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Preferential Solvation of Ni(II) in Water–Solvent Mixtures from ^{13}C NMR Paramagnetic Relaxation Rate

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^{13}C NMR spin-lattice relaxation time of carbon atom on methanol, ethanol, 1-propanol, and dimethyl sulfoxide molecules has been measured for solutions of $Ni(ClO_4)_2$ in these solvents and their mixtures with water. The comparison of the NMR data for solutions with aqueous mixtures and pure solvents gave the number of organic solvent molecules that locate in the first coordination sphere of Ni^{2+} ion. The result shows that Ni^{2+} ion is preferentially hydrated in water–alcohol systems, while in water–dimethyl sulfoxide system, the ion is solvated preferentially with dimethyl sulfoxide.

The preferential solvation of an ion in mixed solvents is an interesting subject in the electrolyte solution chemistry. The detailed information on the structure of solvated ion in a mixed solvent is expected to gain a better understanding of the behavior of ion. The NMR spectroscopy has provided a useful method for investigating local structure in the vicinity of ion. If the signal arising from the solvated solvent molecules is distinguished from that of bulk molecules, the solvation number can be determined directly from integration of the both signals.[1–3] The application of the direct NMR method is, however, confined to systems of high electrolyte concentration and of low rate of solvent exchange. On the other hand, the exchange rate of most ions with moderate number of charge is so high that the NMR spectrum gives a coalesced signal of both the coordinated and bulk molecules. In this case, chemical shift and relaxation rate are utilized to get information on the constitution of coordination sphere of ion.[4–7] This paper reports ^{13}C NMR paramagnetic relaxation rates for carbon atoms of organic solvent molecules caused by Ni^{2+} ion in Ni $(ClO_4)_2$ solution with water–solvent mixtures. The dependence of relaxation rate on concentration was analyzed to deduce the number of organic molecules that locate in the first coordination sphere of Ni^{2+} ion.

Experimental

Commercially available nickel perchlorate hexahydrate was recrystallized from water. The content of water was determined as six mole per formula from cation analysis using a cation-exchange column. The hydrated crystal was used to prepare solutions. Since the mole fraction of Ni(II) was less than 0.001 for solutions in pure organic solvents, a small amount of water accompanied with the crystal will give only a negligible effect on the ^{13}C NMR T_1 (spin-lattice relaxation time) of the solvent molecules. Methanol, ethanol, 1-propanol, and dimethyl sulfoxide (DMSO) were of reagent grade and used without further purification. ^{13}C NMR T_1 was measured by a JEOL FX90Q-FT NMR spectrometer at 35 °C with a standard inversion-recovery technique. The NMR frequency was 22.5 MHz. The error in measuring T_1 was leas than 5%.

Results and Discussion

If we denote the ^{13}C NMR relaxation rate of carbon atoms of solvent molecules located in the first coordination sphere of a paramagnetic ion as $1/T_{1M}$, and that of the bulk solvent as $1/T_{1B}$, then the observed relaxation rate $1/T_1$ is expressed by

$$\frac{1}{T_1} = \frac{X_M}{T_{1M}} + \frac{1-X_M}{T_{1B}}, \tag{1}$$

where X_M denotes the fraction of solvent molecule in the first coordination sphere. X_M is given by

$$X_M = n\frac{C_i}{C_s}, \tag{2}$$

where n is the number of coordinated solvent molecules to Ni^{2+} ion, C_i and C_s are the molar concentrations of ion and solvent molecule, respectively. If we assume that the rate $1/T_{1M}$ and coordination number of Ni^{2+} ion are unchanged in pure and mixed solvent, and that the relationship

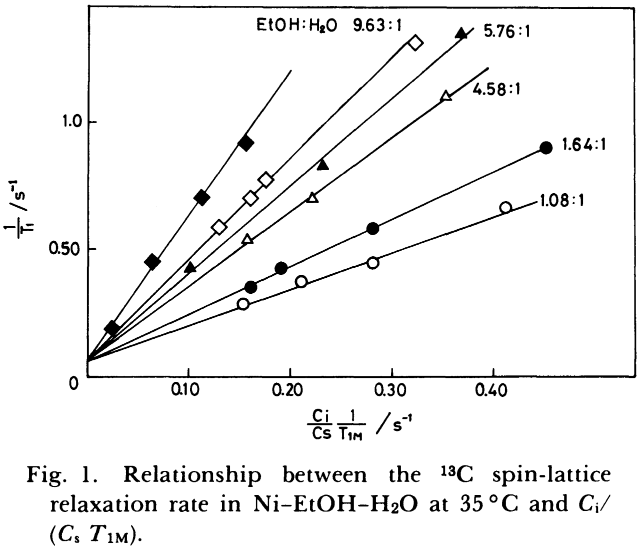

Fig. 1. Relationship between the ^{13}C spin-lattice relaxation rate in Ni–EtOH–H_2O at 35 °C and $C_i/(C_s\,T_{1M})$.

