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Counter Ion Effect on the ^{13}C NMR Paramagnetic Relaxation Rate of Water–Methanol or Water–Dimethyl Sulfoxide Mixed Solvent with Ni(II) Solute

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Synopsis. The paramagnetic-salt induced ^{13}C spin-lattice relaxation rate of solvents methanol and dimethyl sulfoxide was measured for $Ni(ClO_4)_2$, $NiSO_4$, and NiBDS (BDS: *m*-benzenedisulfonate) solutions in 50 wt.% mixture of each of the solvents and water. Relatively small relaxation rates were found for the solutions containing $NiSO_4$. This fact is ascribed to the exclusion of some solvent molecules from the first coordination shell of Ni^{2+} due to the coordination of SO_4^{2-} to Ni^{2+}.

In our previous paper[1)] we have reported the ^{13}C spin-lattice relaxation rate, $1/T_1$, of some alcohol and DMSO molecules in their mixtures with water containing $Ni(ClO_4)_2$. From the data obtained, a conclusion of preferential solvation to Ni^{2+} ion was drawn. In this analysis, ClO_4^- anion was assumed not to coordinate to Ni^{2+} ion directly, and the first coordination sites to be saturated with water and/or solvent molecules. It has been established that in water and DMSO $Ni(ClO_4)_2$ exists as a hexasolvated cation and a non-coordinated ClO_4^- anion.[2,3)] An interesting problem arises when an apparent Ni^{2+}-anion interaction exists. If an anion coordinates to Ni^{2+} directly and replaces some solvent molecules in the first coordination shell where the paramagnetic effect is most predominant, then observed $1/T_1$ is expected to decrease. Sulfate anion-cation interaction in solutions has been investigated by NMR,[4–6)] Raman spectra,[7)] and conductance[8,9)] measurements, etc., and solvent-anion mixed ligand complex formation has been considered to explain these results. In this note the anion effect on the coordination of solvent to Ni^{2+} is investigated by measuring the paramagnetic-ion induced spin-lattice relaxation rate of ^{13}C of methanol and DMSO molecules in their mixtures with water containing $NiSO_4$ or NiBDS (BDS: *m*-benzenedisulfonate). These relaxation rates were compared with those of $Ni(ClO_4)_2$ solutions. Since $NiSO_4$ is not sufficiently soluble in neat solvents, its effect was studied in 50 wt.% aqueous mixtures. NiBDS was chosen for comparison with SO_4^{2-} because it has a divalent anion and has enough solubility in both neat solvent and 50 wt.% aqueous mixtures.

Experimental

The preparation of nickel perchlorate is described in Ref. 1. Commercially-available reagent-grade nickel sulfate was recrystallized from water and dried at room temperature. The water content of the salt was determined as 6 moles per mole of the salt by a total cation analysis using a cation-exchange column. The preparation of NiBDS was based closely on that outlined for CuBDS in Ref. 10. The water content of recrystallized NiBDS was 6 moles per mole of the salt. Methanol and DMSO solvents were both reagent grade and were used without further purification. NMR spectra were recorded on a JEOL FX-90Q FT NMR spectrometer by using the standard inversion-recovery technique at 35 °C. The error in the measurement of T_1 was less than 5%.

Results and Discussion

The observed spin-lattice relaxation rate of solvent nuclei in paramagnetic solution will be a sum of two major contributions:

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

where the first term is for the electron-nuclear relaxation in the first coordination shell and the second term is the diamagnetic relaxation rate. $1/T_{1M}$ and $1/T_{1B}$ are the relaxation rates of the nuclei of the solvent molecules in the first coordination shell and those in the bulk, respectively. X_M denotes the fraction of the coordinated solvent molecules in the first coordination shell, and is expressed as

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

where C_i and C_s are the molar concentrations of the ion and the solvent molecule, respectively, and n is the number of coordinated solvent molecules. For the solution of $Ni(ClO_4)_2$ in neat solvent, Ni^{2+} is assumed to be surrounded by six solvent molecules. $1/T_{1M}$ can be obtained as the slope of plots of observed $1/T_1$ against X_M at low concentrations of Ni^{2+} ion. The $1/T_{1M}$ values thus obtained are 230 s^{-1} for methanol and 110 s^{-1} for DMSO. If $1/T_{1M}$ is assumed not to

