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Spin-Lattice Relaxation Time Measurements of Ions and Water Molecules Containing Spin 1 Nuclei in Lyotropic Liquid Crystalline Systems

Masayasu IIDA*,† and Alan S. TRACEY
Department of Chemistry, Simon Fraser University,
Burnaby, B. C. V5A 1S6, Canada

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Synopsis. The Jeener–Broekaert pulse sequence was applied to the ^{14}N and ^{2}H NMR measurement for studying the dynamic behavior of ions (ammonium and nitrate ions) and water molecules, respectively in lyotropic nematic liquid crystal solutions. The results showed that, in all cases except for the ammonium ion in alkaline solutions, the water molecules and the ions measured gave NMR spectra with properties characteristic of extreme narrowing conditions.

The behavior of ions and water molecules in amphiphilic solutions have been of interest for many years. Nuclear magnetic resonance spectroscopy has provided a powerful tool for the study of specific interactions occuring at the water-amphiphile interface of isotropic micellar and liquid crystalline detergent systems. Relaxation time measurements have been utilized for most investigations on the study of interactions in micellar solutions while the direct observation of quadrupole spittings have been useful in liquid crystalline solutions.[1] When water molecules or ions strongly interact with amphiphiles, two kinds of relaxation times are observed, indicating that a fast anisotropic motion is superposed on a more extensive slow motion.[2] In relaxation studies on liquid crystal systems an application of a phase-shifted, double-quantum pulse sequence on the basis of the Jeener–Broekaert excitation has been known to be useful to determine simultaneously the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$,[3,4] where ω_0 is the nuclear precession frequency. This pulse sequence is applicable to I=1 spin systems and most of the studies hitherto performed have been concentrated on deuterium relaxation of water or of amphiphiles.[5–7] In the present work, the Jeener–Broekaert pulse sequence measurements of the ^{2}H relaxation times of water molecules and of the ^{14}N ones of the NH_4^+ and NO_3^- ions have been carried out to reveal their dynamic behavior at water–amphiphile interfaces in aligned lyotropic liquid crystal systems. The present study is the first example of applying the Jeener-Broekaert pulse sequence to the ions containing ^{14}N nucleus to study their interactions with amphiphiles. The extent of the interactions of the water molecules or the ions with the amphiphiles can be seen through the quadrupole splittings and the activation energies of their rotational motions.

Experimental

Materials. The potassium dodecanoate was prepared from the dodecanoic acid by neutralization with aqueous KOH solution followed by a recrystallization several times from 95% ethanol. Sodium and ammonium decyl sulfates and decylammonium chloride were prepared by the standard methods.[8,9] 1-Decanol was obtained commercially and distilled before use. Ammonium nitrate and $^{2}H_2O$ (99.8% ^{2}H) were also obtained commercially and used directly. The solvent used for the $^{2}H_2O$ dynamic study was 5% $^{2}H_2O$ which was prepared by mixing the above $^{2}H_2O$ with a twice distilled H_2O. For the NO_3^- and NH_4^+ dynamic studies, a twice distilled water was used as a solvent.

NMR Measuements. NMR spectra were obtained on a Bruker WM-400 NMR spectrometer using a multinuclear probe operating at 61.48 MHz for deuterium and at 28.94 MHz for ^{14}N. The spin-lattice relaxation times, T_{1Z} (associated with the return of the Zeeman energy to its equilibrium value) and T_{1Q} (the decay of the quadrupolar energy) were measured using the $(\pi/2)_y$–τ–$(\pi/4)_x$–t_1–$(\alpha)_x$ pulse sequence. This is commonly called the Jeener–Broekaert sequence and has been applied according to the method performed by Vold et al.,[3] where $\tau=1/(2\Delta\nu_Q)$ and $\Delta\nu_Q$ is quadrupolar coupling constant. T_{1Z} and T_{1Q} can be determined from the sum and difference of the line intensities measured as a function of evolution time t_1 where α is fixed as 0.31π. In addition to this, the T_1 (I. R.) value for each sample solution was also determined by the conventional inversion-recovery method. The temperature was maintained with an accuracy of ±0.5 °C by a nitrogen gas flow.

