1852 © 1989 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 62, 1852—1858 (1989) [Vol. 62, No. 6

Variable-Temperature and Variable-Pressure Nitrogen-14 NMR Studies on the Exchange Reaction of Different Nitriles at the Nickel(II) Ion

Masao Ishii, Shigenobu Funahashi,* Koji Ishihara,† and Motoharu Tanaka
Laboratory of Analytical Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464-01

(Received December 5, 1988)

The activation parameters for the exchange reaction of several nitriles at the nickel(II) ion have been determined for the nickel(II) trifluoromethanesulfonate solutions by means of the ^{14}N NMR line broadening method at various temperatures and pressures up to 220 MPa. Values of activation enthalpy ($\Delta H^{\neq}$/kJ mol^{-1}), activation entropy ($\Delta S^{\neq}$/J mol^{-1} K^{-1}), and activation volume at zero pressure ($\Delta V_0^{\neq}$/cm^3 mol^{-1}) for the exchange of various nitriles are respectively as follows: 41.4±0.5, −30±2, and +12.0±0.4 in acetonitrile; 42.0 ±0.4, −25±2, and +13.7±0.5 in propionitrile; 43.3±0.7, −23±2, and +13.1±0.5 in butyronitrile; 43.3±0.5, −19±2, and +12.4±0.6 in isobutyronitrile; 47.1±1.2, −10±4, and +14.4±0.4 in valeronitrile; 51.6±1.9, +4±6, and +13.1±0.6 in benzonitrile. The activation volume varies little in spite of the large variation of the molar volume of nitriles. The activation energy (E_Q/kJ mol^{-1}) and the activation volume at zero pressure ($\Delta V_q^{\neq}$/cm^3 mol^{-1}) for the reorientation of nitrile molecules around the axis perpendicular to the C≡N bond were also determined to be respectively as follows: 7.4±0.1 and +8.3±0.4 for acetonitrile; 8.1±0.1 and +9.5±0.2 for propionitrile; 9.2±0.1 and +9.7±0.3 for butyronitrile; 9.1±0.1 and +11.3±0.2 for isobutyronitrile; 10.7±0.2 and +11.9±0.2 for valeronitrile; 12.5±0.2, and +13.5±0.2 for benzonitrile. Both E_Q and $\Delta V_q^{\neq}$ increase with increasing bulkiness of the substituent to the cyano group.

The volume of activation $\Delta V^{\neq}$ is one of the useful parameters for elucidating the reaction mechanisms.[1-4] The discussion of the reaction mechanism on the basis of $\Delta V^{\neq}$, however, is sometimes still ambiguous, since the effect of the bulkiness of reactants including solvent on the activation volume has not been thoroughly understood.

For the limiting associative (A) mechanism and the limiting dissociative (D) mechanism in the solvent exchange at metal ions, one would expect that the absolute value of the limiting activation volume $|\Delta V^{\neq}_{\mathrm{lim}}|$[3,4] is roughly equal to the molar volume of the solvent V°. Interchange mechanisms (Ia, I, and Id) will give smaller $|\Delta V^{\neq}|$ values. Therefore, not only $\Delta V^{\neq}_{\mathrm{lim}}$ but also $\Delta V^{\neq}$ for Ia and Id mechanisms would be anticipated to vary with the molar volume of solvent even for the same mechanism.

This work has been designed to elucidate the effect of the molar volume of solvent upon the value of $\Delta V^{\neq}$ for the solvent-exchange reaction. We report $\Delta V^{\neq}$ for the exchange of various nitriles at the nickel(II) ion. The utilized nitriles include acetonitrile, propionitrile, butyronitrile, isobutyronitrile, valeronitrile, and benzonitrile. We propose a model for the solvent-exchange reaction based on the volume of activation. In addition, we discuss some microscopic properties of the liquid nitriles obtained from the temperature and pressure dependence of the ^{14}N transverse relaxation time of the neat nitriles.

Experimental

Solvents. Reagent grade acetonitrile (Wako Pure Chemical Industries Co.), propionitrile (Wako), butyronitrile (Tokyo Chemical Industry Co.), isobutyronitrile (Tokyo Chemical), valeronitrile (Tokyo Chemical) were distilled twice after refluxing for 1 h in the presence of P_2O_5 (<2g dm^{-3}). Benzonitrile (Wako) was dried over P_2O_5 for 12 h and distilled twice under reduced pressure.