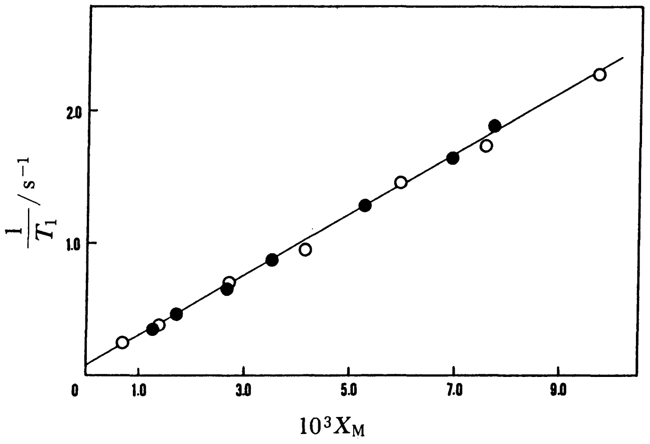

Fig. 1. Plots of ^{13}C spin-lattice relaxation rate as a function of the coordinated solvent fraction, X_M, in methanol. ○: $Ni(ClO_4)_2$,[1)] ●: NiBDS.

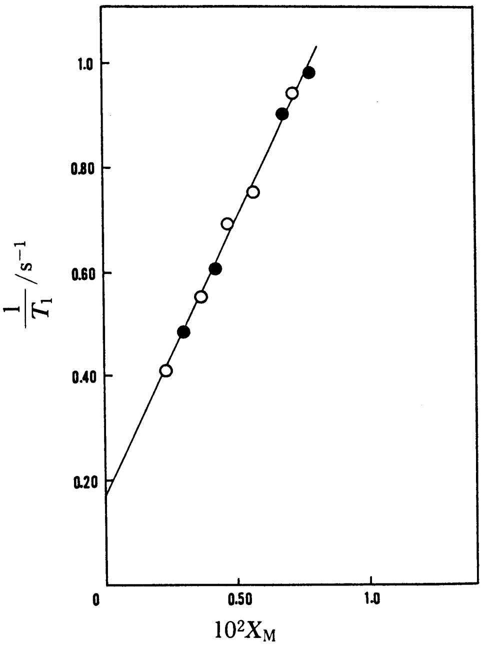

Fig. 2. Plots of ^{13}C spin-lattice relaxation rate as a function of the coordinated solvent fraction, X_M, in DMSO. ○: $Ni(ClO_4)_2$,[1] ●: NiBDS.

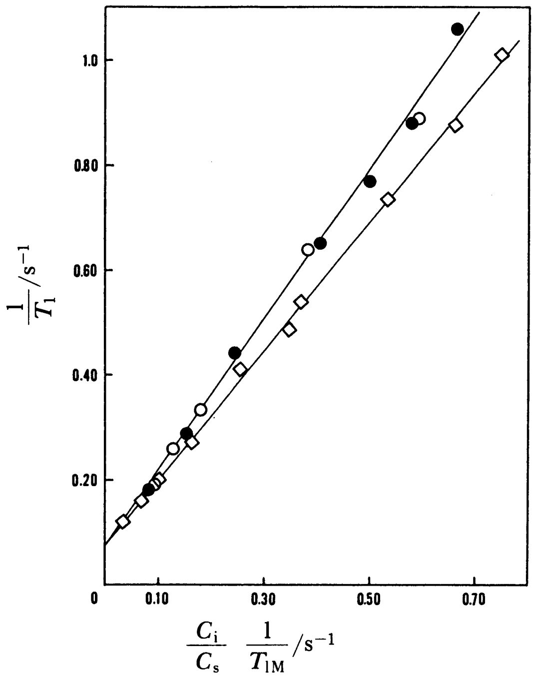

Fig. 3. Plots of ^{13}C spin-lattice relaxation rate versus $C_i/(C_s \cdot T_{1M})$ in water-methanol system. ○: $Ni(ClO_4)_2$, ●: NiBDS, ◇: $NiSO_4$.

