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Effect of Ligand-Exchange Reaction on Longitudinal Magnetization Recovery in Aqueous-Al(III) NMR

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The effect of chemical exchange on the longitudinal magnetization recovery (LMR) was investigated by means of the ^{27}Al NMR in aqueous $Al_2(SO_4)_3$ solution. It was elucidated for the first time that in the case of the rapid ligand-exchange between $[Al(H_2O)_5SO_4]^+$(A) and $[Al(H_2O)_6]^{3+}$(B) the slope of a single exponential decay in the observed LMR gives a slow rate $R_{1,B}(<R_{1,A})$ of the time evolution of the longitudinal magnetization under the presence of energy relaxation as well as chemical exchange. The value of $R_{1,B}$ at the rapid exchange limit becomes equal to $f_A R^*_{1,A} + f_B R^*_{1,B}$ as reported so far, where $R^*_{1,\alpha}$ is energy relaxation rate at site α.

The majority of dynamic studies undertaken by NMR have employed the lineshape measurements with the aid of the theory on the effect of the ligand exchange reaction on the NMR spectrum at a stationary state. The nuclear spin system submitted to the radio-frequency field undergoes, besides the phase relaxation (i.e., spin-spin relaxation), the energy relaxation (i.e., spin-lattice relaxation), whereby the nuclear spins are informed of the temperature of the lattice and come into thermal equilibrium with the lattice. The time evolution of the longitudinal magnetization is controlled by both the energy relaxation rate and the chemical exchange rate. One (KI) of the authors demonstrated the effect of chemical exchange on the energy relaxation and derived an exact solution of the coupled expressions for the time evolution of the individual longitudinal magneitzations of the environments A and B[1] (referred to as I).

The NMR measurements were carried out at various temperatures between 22 °C and 85 °C for aqueous $Al_2(SO_4)_3$ solution (0.18 mol dm^{-3}): the time evolution of the ^{27}Al longitudinal magnetization recovery (LMR) was obtained from the free-induction decays measured by using the inversion recovery method (i.e. π-τ-$\pi/2$),

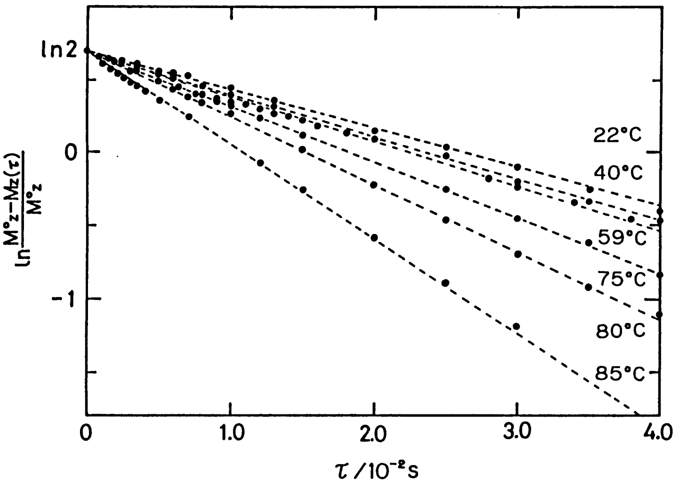

Fig.1. Experimental points of the longitudinal magnetization recovery of aqueous $Al_2(SO_4)_3$ solution between 22 °C and 85 °C. The dashed line is a fit of the data by using a least-square method.

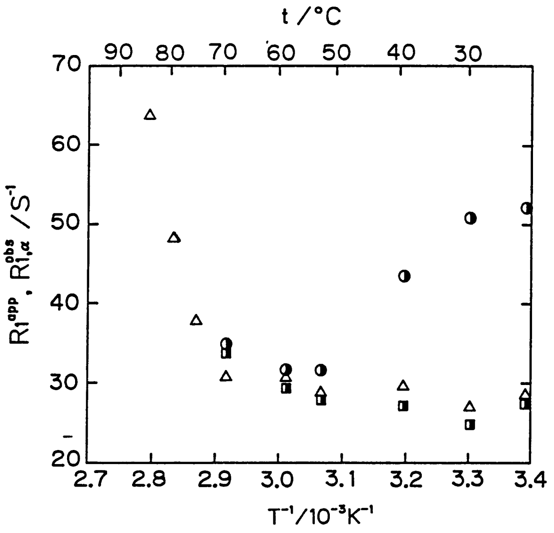

Fig.2. Temperature dependences of R_1^{app}(△), $R_{1,A}^{obs}$ (◐) and $R_{1,B}^{obs}$ (◨); the technique for the measurements of these relaxation rates is mentioned in the text.

