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Solvent Bulkiness Effect on *N,N*-Dimethylformamide Exchange of the *o*-Phenylenediamine-*N,N,N′,N′*-tetraacetatoferrate(III) Complex as Studied by a High-Pressure NMR Method

Masafumi MIZUNO, Shigenobu FUNAHASHI,* Noriyuki NAKASUKA, and Motoharu TANAKA
Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-01

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Synopsis. Activation parameters for solvent exchange of the title complex in *N,N*-dimethylformamide (DMF) have been determined as follows: k (25 °C)=$(3.4\pm0.2)\times10^7$ s^{-1}, $\Delta H^{\neq}=18\pm3$ kJ mol^{-1}, $\Delta S^{\neq}=-40\pm10$ J K^{-1} mol^{-1}, and $\Delta V^{\neq}=10\pm2$ cm^3 mol^{-1}. The positive value of $\Delta V^{\neq}$ indicates that the DMF exchange proceeds via a dissociative interchange mechanism.

Rates for the complexation of d^5 iron(III) ion have been found to be greatly affected by the electron donecity of the bound ligand and the bulkiness of coordinated solvent molecules in several solvents.[1–3] The purpose of this work is to demonstrate the effects of the bound multidentate ligand and the solvent bulkiness on the solvent exchange of iron(III) complexes in terms of activation parameters. Recently we have reported the bound ligand effect on the water exchange of the iron(III) complex with *o*-phenylenediamine-*N,N,N′,N′*-tetraacetate (phdta^{4-}) in aqueous solution.[4] In order to investigate the solvent bulkiness effect on solvent exchange rate, we selected *N,N*-dimethylformamide (DMF) as a bulky solvent.

Experimental

Oxygen-17-enriched DMF was synthesized according to the reference method.[5] The ^{17}O-enriched DMF was purified by distillation over the 4A Molecular Sieves. PhDTA and its iron(III) complex were prepared by the procedures previously described.[4] The preparation of the sample solution for variable-temperature NMR measurement was carried out by the freeze-thaw technique under vacuum. Transfer of the sample solution into a high-pressure NMR tube (o.d. 7 mm) was performed under nitrogen gas in a dry box.[6,7] The concentration of Fe(III)-PhDTA in sample solutions ($C_{\text{Fe(III)-PhDTA}}$) is given in the Figure caption.

Variable-temperature Fourier-transform ^{17}O NMR spectra were measured with JEOL JNM-FX100 and JNM-GX270 NMR instruments operating at 13.50 and 36.63 MHz, respectively. Variable-pressure FT oxygen-17 NMR spectra were obtained with a JEOL-FX100 NMR spectrometer equipped with a high-pressure NMR probe.[6] Temperature and pressure were measured by the same methods as reported previously.[4]

The structure of Fe(III)-PhDTA in the DMF solution should be similar to that in water: The central iron(III) ion is seven-coordinate, with one DMF molecule being solvated.[4] Thus the DMF exchange at the iron(III) complex is expressed by Eq. 1.

$$[\text{Fe(dmf*)(phdta)}]^- + \text{dmf} \rightleftarrows [\text{Fe(dmf)(phdta)}]^- + \text{dmf*}. \quad (1)$$

The exchange rate of solvent molecules between the bulk and the coordination site of a paramagnetic metal ion has been estimated from the transverse relaxation time ($T_{2\text{P}}$) of the bulk solvent nuclei. The solvent ^{17}O NMR line broadening, $(T_{2\text{P}}P_\text{M})^{-1}$, due to the paramagnetic iron(III) complex is expressed as $(T_{2\text{P}}P_\text{M})^{-1}=\pi(\Delta\nu_\text{obsd}-\Delta\nu_\text{solv})P_\text{M}^{-1}$, where $\Delta\nu_\text{obsd}$ and $\Delta\nu_\text{solv}$ are the half-height widths of the ^{17}O NMR spectra of DMF in the bulk in the presence and absence, respectively, of Fe(III)-PhDTA. P_M is the ratio of the number of DMF molecule bound to the iron(III) complex to that of DMF molecules in the bulk. NMR line broadening data were analyzed on the basis of the modified Swift-Connick equation.[4,8]