Components of Liquid Crystals. The lyotropic mesophases used in this study had the general components of detergents, stock solutions containing salts in H_2O (or 5% $^{2}H_2O$) and 1-decanol (except for the decylammonium chloride system). The liquid crystal systems consisted of: 1) Ammonium decyl sulfate/Sodium decyl sulfate/DeOH/H_2O=362 mg/368 mg/81 mg/1008 mg. 2): Decylammonium chloride/ammonium nitrate/acidic (0.04 mol dm^{-3} pyridine–0.06 mol dm^{-3} HCl) H_2O=600 mg/80 mg/1010 mg. 3) Potassium dodecanoate/ammonium nitrate/DeOH/basic (0.08 mol dm^{-3} ethylenediamine–0.03 mol dm^{-3} HBr) H_2O=298 mg/50 mg/50 mg/1010 mg. The pH values of the 1) solution were 5.3 and 10.3 which are controlled by pyridine–HBr in the acidic region or by ethylenediamine–HBr in the alkaline region, respectively. The pH values were 2.5 for the 2) solution and 10.0 for the 3) solution.

Results and Discussion

The quadrupole splittings, $\Delta\nu_Q$, for the $^{14}NH_4^+$, $^{14}NO_3^-$, and $^{2}H_2O$ were measured in the range where a single phase of the nematic lyotropic liquid crystal is present and were used to decide the τ values as stated above. The $\Delta\nu_Q$, values linearly decreased with increasing temperatures. For each system we calculated $\Delta\nu_Q(0)$ ($\Delta\nu_Q$ extrapolated to t=0 °C) and the results are listed in Table 1. For the $^{2}H_2O$ molecule and the counterion in a liquid crystal system, it is generally considered that the magnitude of the $\Delta\nu_Q(0)$ is proportional to the extent of the hydration or the ion-binding if we compare between similar component systems.[1]

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† Present address: Department of Chemistry, Nara Women's University, Nara 630

Table 1. Quadrupole Splittings Being extrapolated to t=0 °C for ^{14}N of NH_4^+, NO_3^-, and ^2H_2O in Some Liquid Crystalline Systems

a) Potassium dodecanoate system (pH 10.0)	i) $^{14}NH_4^+$	ii) $^{14}NO_3^-$	iii) ^2H_2O
$\Delta\nu_Q(0)$/kHz=	4.2±0.3[a]	0.31±0.01	0.15±0.01
b) Decylammonium chloride system (pH 2.5)	i) $^{14}NH_4^+$	ii) $^{14}NO_3^-$	iii) ^2H_2O
$\Delta\nu_Q(0)$/kHz=	1.2±0.1	46±2	0.24±0.02
c) Sodium/ammonium decyl sulfate system			
i) $^{14}NH_4^+$	(pH 5.3)	(pH 10.3)	
$\Delta\nu_Q(0)$/kHz=	1.3±0.1	2.2±0.1[a]	
ii) ^2H_2O (pH 5.3)			
$\Delta\nu_Q(0)$/kHz=0.43±0.02 kHz			

a) These values include the values for the ammonia molecule.

For a single I=1 nucleus, application of the Jeener–Broekaert pulse sequence provides two kinds of the spin-lattice relaxation times associated with the return of the Zeeman energy to its equilibrium value T_{1Z} and the decay of the quadrupolar energy T_{1Q}. These two relaxation times can be expressed by the spectral densities ($J_1(\omega_r)$ and $J_2(\omega_r)$) as follows.[3,4]

$$R_{1Z}=1/T_{1Z}=(e^2qQ/h)^2 3/80(J_1(\omega_r)+4J_2(2\omega_r)), \tag{1}$$

$$R_{1Q}=1/T_{1Q}=(e^2qQ/h)^2 3/80(3\cdot J_1(\omega_r)) \tag{2}$$

where (e^2qQ/h) is the quadrupolar coupling constant.

The usefulness of the application of this method is the ability to simultaneously determine the individual spectral densities of motion, $J_1(\omega_0)$ and $J_2(2\omega_0)$. If water molecules or ions form ion-pairs with amphiphiles so that their motion is restricted, their relaxation times should be frequency dependent and the two spectral densities will have different values. If the interactions do not strongly restrict the motional properties, the relaxation times should be independent of the nuclear precession frequency (extreme narrowing condition), so that J_1 equals J_2. In this case the T_{1Q}/T_{1Z} ratio should be 1.67.