as shown in Fig. 1. The LMR shows a single-exponential decay in spite of some difference in magnitude between ^{27}Al-quadrupole relaxation rates in the first-sphere complex $[Al(H_2O)_5SO_4]^+$ (A) and the hexa-aquo cation $[Al(H_2O)_6]^{3+}$ (B),2) what does the slope of the single-exponential decay (see Fig. 1) mean? Figure 2 shows the temperature dependence of the apparent relaxation rates R_1^{app}, which were obtained from the slope of the logarithmic longitudinal magnetization (LLM) versus the time interval τ between the 180° and 90° pulses (i.e., the dashed lines in Fig. 1). We have found the unexpected results of R_1^{app} as follows: (i) the spectrum shows two discrete lines, ca. 3 ppm apart, from ^{27}Al in A and B sites below 50 °C, but in Fig. 2 all the LLM is linear. (ii) The appreciable increase of R_1^{app} with an increasing temperature is different from the decrease of the quadrupolar-relaxation rates for ^{27}Al with an increasing temperature. In order to make the unexpected results clear, we obtained the longitudinal relaxation rates $R_{1,A}^{obs}$ and $R_{1,B}^{obs}$, which were attributed to both A and B sites, from the time evolution of the intensities of individual lines obtained by Fourier-transform of the free induction decay (see

Fig. 3). The relaxation rate of the B lines is slow compared with that of the A lines. The temperature dependence of $R^{obs}_{1,A}$ and $R^{obs}_{1,B}$, which were estimated as the individual rates of ^{27}Al of the time evolution of each LMR in the $[Al(H_2O)_5SO_4]^+$ and $[Al(H_2O)_6]^{3+}$ species, was also shown in Fig. 2.

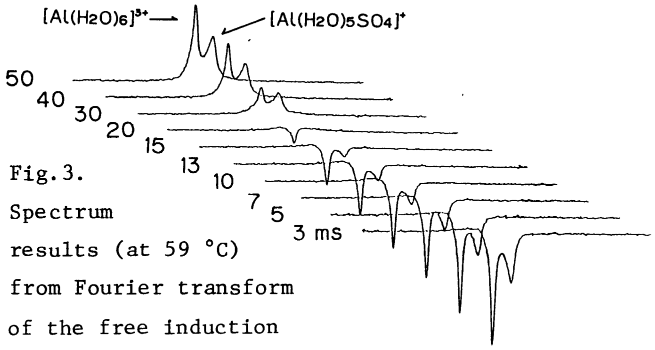

Fig.3. Spectrum results (at 59 °C) from Fourier transform of the free induction decay following the second pulse of a 180°-90° pulse sequence. The time interval between pulses is indicated on the left-hand of the spectrum.

With the aid of the theory on the effect of chemical exchange on LMR we discuss the unexpected and interesting results as follows: (1) R^{app}_1 is roughly equal to $R^{obs}_{1,B}$; (2) at the high temperatures both $R^{obs}_{1,A}$ and $R^{obs}_{1,B}$ become equal to R^{app}_1. The values of R^{app}_1, $R^{obs}_{1,A}$ and $R^{obs}_{1,B}$ can be roughly estimated as the relaxation rates of the time evolution of the magnetizations $M_Z(\tau)$, $M_{Z,A}(\tau)$ and $M_{Z,B}(\tau)$ under the presence of energy relaxation and chemical exchange. According to the theory presented in I, $M_Z(\tau)$ has the form

$$M_Z(\tau) = M_{Z,A}(\tau) + M_{Z,B}(\tau) \tag{1}$$

where

$$M^{\circ}_{Z,A}(\tau) - M_{Z,A} = 2\ [M^{\circ}_{Z,AA}\ \exp(-R_{1,A}\ \tau) + M^{\circ}_{Z,AB}\ \exp(-R_{1,B}\ \tau)] \tag{2}$$

$$M^{\circ}_{Z,B}(\tau) - M_{Z,B} = 2\ [M^{\circ}_{Z,BA}\ \exp(-R_{1,A}\ \tau) + M^{\circ}_{Z,BB}\ \exp(-R_{1,B}\ \tau)] \tag{3}$$