Results and Discussion

Figure 1 shows the temperature dependence of $(T_{2\text{P}}P_\text{M})^{-1}$ for the Fe(III)-PhDTA complex in DMF over the range from −58 to 72 °C. Since the transverse relaxation rate due to the bound DMF in the absence of exchange, $T_{2\text{M}}^{-1}$, is small enough compared with the other relaxation terms over the observable temperature region for the present system, the modified Swift-Connick equation is reduced to Eq. 2:

$$(T_{2\text{P}}P_\text{M})^{-1}=1/(\tau_\text{M}^{-1}\Delta\omega_\text{M}^{-2}+\tau_\text{M}), \quad (2)$$

where τ_M is the residence time of the solvent molecule in the inner sphere of the iron(III) complex and $\Delta\omega_\text{M}$ is the shift between bulk and bound DMF resonances when no exchange occurs. The temperature dependence of $\Delta\omega_\text{M}$ is assumed to be $\Delta\omega_\text{M}=-C_\omega/T$.[9,10] A nonlinear least-squares analysis of the data led to the following parameters by fitting to Eq. 2: $\Delta H^{\neq}$/kJ mol^{-1}, $\Delta S^{\neq}$/

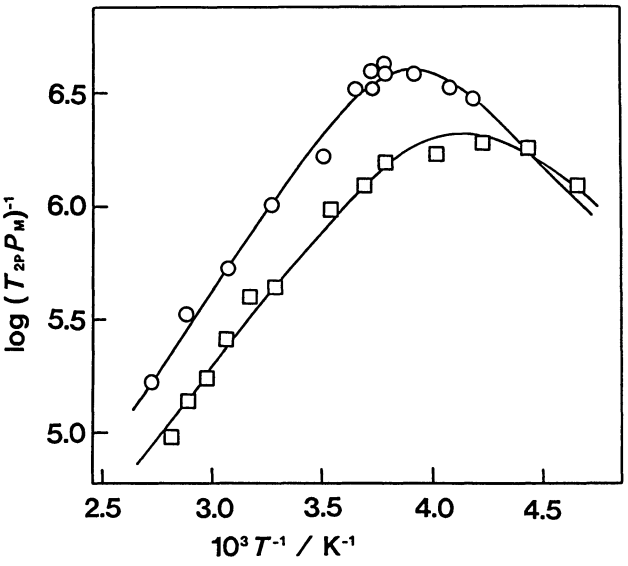

Fig. 1. Variation of the solvent DMF oxygen-17 relaxation rates $(T_{2\text{P}}P_\text{M})^{-1}$ with temperature for Fe(III)-PhDTA in DMF solution. $C_{\text{Fe(III)-PhDTA}}=4.50\times10^{-3}$, 7.03×10^{-3}, and 1.85×10^{-2} mol kg^{-1}. ○: 36.63 MHz ^{17}O; □: 13.50 MHz ^{17}O.

Table 1. Kinetic Parameters for Solvent Exchange on Fe(III) Complexes

	k (25 °C)	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta V^{\neq}$	Ref.
	s^{-1}	kJ mol^{-1}	J K^{-1} mol^{-1}	cm^3 mol^{-1}	
$[Fe(dmf)(phdta)]^-$	3.4×10^7	18±3	−40±10	10±2	This work
$[Fe(dmf)_6]^{3+}$	6.1×10	42.3±4.0	−69.0±13	−0.9±0.2	14
$[Fe(OH_2)(phdta)]^-$	1.2×10^7	26±3	−22±9	4.6±0.2	4
$[Fe(OH_2)_6]^{3+}$	1.6×10^2	64.0±2.5	12.1±6.7	−5.4±0.4	15, 16

