} \qquad (3)$$

Here x_f and x_m are the mole fractions in "free" and micellar environments, respectively, and T_{1f} and T_{1m} are the corresponding T_1's. Since $T_{1f} > T_{1m}$, the reported T_1's are upper limits to the T_1's in the micellar environment. Of course, the difference between T_1 and T_{1m} will depend on the ratio of x_f (essentially equal to the critical micelle concentration) and x_m.

The presence of considerable chain mobility and segmental motion for the associated *n*-alkylammonium ions is consistent with previous ^{13}C studies on micelles[14] and sonicated lecithin vesicles[15] which indicate that the micellar interior possesses fluidity approaching that of a normal liquid hydrocarbon. In other words, the microviscosity in the hydrophobic region of the aqueous micelle is different from the macroscopic viscosity. Fluorescence polarization techniques also suggest this.[23]

Through the range of ammonium ion concentrations used in this study (5–15% to 90–95% in D_2O), both macroscopic solution viscosity and polarity undergo extreme changes. Figures 5–7 show the dependence of ^{13}C T_1 on solution viscosity for the α and ω carbons of the *n*-butyl-, *n*-hexyl-, and *n*-octylammonium ions in D_2O. A linear dependence of T_1 on $1/\eta$ was (at least roughly) obtained for all carbons (*n*-butyl through *n*-octyl). The Stokes-Einstein relation (for idealized solutes) predicts that the plots in Figures 5–7 should have a slope of 1. Only C-1 for the *n*-butylammonium ion has the predicted dependence. With the longer chains the C-1 slopes deviate progressively further from expected behavior. For the decylammonium ion the C-1 carbon is almost independent of concentration in D_2O and of solution viscosity and polarity. It is readily apparent from Figures 5–7 that the dependence of the ω-carbon T_1's on macroscopic viscosity is less than that for the α-carbons. In fact, for the longer chains, T_1's for carbons far removed from the ionic site become completely independent of solution viscosity (see Figure 7). The slopes of such plots for carbons between α and ω fall generally in intermediate positions on the plots.

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Such behavior can be termed a "limiting microviscosity effect." As one proceeds out along an aliphatic chain "anchored" at one end, the motions of carbons (and hence their ^{13}C T_1's) become "decoupled" from motion at the fixed site and also from macroscopic solution characteristics. It is interesting in this regard to note that the T_1 pattern is essentially constant for the last four carbons for many of the cases in Tables I–IV and is equal to that found in a number of chain ends for other, widely varying, systems.[3,4,15,19a] For the free ends of these chains, the pattern of T_1's is unaffected by macroscopic viscosity or the rate of overall reorientation. This behavior is predicted theoretically.[24]

In addition, the relaxation behavior in nonaqueous solution was not related to the macroscopic viscosity. In fact, the solution of *n*-butylammonium ion in CD_2Cl_2–acetone had the lowest viscosity.

Recently, Lyerla, *et al.*,[16] have analyzed ^{13}C τ_{eff} values in a number of *n*-alkanes using a self-consistent treatment which considers alkane carbon motions in terms of contributions from overall and internal rotations, as in eq 2. One then obtains $[\tau(1,j)]^{-1}$, the difference in internal rates of carbon 1 and *j*, from

$$[\tau(1,j)]^{-1} = ({}^{1}\tau_i)^{-1} - ({}^{j}\tau_i)^{-1} \qquad (4)$$

The quantity $[\tau(1,2)]^{-1}$ characterizes the rate of methyl rotation in the alkane case. Application of this treatment to the data for the *n*-alkylammonium ions yields a number of interesting results. Tables I–IV, in addition to the T_1 data, list some corresponding $\tau(\omega,\omega - 1)$ values. In the *n*-butyl case $\tau(4,3)$ goes from 6.2 at 5% to 12 at 95%. Since $\tau(4,3)$ represents the time characterizing methyl group rotation in the *n*-butylammonium ion, one finds that the methyl rotation is restricted as the concentration increases. This may be due to increased steric crowding in the solution structure for this short chain or more probably due to the change in solution polarity and viscosity. Moreover, the lower value at 5% *n*-butylammonium ion, 6.2, is in the range reported by Lyerla, *et al.*,[16] for the alkanes. As chain length increases, the trend toward increasing $\tau(\omega,\omega - 1)$ values with higher ion concentration is still apparent, though to a much smaller degree. Here more $\tau(\omega,\omega - 1)$ values fall in the *n*-alkane range.[16]

The behavior for the longer chains is reasonable, since as chain length increases one might expect the effect of crowding at the ionic site to exert less of an effect on a terminal methyl. It could also be expected that such a methyl would, on the average, be more removed from bulk solvent interactions, making it less susceptible to changes in solvent polarity and viscosity.

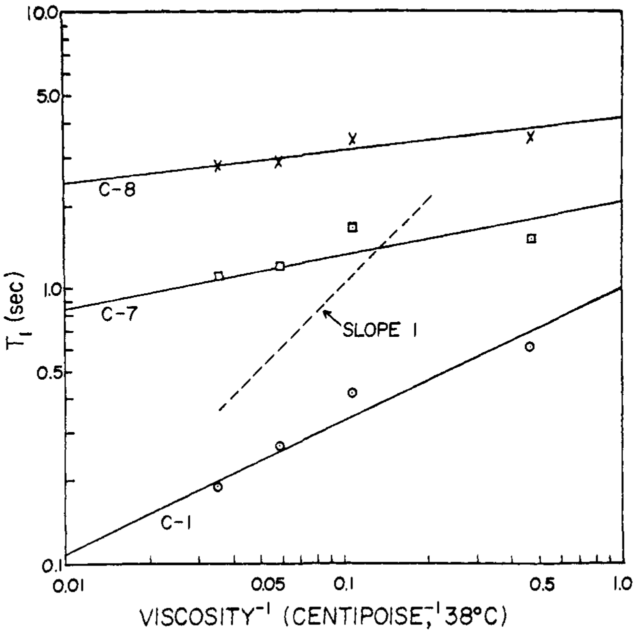

Figure 7. Log-log plot of ^{13}C T_1's *vs.* viscosity^{-1} for *n*-octylammonium ion ($CF_3CO_2^-$) in D_2O at 38° and 25 MHz.

A general method for calculating dipolar T_1's in molecules with multiple internal motions and both isotropic overall reorientation has been developed.[24–26] The theory predicts that, beyond carbons four or five (from the site of restriction), the decay of the autocorrelation function can be described by a single time constant. The theory also indicates that the diffusion coefficient for overall reorientation can be varied over a wide range without affecting the decay of the autocorrelation functions of carbons beyond the fourth carbon provided that each internal motion is faster than the overall reorientation. The variation of T_1 along the chain is determined only by the pattern of internal motion. The diffusion coefficient for rotation about the *i*th bond would be calculable empirically from the "apparent" correlation times obtained from the T_1 values of the *i*th and ($i - 1$)th carbon atoms, as is essentially done in the Lyerla[16] treatment. The results presented in this paper are consistent with the above predictions.

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