[Ni(H$_2$O)$_6$](CF$_3$SO$_3$)$_2$. Trifluoromethanesulfonic acid (50 g, Wako) was added dropwise to basic nickel(II) carbonate (20 g, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$, Wako) suspended in 50 cm^3 water. The resulting mixture was heated to complete the reaction and to concentrate the solution. Finally, the green salt yielded by cooling the solution was recrystallized from water and dried under vacuum at room temperature. Found: C, 5.20; H, 2.63%. Calcd for $[Ni(H_2O)_6](CF_3SO_3)_2$: C, 5.17; H, 2.60%.

Sample Preparation. Nitrile solutions of nickel(II) trifluoromethanesulfonate were prepared by dissolving the hydrated nickel(II) trifluoromethanesulfonate (ca. 4 g) in respective nitriles (ca. 60 cm^3) and removing the water under reflux for about 5 h in the modified Soxhlet extractor with Molecular Sieves 4A in the thimble.[5,6] The reflux was repeated two or three times with freshly activated molecular sieves. The nickel(II) concentration of each stock solution was determined by EDTA titration with TAMSMB (2-(2-thiazolylazo)-4-methyl-5-(sulfomethylamino)benzoic acid) as an indicator.[7] The content of water in sample solutions as determined by the Karl-Fischer titration was less than 5×10^{-3} mol kg^{-1} that corresponded to at most less than 0.05 mol/mol of Ni^{2+}.

The dilution of the stock solution and the transfer of the sample solution into an NMR tube were carried out under dry nitrogen gas in a dry box. The sample solutions for variable-temperature NMR measurement were degassed and sealed on a standard vacuum line. The nickel(II) concentrations of the NMR sample solutions were ranged over 2×10^{-2}—2×10^{-1} mol kg^{-1}.

Variable-Temperature ^{14}N NMR Measurement. ^{14}N NMR measurements were performed at various temperatures on a JEOL JNM-GX270 FT-NMR spectrometer operating at 19.51 MHz. The pulse width was 31 μs (90°) and

---

† Present address: Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku, Tokyo 160.

pulse repetition time was typically 0.15 s. The number of scans was varied between 300 and 30000 depending on the line width. An 8 mm o.d. NMR sample tube was inserted into a 10 mm o.d. NMR tube containing a lock solvent (CD_3OD or D_2O) and nitromethane as a chemical shift standard. The temperature was measured by a substitution technique using a thermistor (D111-1031 or D641, Takara Thermistor Co.). About 15 to 30 min were required for the temperature equilibration of the sample solution and the temperature stability was ±0.2 K.

Variable-Pressure ^{14}N NMR Measurement. For variable-pressure NMR experiments, a multinuclear NMR probe designed for a wide-bore superconducting magnet (6.34 Tesla) of a JEOL JNM-GX270 FT-NMR spectrometer has been newly constructed. The pressure vessel consisting of four separable parts is illustrated in Fig. 1A. The pressure pipe (1) is made of nonmagnetic titanium alloy, around which spiral is cut. A Dewar vessel (e) covers it to insulate the heat. The thermostating gas is flowed along the spiral in order to adjust the temperature in the pressure vessel. An adapter (2) made of titanium alloy is attached to facilitate insertion and withdrawal of the sample tube. Four leading wires for a saddle-shaped coil and a copper-constantan thermocouple are introduced into the electrical terminal (3). The pressure seal at this part is achieved with the cone-type seal using small copper cones covered with Daiflon (poly(chlorotrifluoroethylene), Daikin-Kogyo Co.) for insulation, and at other parts the pressure sealing is accomplished with standard cone-type seals and O-ring seals. The internal housing (4) made of titanium alloy is the guide for the sample tube and also reduces the volume of pressure-transmitting liquid filled in the pressure vessel. The pressure vessel is connected through the flexible tube (a) to a pressure-generating system[8] consisting of a high-pressure generating pump (KBP56, Hikarikouatsu) and Heise Bourdon gauges. The pressure-transmitting liquid used in this work was Daifloil #1 (poly(chlorotrifluoroethylene), Daikin-Kogyo Co.).