Table 2. Temperature Dependences of ^{14}N Relaxation Times of NH_4^+ and NO_3^- in the Potassium Dodecanoate Liquid Crystals

i) $^{14}NH_4^+$ (pH 10.0)[a]		ii) $^{14}NO_3^-$ (pH 10.0)[b]		
T/K	T_1(I.R.)/ms	T_1(I.R.)/ms	T_{1Q}/ms	T_{1Z}/ms
288	11	68	125	71
290	11	75	130	72
293	13	—	—	—
295	13	88	135	91
300	14	96	148	100
302	14	—	—	—
305	15	112	189	110

a) ΔE_a/kJ mol^{-1}=13±2. b) ΔE_a/kJ mol^{-1}=20±2; T_{1Q}/T_{1Z}=1.7±0.1.

Table 3. Temperature Dependences of ^{14}N Relaxation Times of NH_4^+ in the Decylammonium Chloride Liquid Crystals (pH 2.5)

T/K	T_1(I.R.)/s	T_{1Q}/s	T_{1Z}/s
285	0.84	1.43	0.85
288	0.88	1.51	0.90
290	0.93	1.55	0.94
293	0.99	1.57	1.00
296	1.03	1.65	1.00
298	1.05	1.68	1.03

ΔE_a/kJ mol^{-1}=13±2; T_{1Q}/T_{1Z}=1.6±0.1.

Table 4. Temperature Dependences of the Relaxation Times of $^{14}NH_4^+$in Sodium/Ammonium Decyl Sulfate Liquid Crystal

T/K	i) pH=5.3[a] T_1(I.R.)/s	T_{1Q}/s	T_{1Z}/s	ii) pH=10.3[b] T_1(I.R.)/ms
281	0.18	0.30	0.17	3.3
285	0.23	0.42	0.25	3.6
289	0.29	0.45	0.27	4.0
293	0.31	0.53	0.33	4.4
297	0.40	0.61	0.36	4.8
300	0.45	0.73	0.41	5.1

a) ΔE_a/kJ mol^{-1}=33±2; T_{1Q}/T_{1Z}=1.7±0.1. b) ΔE_a/kJ mol^{-1}=16±3.

Table 5. Temperature Dependences of the Relaxation Times of ^2H_2O in the Decylammonium Chloride Liquid Crystal (pH 2.5)

T/K	T_1(I.R.)/s	T_{1Q}/s	T_{1Z}/s
285	0.24	0.40	0.25
288	0.28	0.49	0.29
293	0.33	0.51	0.32
296	0.36	0.58	0.34
299	0.43	0.71	0.42

ΔE_a/kJ mol^{-1}=28±4; T_{1Q}/T_{1Z}=1.65±0.05.

According to the method proposed by Vold and Vold,[3,4] we obtained values of T_{1Q} and T_{1Z} for ^2H_2O and $^{14}NH_4^+$ in various systems with varying temperatures. The results are listed in Tables 2—5 together with T_1 values obtained by the inversion-recovery method. A correspondence between the T_{1Z} and the T_1 (I.R.) value in all cases are satisfactory. We can thus use two kinds of the spin-lattice relaxation times to calculate the T_{1Q}/T_{1Z} ratios and to check whether the extreme narrowing condition is fulfilled or not. The values obtained (listed in the bottom rows of Tables 2—5) show that the ratios coincide with 1.67 within the experimental error in all the cases. It has also been shown for some micellar solutions[10] and for an aqueous sodium dibutyl phosphate lamellar mesophase[11] that the extreme narrowing condition is fulfilled for counterions or water molecules. To compare the extent of the ion binding or the hydration, we calculated activation energies for effective correlation times, τ_{eff}, related with the relaxation rates, R_1. The temperature dependency of R_1 will correspond to that of τ_{eff},[12] which may show an Arrhenius behavior. We obtained the activation energy for τ_{eff} from the Arrhenius plot of $1/T_1$, where we used T_1 values obtained through inversion-recovery method because these values

Table 6. Temperature Dependences of the Relaxation Times of ^2H_2O in the Sodium Decyl Sulfate Liquid Crystal (pH 5.3)

T/K	T_1(I.R.)/s
285	0.22
289	0.25
293	0.28
297	0.31
300	0.35

ΔE_a/kJ mol^{-1}=22±1.

will be of higher accuracy than the corresponding T_{1Z} values. The Arrhenius plots for all the systems were approximately linear in the temperature range utilized here and the activation energies were obtained as listed in the bottom rows of Tables 2—6. We can generally say, when comparing similar component systems, that larger activation energies are required for the reorientation of the ions or molecules if they interact with the amphiphiles as for instance, NH_4^+/decylammonium mesophase (pH 2.5), E_a=13±2 kJ mol^{-1} vs. NH_4^+/decyl sulfate mesophase (pH 5.3), E_a=33±2 kJ mol^{-1}. Clearly the activation energies increase if the ions or molecules interact more strongly and also the $\Delta\nu_Q$ values of the nuclei of interest also increase with increasing interactions with the amphiphiles.