change when water or anion occupies several of the six coordinate sites of Ni^{2+}, the number of coordinated solvent molecules is obtained from the slope of plots of $1/T_1$ against $C_i/(C_s \cdot T_{1M})$ at low Ni^{2+} concentrations. In Figs. 1 and 2, the $1/T_1$ values of $Ni(ClO_4)_2$ and NiBDS are plotted as a function of X_M in methanol and DMSO, respectively. In both the figures, the plots appear to fall on a common straight line. The same mention can be made for the aqueous methanol and aqueous DMSO systems. In Figs. 3 and 4, the $1/T_1$ values in 50 wt.% aqueous methanol and DMSO, respectively, are plotted versus $C_i/(C_s \cdot T_{1M})$. In both the figures, the plots for $Ni(ClO_4)_2$ and NiBDS appear to fall on their respective common straight lines. Thus for the NiBDS solutions, the possibility that BDS^{2-} replaces the solvent molecules in the first coordination shell may be considered negligible as with ClO_4^- in both neat and aqueous mixtures. The number, n, of the solvent molerules locating in the inner shell of Ni^{2+} is obtained as the slope of the plots shown in Figs. 3 and 4. For 50 wt.% methanol n=1.4 and for 50 wt.% DMSO n=1.1. Since the n values expected from the overall solvent composition are 2.2 and 1.1, respectively, the Ni^{2+} ion is solvated preferentially by water in 50 wt.% methanol, while no preferential solvation is found in 50 wt.% DMSO. On the other hand, in the case of $NiSO_4$, the downward deviation from the plots of $Ni(ClO_4)_2$ is apparent in both the aqueous mixtures. The deviation may be ascribed to the replacement of some solvent molecules by SO_4^{2-} anion in the inner shell of Ni^{2+} ion. The difference in the values between $Ni(ClO_4)_2$ and $NiSO_4$ is 0.3 for water-methanol and 0.2 for water-DMSO, so about 0.3 methanol or 0.2 DMSO molecule is considered to be replaced by SO_4^{2-} in forming the inner shell complex. If SO_4^{2-} anion could replace not only nonaqueous solvent molecules but also water molecules, SO_4^{2-} anion would replace more than 0.3 or 0.2 solvent molecule (nonaqueous or water) in the inner shell. Bechtold et al.[6] studied the Ni(II)-SO_4^{2-} interaction by ^{17}O NMR in aqueous solution. According to their results, $Ni(H_2O)_6^{2+}$ is the most predominant species, which occupies about 90% of the total Ni species at temperatures near 35 °C. The pres-

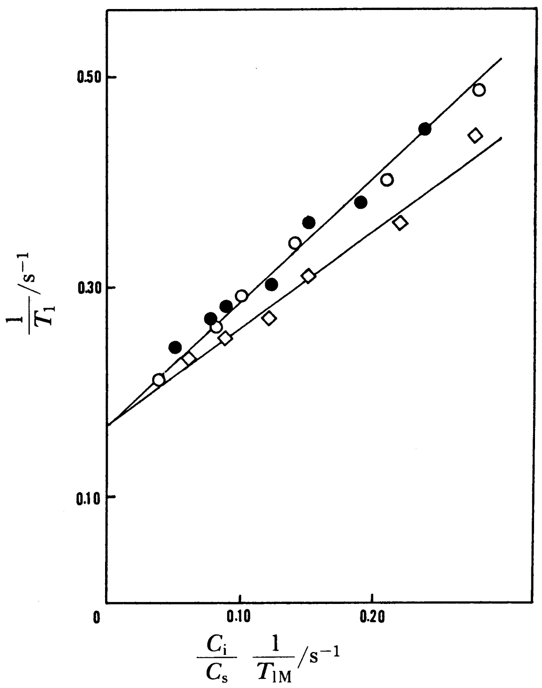

Fig. 4. Plots of ^{13}C spin-lattice relaxation rate versus $C_i/(C_s \cdot T_{1M})$ in water-DMSO system. ○: $Ni(ClO_4)_2$, ●: NiBDS, ◇: $NiSO_4$.

ent work has given a still higher percentage of the inner-shell complex containing SO_4^{2-}. The addition of nonaqueous solvent may enhance the coordination of SO_4^{2-} anion to Ni^{2+} ion directly. These tendencies are also found in $Al_2(SO_4)_3$-water-nonaqeous solvent systems from ^{27}Al NMR spectra.[4,5] Sulfate anion is a compact divalent anion, while BDS^{2-} is of much larger size and its minus charge is localized to some extent on the functional group. The difference in size and charge distribution would be one of proper explanations for the marked difference in behavior between SO_4^{2-} and BDS^{2-}. Hallada and Atkinson[8] reported a conductance work on MnBDS and $MnSO_4$ in aqueous methanol. The ion association constants evaluated from conductance data of $MnSO_4$ are much larger than those of MnBDS throughout in the solvent composition range studied. Similar results were obtained with systems of $CuSO_4$ and CuBDS in aqueous dioxane.[9] The difference between the ion association constants of the sulfate and the BDS salt may be ascribed to the feasibility of the inner shell coordination of sulfate anion.

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