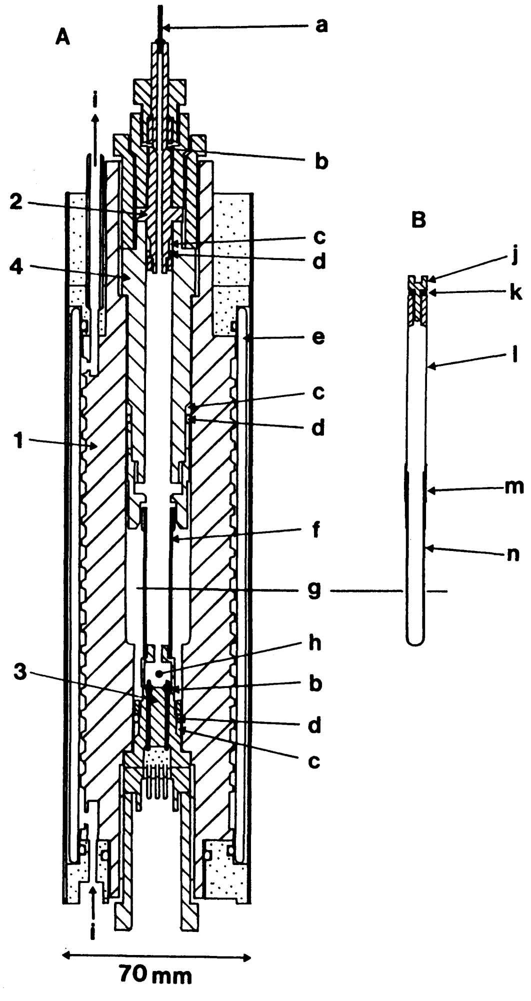

Fig. 1. High-pressure vessel and NMR sample tube for high-pressure NMR experiments.
(A) High-pressure vessel. 1, pressure pipe (titanium alloy); 2, adapter (titanium alloy); 3, electrical terminal; 4, internal housing (titanium alloy); a, flexible tube (SUS316); b, cone-type seal; c, backup ring (Teflon); d, O-ring (Viton); e, Dewar vessel; f, bobbin (glass); g, r.f. coil center; h, copper-constantan thermocouple; i, thermostating gas flow. (B) Sample tube. j, screw (Teflon); k, O-ring (silicone); l, flexible Teflon cap; m, contractive Teflon tube; n, 7 mm o.d. glass tube.

The sample tube, illustrated in Fig. 1B, is filled with the sample solution. It consists of a 7 mm o.d. glass tube and a flexible Teflon cap, both of which are connected with a contractive Teflon tube. At the top a silicone O-ring and Teflon screw are attached.

Before carrying out the high-pressure experiment, the temperature of the sample was measured by a substitution technique using a thermistor, and monitored with a thermocouple introduced into the pressure vessel during the high-pressure experiments. About 5 h were required for the complete temperature equilibration and the temperature stability over several hours was ±0.2 K.

Results and Discussion

Structure of Solvated Ni(II) Ion in Nitrile. The crystal structure of $[Ni(CH_3CN)_6](SbF_6)_2$[9] and $[Ni(CD_3CN)_6](SbF_6)_2$[10] has been determined by the X-ray diffraction method; the nickel(II) ion is octahedrally coordinated by six acetonitrile molecules with the Ni–N–C angle of 175°. The electronic absorption spectra of $Ni(BF_6)_2$,[11] $Ni(MF_6)_2$ (M=Sb, Bi),[10] and $Ni(ClO_4)_2$[6] in acetonitrile are characteristic of an octahedrally coordinated Ni^{2+} ion. The solvation number of 6 for nickel(II) ion in acetonitrile has also been confirmed by means of ^{1}H NMR.[12,13]

In Fig. 2 are shown the electronic absorption spectra of solutions of $Ni(CF_3SO_3)_2$ in various nitriles which were recorded on a UV-265FW spectrophotometer (Shimadzu) and a U-3400 spectrophotometer (Hitachi). The spectrum of acetonitrile solution is very similar to those reported,[6,10,11] and the spectra of the other nitrile solutions are also characteristic of the octahedrally coordinated Ni^{2+} ion, although the slight band shift is observed. Therefore, we can safely state that Ni^{2+} ion is octahedrally coordinated by the nitrile molecules in all solutions investigated.