Only in the case of the ammonium ion in alkaline solutions where formation of the ammonia is appreciable,[13)] the ratios obtained were significantly smaller than 1.67 and were around 1.3—1.4. Since the ammonia molecules can be considered to be also under extreme narrowing condition, the T_{1Q}/T_{1Z} ratio for the ammonium ion in alkaline solution is also expected to be close to 1.67. The significantly smaller values of the ratio obtained here may, therefore, arise from the effect of the rapid exchange between the ammonium ion and the ammonia molecule, whose ^{14}N nuclear quadrupolar coupling constants are quite different.[14)] Since the coincidence of the T_{1Z} values with the corresponding T_1 (I.R.) values was better than that of the T_{1Q}/T_{1Z} values with 1.67 in these cases, the difference in the latter values can be attributed to a larger effect of the exchange on the T_{1Q} values than the T_{1Z} values. The T_{1Q} value obtained for the ammonium ion in the alkaline solution thus may be different from that defined in Eq. 2. Although the analysis of the result for this system in detail seems to be complicated, the activation energy for the ^{14}N relaxation rate obtained by the inversion-recovery method can be a measure for the extent of the interaction of the ammonium ions with the amphiphiles: As shown in Table 4, the activation energy in the acidic solution is appreciably larger than that in the alkaline solution and this result is consistent with the fact that the interaction of the ammonia molecules with the anionic amphiphiles is slight due to an absence of the electrostatic interactions.

In conclusion, this application of the Jeener–Broekaert pulse sequence to study the dynamic behavior of the nitrate and ammonium ions and the water molecules showed that these systems in most cases undergo the extreme narrowing of their NMR signals. It was not possible to ascertain if they undergo slow motions within the water-amphiphile interface. The activation energies for their reorientational motions, however, described the extent of the binding of the ions and water molecules to the amphiphiles.

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References

1) B. Lindman, "NMR of Newly Accessible Nuclei," Vol. 1, (1983).

2) T. C. Farrar and E. D. Becker, "Pulse and Fourier Transform NMR," Academic Press, New York (1971), Chap. 4.

3) R. R. Vold, "NMR of Liquid Crystals," ed by J. W. Emsley, D. Reidel, Dondrecht (1985), pp. 260—275.

4) R. R. Vold and R. L. Vold, "Liquid Crystals and Ordered Fluids,," ed by A. C. Griffin and J. F. Johnson, Plenum, New York (1984), Vol. 4, pp. 561—578.

5) J. P. Jacobson and K. Schaumburg, *J. Magn. Reson.*, **24**, 173 (1976).

6) T. C. Wong and K. R. Jeffrey, *Mol. Phys.*, **46**, 1 (1982).

7) K. R. Jeffrey, T. C. Wong, and A. P. Tulloch, *Mol. Phys.*, **52**, 307 (1984).

8) L. W. Reeves and A. S. Tracey, *J. Am. Chem. Soc.*, **97**, 5729 (1975).

9) K. Radley and A. S. Tracey, *Mol. Cryst. Liq. Cryst. Lett.*, **1**, 95 (1985).

10) E. Sjöblom and U. Henriksson, *J. Phys. Chem.*, **86**, 4451 (1982).

11) C. Chachaty and J. P. Quaegebeur, *Mol. Phys.*, **52**, 1081 (1984).

12) A. M. de P. Nicholas and R. E. Wasylishen, *J. Phys. Chem.*, **89**, 5446 (1985); A. M. de P. Nicholas and R. E. Wasylishen, *Can. J. Chem.*, **65**, 951 (1987).

13) "Stability Constants of Metal-Ion Complexes," ed by Silllén; The Chemical Society; Burlington House, London (1964), p. 150.

14) "Multinuclear NMR," ed by J. Mason, Plenum, New York (1987), p. 346.