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Variable Pressure and Temperature Nuclear Magnetic Resonance Study of Solvent Exchange on Manganese(II) Ion in N,N-Dimethylformamide. Influence of Solvent Molecular Size on Solvent Exchange Mechanism

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The solvent exchange rates for manganese(II) ion in DMF have been measured at various pressures up to 300 MPa by the high-pressure oxygen-17 NMR line-broadening method. The activation volume of 1.6 ± 0.5 $cm^3\ mol^{-1}$ points to an interchange mechanism operative in the exchange process. This is discussed in terms of the bulkiness of DMF.

The activation volume, $\Delta V^{\ddagger}$, for solvent exchange has proved to be particularly diagnostic of activation mode for solvent exchange on metal ions.[1,2] Merbach has claimed on the basis of the values of activation volumes that for the first-row bivalent transition-metal ions in water and methanol the activation mode for solvent exchange changes from associative (I_a) for Mn^{2+} to dissociative (I_d) for Ni^{2+} with increase in atomic number, and that this trend in mechanistic variation appears to persist in other solvent also.[1] Available values of activation volumes for solvent exchange on manganese(II) ion are in fact negative (-5.4 ± 0.1 $cm^3\ mol^{-1}$ in water,[3] -7.0 ± 0.4 $cm^3\ mol^{-1}$ in acetonitrile,[4] -5.0 ± 0.2 $cm^3\ mol^{-1}$ in methanol[5]). Therefore, the mechanism of the solvent exchange on manganese(II) ion in these solvents should be associative interchange (I_a).

By the high-pressure stopped-flow method, we have measured the activation volumes for the complexation of iron(III) ion in aqueous and nonaqueous media.[6-8] The complexation of hexaaquairon(III) ion in water was considered to proceed via an associative mode of activation because of negative volumes of activation, and on the other hand in nonaqueous solvents the activation volume for complexation does vary to a large extent with entering ligands and coordinated solvents: the bulkiness of reactants is reflected to a large extent in the activation volume for the complexation with an associative character in water than for the complexation with a dissociative character in aqueous solution. More recently, aluminum(III), gallium(III), and indium(III) ions with isoelectronic configurations in the same column of the periodic table were chosen to investigate selectively the size effect of metal ions on the complexation mechanism: the larger the ionic radius, the less dissociative the mechanism.9) As a result, quite similarly, the more bulky the solvent, the more dissociative the activation process for metal complex formation. In this work, in order to look at the influence of bulkiness of solvent on solvent exchange mechanism on the basis of activation volume, we have investigated solvent exchange rates for manganese(II) ion in N,N-dimethylformamide (DMF) as a bulky solvent by the high-pressure NMR method.

The crystals of $[Mn(dmf)_6](ClO_4)_2$ were prepared of which the composition was confirmed by elemental analyses. The preparation of NMR sample solutions was carried out on a standard vacuum line.10) The transfer of the sample solution into a high-pressure NMR tube (o.d. 7 mm) was performed under nitrogen gas in a dry box. Variable-temperature Fourier-transform oxygen-17 NMR spectra at natural abundance were obtained with JEOL-FX100, JEOL-GX270 and JEOL-GX400 instruments operating at 13.51 MHz, 36.64 MHz, and 54.21 MHz, respectively. Variable-pressure FT oxygen-17 NMR spectra were recorded on a JEOL-GX270 spectrometer. For the high-pressure experiments, a multinuclear NMR probe has been built which fits into the wide-bore of the 6.34 Tesla superconducting magnet.11) The pressure vessel has been tested up to 350 MPa.

The solvent NMR line broadening, $(T_{2P}P_M)^{-1}$, due to the paramagnetic ion is expressed as $(T_{2P}P_M)^{-1} = \pi(\Delta\nu_{obsd} - \Delta\nu_{solv})P_M^{-1}$, where $\Delta\nu_{obsd}$ and $\Delta\nu_{solv}$ (Hz) are the half-height widths of the NMR spectra of DMF in the presence and absence, respectively, of the manganese(II) ion, and P_M is the mole fraction of DMF molecules bound to the manganese(II) ion. We measured the NMR spectra of sample solutions with two different concentrations ($P_M = 1.56 \times 10^{-4}$ and 9.15×10^{-4}) of manganese(II) perchlorate at various temperatures (-30 — 50 °C). The observed line widths $(\Delta\nu_{obsd} - \Delta\nu_{solv})$ are excellently proportional to the manganese(II) ion concentrations. The temperature dependence of line broadening is shown in