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Table 1. ^{13}C Spin-Lattice Relaxation Time in $Ni(ClO_4)_2$-CH_3OH-H_2O System

$X(H_2O)$	Ni :	CH_3OH :	H_2O	T_1/s	Slope
0.70	0.00148	0.430	1	1.05	0.78
	0.00113	0.430	1	1.43	
	0.000603	0.430	1	2.48	
	0.000448	0.430	1	3.21	
0.50	0.000930	0.992	1	2.27	1.9
	0.000521	0.992	1	3.56	
	0.000352	0.992	1	4.71	
0.40	0.00102	1.51	1	2.46	2.5
	0.000585	1.51	1	3.61	
	0.000358	1.51	1	5.28	
0.30	0.00188	2.35	1	1.83	3.4
	0.00143	2.35	1	2.32	
	0.000874	2.35	1	3.37	
0.21	0.00351	3.67	1	1.32	3.8
	0.00306	3.67	1	1.50	
	0.00251	3.67	1	1.84	
	0.00121	3.67	1	3.25	
0.13	0.00582	6.70	1	1.19	4.7
	0.00346	6.70	1	1.94	
	0.00317	6.70	1	2.13	
	0.00152	6.70	1	3.64	
0	0.000877	1	0	0.89	
	0.000688	1	0	1.06	
	0.000447	1	0	1.67	
	0.000228	1	0	2.62	
	0.000111	1	0	4.09	

Table 2. ^{13}C Spin-Lattice Relaxation Time in $Ni(ClO_4)_2$-C_2H_5OH-H_2O System

$X(H_2O)$	Ni :	C_2H_5OH :	H_2O	T_1/s	Slope
0.48	0.00315	1.08	1	1.50	1.5
	0.00219	1.08	1	2.23	
	0.00159	1.08	1	2.67	
	0.00118	1.08	1	3.44	
0.38	0.00529	1.64	1	1.10	1.8
	0.00333	1.64	1	1.69	
	0.00224	1.64	1	2.33	
	0.00162	1.64	1	2.84	
0.18	0.0116	4.58	1	0.90	2.9
	0.00715	4.58	1	1.39	
	0.00510	4.58	1	1.82	
0.15	0.0153	5.76	1	0.73	3.5
	0.00953	5.76	1	1.19	
	0.00317	6.76	1	2.13	
0.094	0.0232	9.63	1	0.75	4.2
	0.0119	9.63	1	1.28	
	0.0111	9.63	1	1.40	
	0.00895	9.63	1	1.69	
0	0.00103	1	0	1.07	
	0.000775	1	0	1.39	
	0.000361	1	0	2.19	
	0.000132	1	0	4.94	

Table 3. ^{13}C Spin-Lattice Relaxation Time in $Ni(ClO_4)_2$-*n*-C_3H_7OH-H_2O System

$X(H_2O)$	Ni :	*n*-C_3H_7OH :	H_2O	T_1/s	Slope
0.50	0.00199	1.00	1	2.80	0.61
	0.00128	1.00	1	3.32	
	0.00100	1.00	1	3.74	
	0.000647	1.00	1	4.27	
0.40	0.00325	1.51	1	2.07	0.96
	0·00252	1.51	1	2.56	
	0.00172	1.51	1	3.05	
	0.00139	1.51	1	3.29	
0.30	0.00506	2.30	1	1.63	1.3
	0.00281	2.30	1	2.45	
	0.00220	2.30	1	2.80	
0.21	0.0632	3.77	1	1.62	1.8
	0.0352	3.77	1	2.58	
	0.00262	3.77	1	2.78	
0.099	0.0150	9.08	1	1.22	2.8
	0.00952	9.08	1	1.83	
	0.00831	9.08	1	1.93	
0	0.00150	1	0	0.66	
	0.00110	1	0	0.92	
	0.000627	1	0	1.32	
	0.000263	1	0	2.45	
	0.000158	1	0	3.64	

Table 4. ^{13}C Spin-Lattice Relaxation Time in $Ni(ClO_4)_2$-$(CH_3)_2SO$-H_2O System