Transverse Relaxation Time of ^{14}N in Neat Nitrile. Transverse relaxation time T_2 of nitrogen-14 in neat

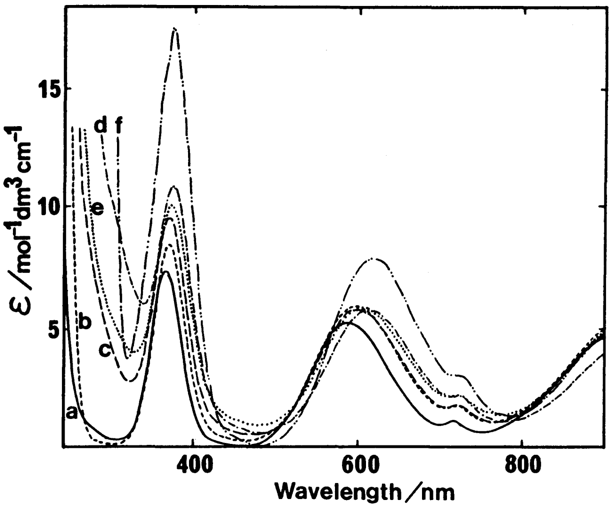

Fig. 2. Electronic absorption spectra of $Ni(CF_3SO_3)_2$ nitrile solutions. a (———), acetonitrile solution; b (---------), propionitrile solution; c (——— —), butyronitrile solution; d (— · —), isobutyronitrile solution; e (·········), valeronitrile solution; f (—··—), benzonitrile solution.
The values of ε are somewhat ambiguous, since the concentrations of the solution in the unit of mol kg^{-1} are transformed into the unit of mol dm^{-3} using the density of the neat solvent.

nitrile is evaluated from the half-height width of the ^{14}N NMR spectrum ($T_2=(\pi\Delta\nu)^{-1}$). Since reorientation of acetonitrile molecules around the axis perpendicular to the C≡N bond in the liquid state is very rapid, ^{14}N ($I=1$) transverse relaxation rate (T_2^{-1}) of acetonitrile is equal to the longitudinal relaxation rate (T_1^{-1}),[14] and these are expressed as follows:

$$T_1^{-1}=T_2^{-1}=\frac{3}{2}\pi^2\chi^2\left(1+\frac{1}{3}\xi^2\right)\tau_q \qquad (1)$$

where χ/Hz is the quadrupole coupling constant ($\chi=e^2Qq/h$), τ_q/s is the correlation time characterizing the reorientation about the axis perpendicular to the C≡N bond and ξ is the asymmetry parameter. This equation is valid for the ^{14}N nuclear relaxation in all the studied nitriles. The temperature and pressure dependence of the relaxation time may be attributable to the variation of τ_q.[14,15]

The temperature dependences of T_2 for ^{14}N of nitriles are shown in Fig. 3. The data were conventionally analyzed by using Eq. 2:

$$\ln T_2=\ln T_2^{298.2}-E_Q(1/T-1/298.2)/R \qquad (2)$$

where $T_2^{298.2}$ and E_Q refer to T_2 at 298.2 K and the activation energy for the reorientation, respectively. The values of $T_2^{298.2}$ and E_Q for acetonitrile are in good agreement with the literature values.[6,14,16] The obtained parameters are listed in Table 1.

By using Eq. 1, we can estimate values of the rate constant (τ_q^{-1}) of the reorientation for some nitriles of which the values of χ and ξ are available; values of τ_q^{-1}

