^{17}O NMR Study of Aqueous Electrolyte Solutions; Effect of KCl and NaCl on the ^{17}O NMR Parameters of Water

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Synopsis. The aqueous solutions containing KCl or NaCl at various concentrations have been studied by ^{17}O NMR. The line width of the signal increases and decreases with an addition of KCl above and below 55 °C, respectivly, and these results indicate that the effect of KCl on the water structure depends on temperature.

The chemical shift changes induced on the ^{17}O NMR signal of water by an addition of salts such as KCl and NaCl have been used to study interaction between H_2O and solute molecules.[1,2] Hydrogen bonding network among water molecules and motion of water molecule have been investigated from the line width of its ^1H or ^{17}O NMR signal[3,4] and their spin-lattice (T_1) or/and spin-spin relaxation time (T_2), respectively.[5–11]

In this report, we have studied the effects of KCl and NaCl on the ^{17}O NMR parameters of water. The line width decreases with an addition of KCl below 55 °C. On the contrary, above this temperature, it increases with an addition of KCl. These results indicate that KCl acts as water structure breaking and forming salt, below and above 55 °C, respectively.

Experimental

Materials. H_2O was prepared by distillation of deionized water. D_2O was purchased from MSD Isotopes and used as received. KCl and NaCl were obtained from Sigma Chemical Co. and they were dried under reduced pressure at 150 °C for 24 h before use.

NMR Measurement. All ^{17}O NMR experiments were carried out using JEOL GSX-270 spectrometer operating at the resonance freaqency of 36.6 MHz. The spectra were recorded with proton decoupling, and the signal to noise ratio of the spectra was improved by apodization which introduced 10 Hz line broadening. The chemical shifts are given in parts per million (ppm) and the ^{17}O NMR signal of D_2O at 35 °C was used as a reference (0 ppm). T_1 values were determined by using a saturation recovery method[12] and T_2 was calculated from the line width of the signal.

Results and Discussion

Chemical Shifts. The chemical shift change for the ^{17}O NMR signal of water is plotted against the concentration of salt at 35 °C in Fig. 1. The plots for KCl and NaCl exhibit straight lines, over the salt concentration range examined, with the slope [∂(ppm)/∂(mol dm^{-3})] of 0.80 and 0.45, respectively. The ^{17}O NMR signal moves toward downfield with the addition of salt. Since K^+ and Na^+ are known to shift the signal upfield, the observed downfield shift of the signal is attributed to the large downfield shift effect of Cl^-.[1,2] Hence, the smaller slope of the plot for NaCl, compared with that for KCl, indicates that the upfield effect of Na^+ is larger than that of K^+.

Relaxation Times. Relaxation parameters measured under various conditions are summarized in Table 1. T_1 of ^{17}O NMR signal of H_2O was determined to be

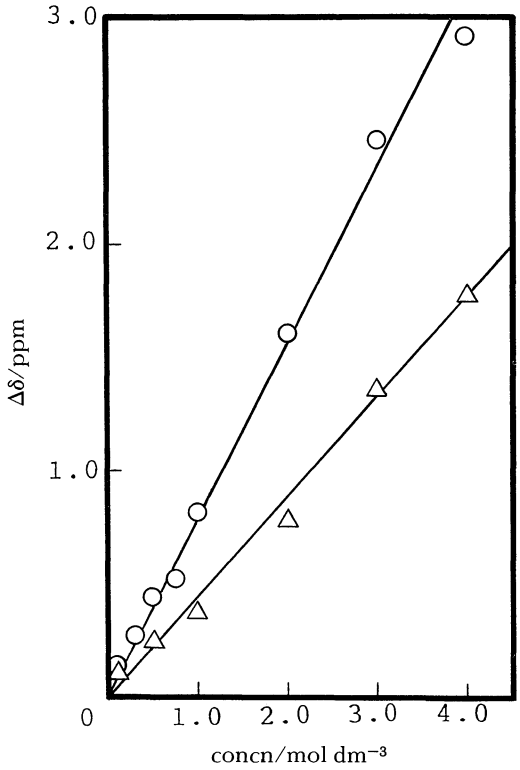

Fig. 1. Plot of observed chemical shift for the ^{17}O NMR signal of D_2O against the concentration of salt added at 35 °C. KCl (○), and NaCl (△).