$X(H_2O)$	Ni :	$(CH_3)_2SO$:	H_2O	T_1/s	Slope
0.60	0.00158	0.660	1	0.97	2.9
	0.00102	0.660	1	1.40	
	0.000707	0.660	1	1.75	
0.50	0.00240	1.02	1	0.81	3.9
	0.00190	1.02	1	0.96	
	0.00106	1.02	1	1.51	
	0.000735	1.02	1	1.98	
0.35	0.00723	1.86	1	0.43	4.7
	0.00300	1.86	1	0.92	
	0.00161	1.86	1	1.58	
0.21	0.00978	3.81	1	0.57	5.2
	0.00620	3.81	1	0.86	
	0.00309	3.81	1	1.50	
0.10	0.0162	8.96	1	0.76	5.5
	0.0112	8.96	1	1.07	
	0.00783	8.96	1	1.45	
	0.00536	8.96	1	1.85	
0	0.00119	1	0	1.04	
	0.000782	1	0	1.46	
	0.000598	1	0	1.81	
	0.000325	1	0	2.80	

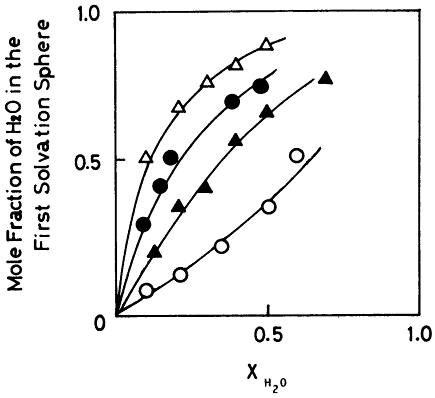

Fig. 2. Relationship between the mole fraction of H_2O in the first solvation sphere and H_2O mole fraction of the solvent at 35 °C. ○: DMSO-H_2O, ▲: MeOH-H_2O, ●: EtOH-H_2O, △: *n*-PrOH-H_2O.

between $1/T_1$ and $C_i/(C_sT_{1M})$ is linear at low concentration of Ni^{2+} ion, slope gives n directly. The coordination number, n, of Ni^{2+} ion in pure solvent was assumed to be six,[9–11] then $1/T_{1M}$ values were obtained from data for pure organic solvent solution. Figure 1 shows the plots for ethanol (C1) carbon in water–ethanol systems, which appear to be linear. Tables 1—4 give the observed T_1 and the slopes for water-methanol, -ethanol (C1), -1-propanol (C1), and -DMSO, respectively. The variation of the composition of the first coordination sphere is shown in Fig. 2 as a function of the composition of bulk solvent. Figure 2 shows that Ni^{2+} ion is preferentially solvated with DMSO in water-DMSO system, while Ni^{2+} in water-alcohol mixture is preferentially hydrated. The magnitude of the preferential hydration increases with the increase in the chain length of alcohol molecules. The behavior of this preferential solvation in water–methanol system is consistent qualitatively with the result obtained by a kinetic study of solvated Ni^{2+} ion reacting with ammonia in water-methanol system.[12] The tendency of solvation in water–methanol mixture has been reported for other ions: Preferential solvation of Eu^{3+} was investigated by luminesence lifetime method[13] and those of Na^+ and Rb^+ were examined by ^{23}Na and ^{87}Rb spin-lattice relaxation rate.[5,6] A coordination ability of DMSO competing with water was demonstrated in $Al(ClO_4)_3$–DMSO–water system by direct ^1H NMR peak integration method.[1–3] ^{23}Na chemical shift and spin-lattice relaxation rate showed that Na^+ ion is solvated preferentially with DMSO in water–DMSO system.[5,7] Luminesence lifetime study of Eu^{3+} in water–DMSO system resulted in preferential solvation with DMSO.[13] ^{23}Na and ^1H NMR chemical shift studies also showed that Na^+ is solvated preferentially with DMSO in binary mixtures of DMSO with nitromethane, acetonitrile, pyridine, and 1-propanol.[7,8] It seems that solvation tendency is not expressed by the Gutmann donor number.[14,15] As for the solvation of Ni^{2+} ion, Munakata et al. have proposed the coordination power to express the solvent donor ability from electronic spectra of Ni^{2+} ion in various binary mixed solvents.[16] The present results agree qualitatively with the order proposed by them. The solvent used in our experiments is confined to solvent rich compositions because of the difficulty of ^{13}C NMR T_1 measurement in low contents of organic species. The measurement by a high field NMR spectrometer or the use of ^{13}C-enriched solvent will overcome the difficulty. The effect of perchlorate counter ion is completely ignored. Since the measurement was carried out in low electrolyte concentration, the effect of counter ion is considered to be small. The measurement with other counter ions will confirm the assumption.

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