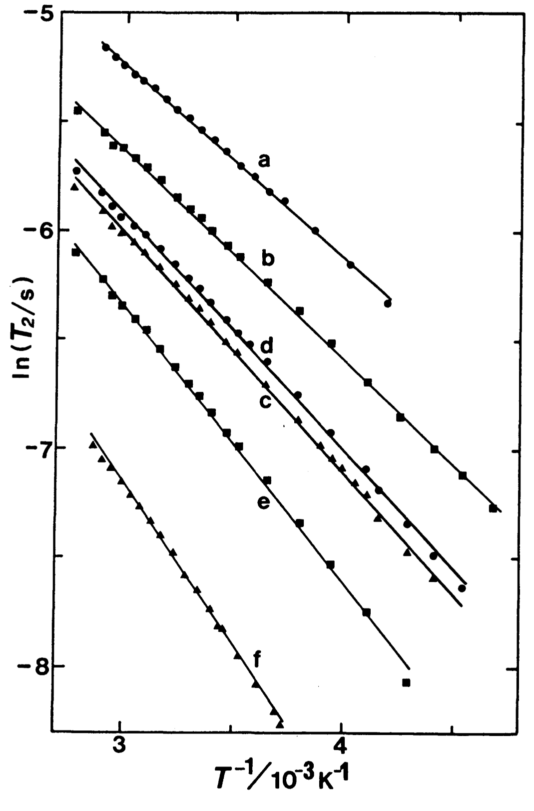

Fig. 3. Temperature dependences of T_2/s for ^{14}N of nitriles. a, acetonitrile; b, propionitrile; c, butyronitrile; d, isobutyronitrile; e, valeronitrile; f, benzonitrile.

Table 1. Transverse Relaxation Time of ^{14}N and Activation Parameters for Reorientation of Nitrile[a)]

Solvent	$T_2^{298.2}$	E_Q	$\Delta V_q^{\ddagger}$		$10^2\Delta\beta_q^{\ddagger}$	$V^{ob)}$
	s	kJ mol⁻¹	cm³ mol⁻¹		cm³ mol⁻¹ MPa⁻¹	cm³ mol⁻¹
Acetonitrile	3.88×10⁻³	7.4±0.1	+8.3±0.4	(332 K)	+2.0±0.4	52.9
Propionitrile	2.56×10⁻³	8.1±0.1	+9.5±0.2	(330 K)	+2.0±0.2	70.9
Butyronitrile	1.66×10⁻³	9.2±0.1	+9.7±0.3	(329 K)	+1.5±0.3	87.9
Isobutyronitrile	1.82×10⁻³	9.1±0.1	+11.3±0.2	(328 K)	+2.2±0.2	90.3
Valeronitrile	1.12×10⁻³	10.7±0.2	+11.9±0.2	(329 K)	+2.4±0.2	104.6
Benzonitrile	4.59×10⁻⁴	12.5±0.2	+13.5±0.2	(332 K)	+2.0±0.2	103.1

a) Errors quoted are standard deviations. b) Molar volume at 298.2 K. Calculated using the data taken from J. A. Riddick, W. B. Bunger, and T. K. Sakano, "Organic Solvents," 4th ed, Wiley-Interscience, New York (1986).

at 298.2 K and corresponding $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are 8.0×10^{11} s^{-1}, 5.0 ± 0.1 kJ mol^{-1}, and -0.3 ± 0.4 J mol^{-1} K^{-1} ($\chi=3.738$ MHz, $\xi=0.46\times10^{-2}$)[17] for acetonitrile, 5.4×10^{11} s^{-1}, 5.8 ± 0.1 kJ mol^{-1}, and -1.0 ± 0.4 J mol^{-1} K^{-1} ($\chi=3.776$ MHz, $\xi=2.08\times10^{-2}$)[17] for propionitrile, and 1.0×10^{11} s^{-1}, 9.9 ± 0.2 kJ mol^{-1}, and -1.0 ± 0.6 J mol^{-1} K^{-1} ,($\chi=3.885$ MHz, $\xi=10.73\times10^{-2}$)[18] for benzonitrile. It is to be noted that the reorientation of these nitriles is characterized by very small entropy values. Since χ values in different nitriles change no more than a few percent and the contribution of $\xi^2/3$ is negligibe,[14] the difference of τ_q is considered to be exclusively responsible for the difference of T_2. Therefore the rate of reorientation is in the order: acetonitrile > propionitrile > isobutyronitrile≃butyronitrile > valeronitrile > benzonitrile.