Table 1. T_1, T_2*[a], and τ_c[b] of the ^{17}O NMR of Water

	H_2O	D_2O		D_2O/1.0 mol dm^{-3} KCl	
	35 °C	35 °C	75 °C	35 °C	75 °C
T_1/ms	6.2±1.0	7.9±1.0	14.3±0.7	8.2±1.0	12.1±0.7
T_2*/ms	6.1±0.3	4.8±0.2	9.1±0.6	5.3±0.3	8.2±0.5
τ_c/ps	2.9±0.5	2.3±0.3	1.2±0.1	2.2±0.3	1.5±0.1

a) Calculated from the observed line width. b) Estimated from the determined T_1 value with $e^2qQ/\hbar$=7.7 MHz.[7]

6.2±1.0 ms at 35 °C. This value is almost comparable to the previously reported value.[5] The apparent spin-spin relaxation time (T_2*) was calculated to be 6.1±0.3 ms from the line width of 52.5 Hz at 35 °C. Hence, T_2 is nearly equal to T_1 at this temperature. When T_1=T_2, i.e., a rapid motional limit, T_1^{-1} (T_2^{-1}) of ^{17}O nucleus is given by[13]

$$T_1^{-1} = T_2^{-1} = (3/125)(1 + \eta^2/3)(e^2qQ/\hbar)^2\tau_c$$

where η is an asymetric parameter of the electrical field gradient around ^{17}O nucleus and is known to be negligibly small for bulk water molecule.[14] $e^2qQ/\hbar$ is the quadrupole coupling constant of ^{17}O nucleus and τ_c is the correlation time of water molecule. The $e^2qQ/\hbar$ value for both H_2O and D_2O have been reported to be 7.7±0.1 MHz at temperature from 5 to 95 °C.[6,7] Since the $e^2qQ/\hbar$ is expected to be independent of the salt concentration, change in relaxation times is attributed to alteration of τ_c. T_1 is larger than T_2* for D_2O samples and this may be attributed to the D–O scalar coupling, although its magnitude is modulated by the dynamic process of deuterium exchange.

Effect of Salt Concentration on the Line Width. The line width of ^{17}O NMR signal of D_2O is plotted against KCl concentration in Fig. 2. At 55 °C, the line width is independent of KCl concentration. At lower temperature (35 °C), the line width decreases with increasing KCl concentration and reaches a steady-state value (ca. 59 Hz). On the contrary, at higher temperature (75 °C), the line width increases with KCl concentration and reaches another steady-state value

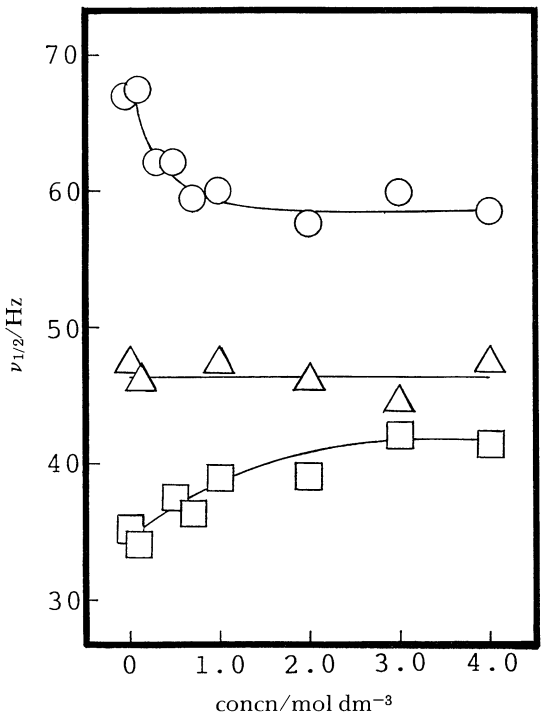

Fig. 2. Plot of the observed line width for the ^{17}O NMR resonance of D_2O against the concentration of KCl. 35 °C (○), 55 °C (△), and 75 °C (□).