For the symbols refer to I. The rate $R_{1,A}$ ($>R_{1,B}$) for time-dependent processes of energy relaxation as well as chemical exchange and the coefficients in Eqs. 2 and 3 are expressed in terms of the energy relaxation rate $R^*_{1,A}$($R^*_{1,B}$) at site A (site B), the lifetime of each chemical exchange (τ_A and τ_B) and each fractional population (f_A and f_B), as shown in Eqs. 8-10 and Eqs. 13-17 in I. The coefficients in Eqs. 2 and 3 were calculated as a function of $R^*_{1,A}\tau_A$ in the case of $R^*_{1,A}/R^*_{1,B}=25$ and $f_A/f_B=3$, as shown in Fig. 4. In the rapid exchange (i.e. $R^*_{1,A}\tau_A<1$) above ca. 60 °C the time evolution of $M_Z(\tau)$ and $M_{Z,\alpha}(\tau)$(α=A or B) was given by

$$M^{\circ}_Z - M_Z = 2M^{\circ}_Z\ \exp(-R_{1,B}\ \tau) \tag{4}$$

$$M^{\circ}_{Z,\alpha}(\tau) - M_{Z,\alpha} = 2M^{\circ}_{Z,\alpha}\ \exp(-R_{1,B}\ \tau) \tag{5}$$

This is because $M^{\circ}_{Z,AB}/M^{\circ}_Z$ and $M^{\circ}_{Z,BB}/M^{\circ}_Z$ approach f_A and f_B, respectively, and $M^{\circ}_{Z,AA}/M^{\circ}_Z$ and $M^{\circ}_{Z,BA}/M^{\circ}_Z$ approach zero (see Fig. 4). Thus the result of $R^{app}_1 \approx R^{obs}_{1,\alpha}$

(α=A or B) $\approx R_{1,B}$ above ca. 60 °C (see Fig. 2) can be explained by Eqs. 4 and 5. For the rapid exchange limit the slow rate $R_{1,B}$ becomes equal to $f_AR^*_{1,A} + f_BR^*_{1,B}$ and the fast rate $R_{1,A}$ to $\tau_A^{-1} + \tau_B^{-1} + f_BR^*_{1,A} + f_AR^*_{1,B}$ (see Eqs. 8 - 10 in I). The value of R_1^{app} which we can observe at the rapid exchange limit means an average value $f_AR^*_{1,A} + f_BR^*_{1,B}$, as reported so far,[3] because of $R_1^{app}=R_{1,B}$ (see Eq. 4) and $R_{1,B}=f_AR^*_{1,A} + f_BR^*_{1,B}$. In the rapid exchange limit we can observe just one Lorentzian spectrum characterized by the average environment which a spin sees[4] and a single exponential decay of the LLM means a slow rate $R_{1,B}$ ($<R_{1,A}$).

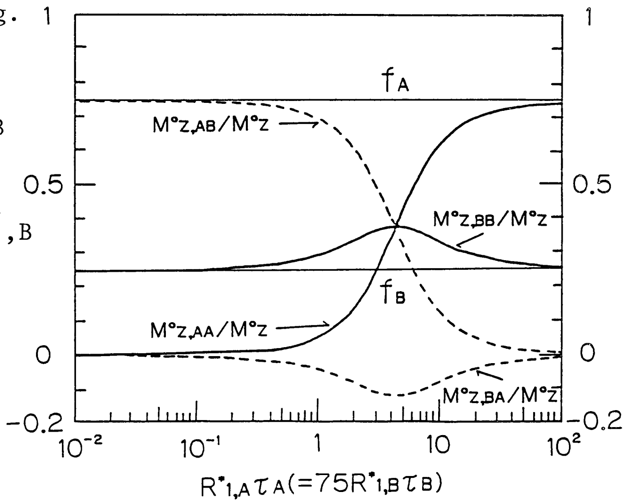

Fig.4 The dependence of $R^*_{1,A}\tau_A$ (or $R^*_{1,B}\tau_B$) on the coefficients in Eqs. 2 and 3 under the conditions of $R^*_{1,A}/R^*_{1,B} = 25$ and $f_A/f_B = 3$.

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