Plots of $\ln T_2$ vs. pressure are shown in Fig. 4. Since all plots are slightly curved, the data were analyzed according to the quadratic equation:

$$\ln T_2 = \ln T_2{}^0 - \Delta V_q{}^{\neq} P/RT + \Delta\beta_q{}^{\neq} P^2/2RT \qquad (3)$$

where $\Delta V_q{}^{\neq}$ is the activation volume for the reorientation by rotation about the axis perpendicular to the C≡N bond at zero pressure and $\Delta\beta_q{}^{\neq}$ is the compressibility coefficient of activation. The parameters obtained are listed in Table 1 together with the molar volume of the solvent V°. The value of $\Delta V_q{}^{\neq}$ for acetonitrile ($+8.3\pm0.4$ cm^3 mol^{-1}) is in excellent agreement with that ($+8.5\pm1.4$ cm^3 mol^{-1}) obtained by Bull and Jonas[15] and the agreement is fair with the value ($+6.4\pm0.2$ cm^3 mol^{-1}) obtained by Swaddle et al.[6] There is a trend that $\Delta V_q{}^{\neq}$ increase slightly with the increase of V°. In conclusion, correlation time, activation energy, and activation volume for reorientation increase with increasing bulkiness of substituent to the cyano group.

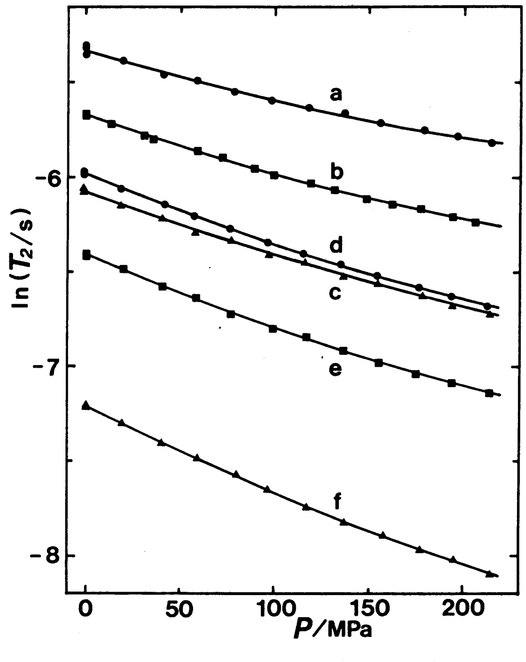

Fig. 4. Pressure dependences of T_2/s for ^{14}N of nitriles. a, acetonitrile; b, propionitrile; c, butyronitrile; d, isobutyronitrile; e, valeronitrile; f, benzonitrile.

Solvent Exchange at the Nickel(II) Ion in Nitrile. The rate for rapid solvent exchange between the bulk and the coordination site of a paramagnetic metal ion can be derived from the transverse relaxation rate of the bulk solvent nuclei.[19–21] The nitrile ^{14}N line broadening, $(T_{2p}P_M)^{-1}$, caused by the interaction with the nickel(II) ion can be expressed as Eq. 4:

$$(T_{2p}P_M)^{-1} = \pi(\Delta\nu_{\rm obsd} - \Delta\nu_{\rm solv})P_M{}^{-1} \qquad (4)$$

where P_M is the ratio of the number of nitrile molecules bound to nickel(II) to that in the bulk, $\Delta\nu_{\rm obsd}$ and $\Delta\nu_{\rm solv}$ are the full widths at half-height of the ^{14}N NMR signal for the bulk nitrile of the nickel(II) nitrile solution and of the neat nitrile, respectively. For $P_M \ll 1$, $(T_{2p}P_M)^{-1}$ is given by the modified Swift-Connick equation (Eq. 5):[19–21]

$$\frac{1}{T_{2P}P_M} = \frac{1}{\tau_M}\,\frac{T_{2M}{}^{-2} + (T_{2M}\tau_M)^{-1} + \Delta\omega_M{}^2}{(T_{2M}{}^{-1} + \tau_M{}^{-1})^2 + \Delta\omega_M{}^2} + \frac{1}{T_{2O}} \qquad (5)$$

in which symbols have their usual meaning.[22] We measured the NMR spectra of sample solutions with two or three different concentrations of nickel(II) trifluoromethanesulfonate at various temperatures. The observed line widths $(\Delta\nu_{\rm obsd} - \Delta\nu_{\rm solv})$ are excellently proportional to the P_M value. The temperature dependences of $(T_{2P}P_M)^{-1}$ for the nitrile solutions of $\rm Ni(CF_3SO_3)_2$ are shown in Fig. 5. Since $\Delta\omega_M{}^2 \gg \tau_M{}^{-2}$, $T_{2M}{}^{-2}$ over the temperature range of our experiment, Eq. 5 is simplified to Eq. 6:

$$(T_{2P}P_M)^{-1} = \tau_M{}^{-1} + T_{2O}{}^{-1} \qquad (6)$$

where $\tau_M{}^{-1}$ is equivalent to the rate constant $k_{\rm ex}$ for the solvent-exchange reaction ($k_{\rm ex} = k_BT/h \exp(-\Delta H^{\neq}/RT + \Delta S^{\neq}/R)$) and $T_{2O}{}^{-1}$ ($= C_O/T \exp(E_O/RT)$) is the relaxation term due to the interaction in the outer sphere of the nickel(II) ion. We analyzed the data according to Eq. 6 by a least-squares fitting and obtained the kinetic parameters listed in Table 2.

The variable-pressure ^{14}N NMR experiments have been performed at about 330 K where the outer-sphere contribution $T_{2O}{}^{-1}$ is negligible so that $(T_{2P}P_M)^{-1}$ is exclusively ascribed to the solvent-exchange contribution $\tau_M{}^{-1}$. The pressure dependences of $k_{\rm ex(p)}$ ($=\tau_M{}^{-1} = (T_{2P}P_M)^{-1}$ at a given temperature) are presented in Fig. 6. $k_{\rm ex(p)}$ can be expressed as Eq. 7:

$$\ln k_{\rm ex(p)} = \ln k_{\rm ex(0)} - \Delta V_0{}^{\neq} P/RT + \Delta\beta^{\neq} P^2/2RT \qquad (7)$$

where $k_{\rm ex(0)}$ is the rate constant at zero pressure, $\Delta V_0{}^{\neq}$is the volume of activation at zero pressure, and $\Delta\beta^{\neq}$ is the compressibility coefficient of activation. The kinetic parameters are evaluated by a least-squares fitting of the data to Eq. 7 and are listed in Table 2. The $\Delta V_0{}^{\neq}$ value for the reaction in acetonitrile is in good agreement with that obtained by Merbach et