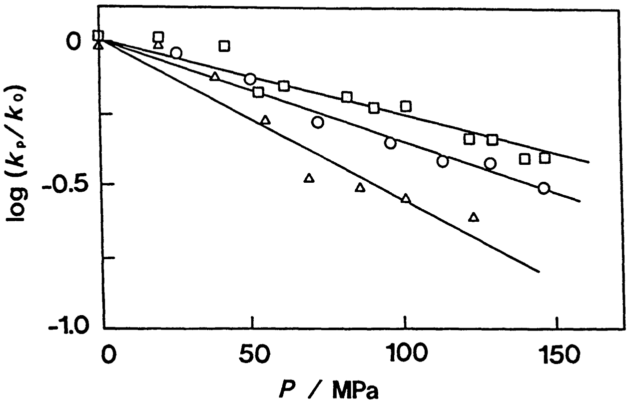

Fig. 2. Pressure dependence of $\log k_P$ for DMF exchange of the Fe(III)-PhDTA complex at −23.4 °C (△), 27.0 °C (○), and 61.3 °C (□). $C_{Fe(III)\text{-}PhDTA}=2.16\times10^{-2}$ mol kg^{-1}.

J K^{-1} mol^{-1}, and C_ω/K rad s^{-1} are 16.1±0.8, −51±3, and $(1.03\pm0.06)\times10^9$ for 13.50 MHz and 20.9±0.9, −33±3, and $(2.05\pm0.09)\times10^9$ for 36.63 MHz, respectively. These values obtained were used for drawing the solid curves in Fig. 1. The enthalpy and entropy of activation for DMF exchange on Fe(III)-PhDTA were determined to be 18±3 kJ mol^{-1} and −40±10 J K^{-1} mol^{-1}, respectively, taking experimental errors into account.

Since the definite chemical exchange region was not observed, we estimated the activation volume according to the following procedure. The solvent electrostriction acting on the primary coordination sphere may result in a large compression, typically of the order of gigapascals,[11] so that an externally applied pressure of about 150 MPa will not produce any noticeable changes in bond lengths. Therefore, the scalar coupling constant (A)[12] which depends on the distance between the iron(III) ion and the oxygen nucleus is not expected to vary to an appreciable extent in the present pressure experiments. Consequently, we calculated the k_P values at various pressures at three different temperatures, assuming that $\Delta\omega_M$ is independent of pressure as has been demonstrated by Merbach et al.[13] Values of $\ln(k_P/k_0)$ are plotted against P in Fig. 2. The activation volume at the respective temperature was obtained as follows: $\Delta V^{\neq}=11.9\pm2.6$ (−23.4 °C), 8.7±1.0 (27.0 °C), and 8.6±1.1 cm^3 mol^{-1} (61.3 °C). Taking into account experimental errors, the mean value of $\Delta V^{\neq}$ should be 10±2 cm^3 mol^{-1}.

The exchange of DMF on the Fe(III)-PhDTA complex is much faster than the solvent exchange on the hexa(solvento)iron(III) ion in water and DMF (see Table 1). This fact comes mainly from the difference in activation enthalpy. The values of $\Delta V^{\neq}$ for the solvent exchange on the hexa(solvento)iron(III) ion are negative, while those of the Fe(III)-PhDTA complex are positive both in water and DMF: The solvent exchange proceeds via an associative interchange mechanism for the former, while a dissociative interchange mechanism is operative for the latter. Since a ligand with electron donecity such as phdta^{4-} binds to the iron(III) ion, the electron density of the iron(III) atom should increase and the bond between the metal ion and a coordinated DMF molecule may be weakened (the bound ligand effect). The solvent exchange of the Fe(III) complex with electron-donating ligand proceeds much faster and more dissociatively than that on the hexa(solvento)-iron(III) ion. The more positive activation volume for the DMF exchange may be attributed to the bulkiness of a DMF molecule compared with a water molecule. In bulkier solvents, a coordinated leaving solvent molecule may be forced to leave partly the inner sphere of the central metal ion due to steric hindrance before an entering solvent starts to coordinate (solvent bulkiness effect). In conclusion, this study has clearly demonstrated that both the bound ligand effect and the solvent bulkiness effect make the activation mode less associative for the solvent exchange of Fe(III)-PhDTA in DMF.

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