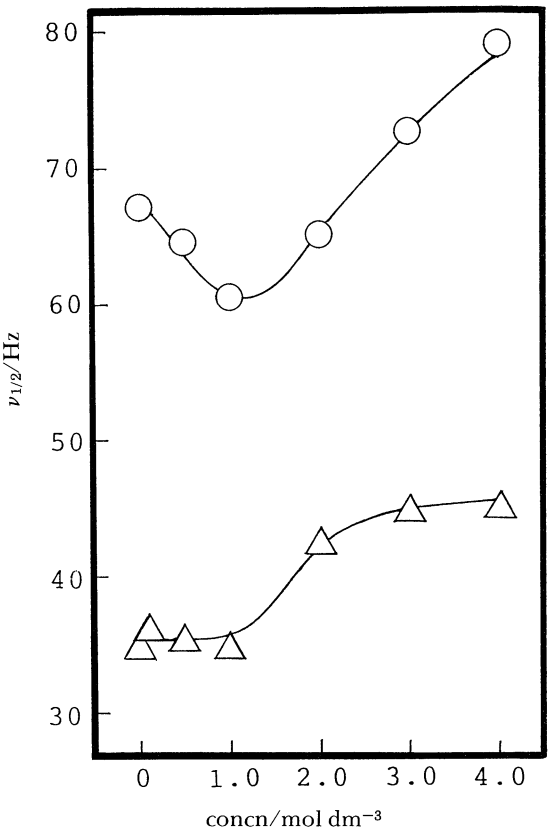

Fig. 3. Plot of the observed line width for the ^{17}O NMR resonance of D_2O against the concentration of NaCl. 35 °C (○), and 75 °C (△).

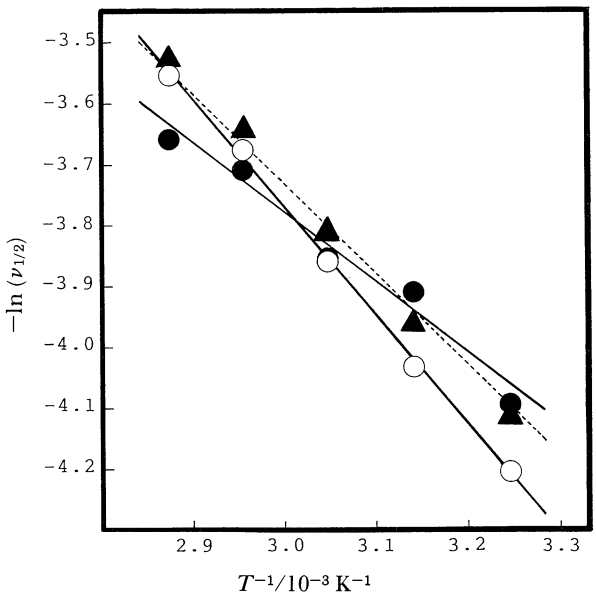

Fig. 4. Arrhenius plots for the observed line width of the ^{17}O NMR resonance of D_2O (○), D_2O containing 1.0 mol dm^{-3} of KCl (●), and NaCl (▲). The $\Delta E^{\neq}$ values determined from these plots are 10 (D_2O without salt), 15 (D_2O containing KCl), and 12 kJ mol^{-1} (D_2O containing NaCl).

(ca. 40 Hz). A similar plot for the D_2O solution containing NaCl is shown in Fig. 3. The line width of the signal at 75 °C seems to be independent of NaCl concentration below 1.0 mol dm^{-3}. But an anomalous behavior is observed above 1.0 mol dm^{-3}.

Effect of Temperature on the Line Width. Figure 4 shows the Arrhenius plots of the line width of the ^{17}O NMR signal for D_2O with and without salts in the temperature range from 35 to 75 °C. The Arrhenius plot for T_1 of ^{17}O NMR signal of water (from −14 to 180 °C) has shown to deviate from a straight line.[8] However, the plots in Fig. 4 exhibit straight lines in the temperature range studied. These two lines in Fig. 4 cross with each other at $3.0\times10^{-3}K^{-1}$ (ca. 55 °C), indicating that the line width decreases and increases below and above 55 °C, respectively, as discussed above. This result also confirms the KCl concentration independency of the line width at 55 °C. It has been reported from the ^1H NMR studies that K^+, Na^+, and Cl^- in H_2O act as water structure breaking ions at room temperature.[15] In Fig. 2, such an effect of KCl is clearly observed below 55 °C. On the contrary, above 55 °C, the increase of the line width by an addition of KCl is interpreted as an increase of τ_c, indicating that the added ions inhibit molecular motion of water, i.e., KCl acts as a water structure forming salt above 55 °C.

For NaCl solution, similar experiments were performed. The temperature where the Arrhenius plot for D_2O solution containing 1.0 mol dm^{-3} of NaCl crosses with that for D_2O is 2.9×10^{-3} K^{-1} (ca. 75 °C), reflecting that the line width is independent of NaCl concentration up to 1.0 mol dm^{-3}.

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