Fig. 1. Over the present temperature range, the observed transverse relaxation rate is independent of the observed frequencies of 13.51 MHz, 36.64 MHz and 54.21 MHz, and controlled by the chemical exchange: $(T_{2p}P_M)^{-1} = \tau_M{}^{-1}$, where τ_M is the mean lifetime of the observed oxygen-17 of DMF in the first coordination sphere of the manganese(II) ion.[10] The solvent exchange rate constant k is equal to $\tau_M{}^{-1} = (k_BT/h)\exp(-\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R)$. Activation parameters for the solvent exchange were determined to be $k = (2.7 \pm 0.2) \times 10^6\ s^{-1}$ at 25.0 °C, $\Delta H^{\ddagger} = 35.8 \pm 0.6$ kJ mol^{-1}, and $\Delta S^{\ddagger} = -2 \pm 2$ J $mol^{-1}\ K^{-1}$. We measured the NMR spectra of sample solutions at 36.3 °C at various pressures up to 300 MPa. Logarithmic values of the ratio of rate constant (k_P) at P MPa to rate constant (k_0) at 0 MPa are

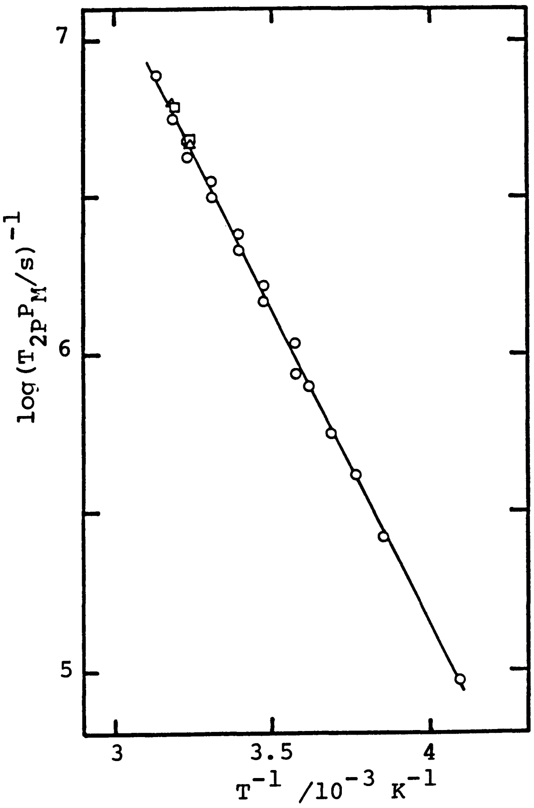

Fig. 1. Temperature dependence of $\log(T_{2p}P_M)^{-1}$ for the oxygen-17 of bulk DMF in the presence of manganese(II) ion at 13.51 MHz (△), 36.64 MHz (○), and 54.21 MHz (□). The solid line is calculated by using the obtained values.

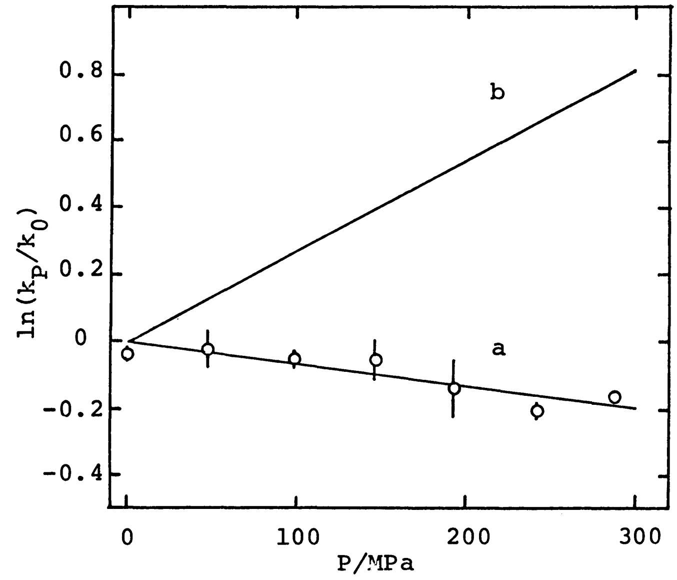

Fig. 2. Pressure dependence of the rate constant for the DMF exchange on manganese(II) ion at 36.3 °C and $P_M = 1.96 \times 10^{-4}$. Each point is an average of values obtained for two sample solutions prepared independently. Each bar indicates the maximum deviation. Errors for rate constants are less than 8%. Solid line a is calculated by using the obtained $\Delta V^{\ddagger}$ for the DMF exchange. Solid line b is drawn according to the $\Delta V^{\ddagger}$ of $-7.0\ cm^3\ mol^{-1}$ for the acetonitrile exchange.[4]

plotted against pressure in Fig. 2. The volume of activation is given by $\Delta V^{\ddagger} = -RT(\partial \ln k/\partial P)_T$. We determined $\Delta V^{\ddagger} = 1.6 \pm 0.5\ \mathrm{cm^3\ mol^{-1}}$ at 36.3 °C.

This small but positive activation volume for the DMF exchange on manganese(II) ion is attributed to the bulkiness of DMF. In bulkier solvents, a coordinated solvent molecule may be forced to leave partly the inner sphere of the central metal ion due to steric hindrance until an entering solvent starts to coordinate. In conclusion, this study clearly demonstrates that the increase in crowding at the metal center causes the activation mode to be less associative: the mechanism changes from I_a to I on going from small-size solvent such as H_2O, CH_3OH, or CH_3CN to bulky DMF.

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