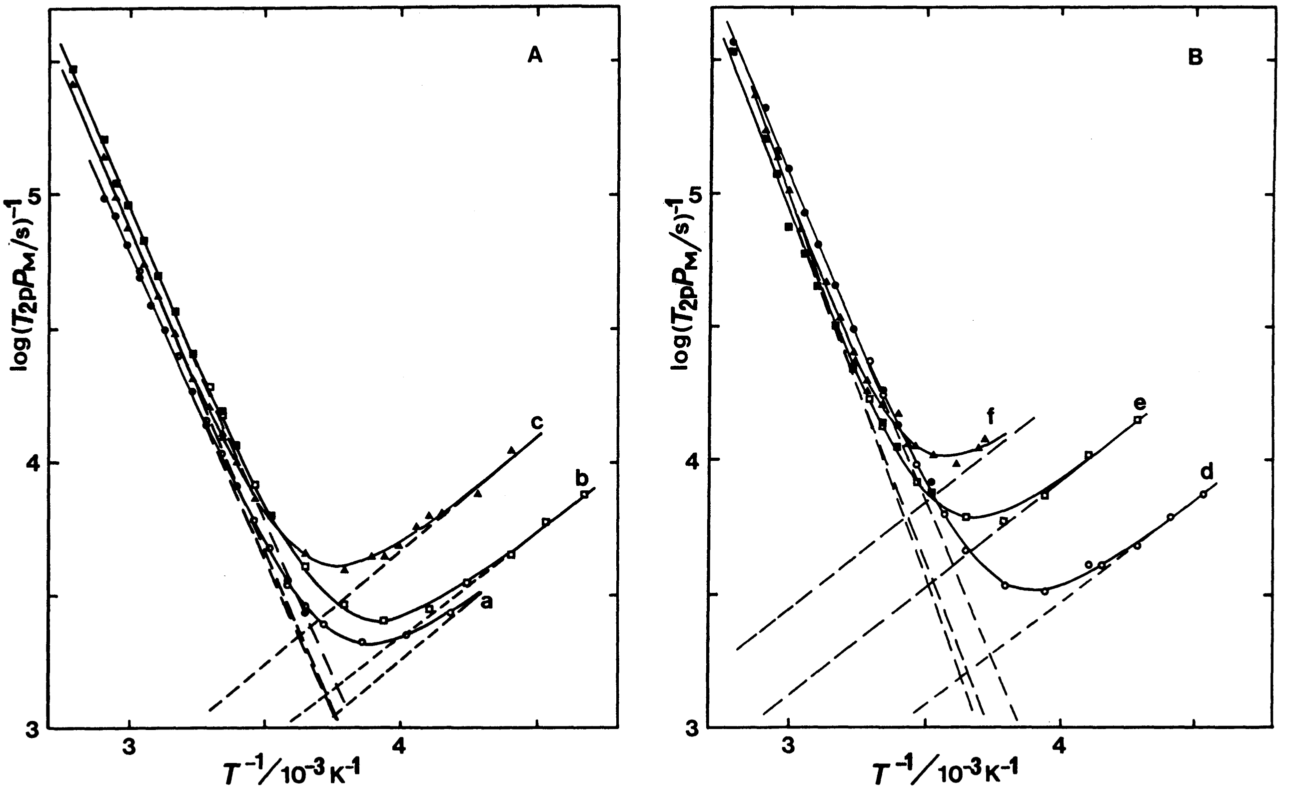

Fig. 5. Temperature dependences of $(T_{2P}P_M)^{-1}/s^{-1}$.
(A) a, acetonitrile solution (●: P_M=1.49×10^{-2}, ◐: P_M=3.19×10^{-2}, ○: P_M=4.39×10^{-2}); b, propionitrile solution (■: P_M=2.27×10^{-2}, □: P_M=5.73×10^{-2}); c, butyronitrile solution (▲: P_M=2.12×10^{-2}, △: P_M=4.24×10^{-2}). (B) d, isobutyronitrile solution (●: P_M=2.06×10^{-2}, ○: P_M=3.80×10^{-2}); e, valeronitrile solution (■: P_M=2.07×10^{-2}, □: P_M=4.19×10^{-2}); f, benzonitrile solution (▲: P_M=1.63×10^{-2}, △: P_M=4.505×10^{-2}). Dashed lines show the contribution of τ_M^{-1} and T_{2O}^{-1}.

Table 2. Kinetic Parameters for Nitrile Exchange at Nickel(II)[a]

Solvent	$k_{ex}^{298.2}$	$\Delta H^{\ne}$	$\Delta S^{\ne}$	$\Delta V_0^{\ne}$		$10^2\Delta\beta^{\ne}$
	s^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}	cm^3 mol^{-1}		cm^3 mol^{-1} MPa^{-1}
Acetonitrile	6.24×10^3	41.4±0.5	−30±2	+12.0±0.4	(332 K)	4.0±0.3
Propionitrile	1.33×10^4	42.0±0.4	−25±2	+13.7±0.5	(330 K)	2.3±0.2
Butyronitrile	1.04×10^4	43.3±0.7	−23±2	+13.1±0.5	(329 K)	4.1±0.4
Isobutyronitrile	1.59×10^4	43.3±0.5	−19±2	+12.4±0.6	(328 K)	3.8±0.6
Valeronitrile	9.99×10^3	47.1±1.2	−10±4	+14.4±0.4	(329 K)	5.0±0.4
Benzonitrile	9.38×10^3	51.6±1.9	+4±6	+13.1±0.6	(332 K)	6.3±0.6

a) Errors quoted are standard deviations.

al. (+11.3±1.0 cm^3 mol^{-1}).[23)]

In spite of the large variation of V° of the nitriles (53—105 cm^3 mol^{-1}), little change is observed in the activation volumes for the solvent exchange at nickel(II) (12.0—14.4 cm^3 mol^{-1}): the molar volume of solvent itself has little influence upon $\Delta V^{\ne}$ for the exchange reaction of nitriles.

In order to consider the activation volume for the solvent exchange at a metal ion, we now define the inner sphere of the solvated metal ion as the sphere into which the solvent molecules in the bulk can not penetrate at the initial state (see Fig. 7). The activation volume for the solvent exchange is thought to be the difference between the volume V_d that the leaving solvent loses in the inner sphere and the volume V_a that the entering solvent gets in the inner sphere at the transition state, as illustrated in Fig. 7. According to the molecular model constructed with van der Waals's radii of atoms, the nitrile molecules in the bulk can penetrate into the gaps among the bound nitriles without any steric hindrance regardless of the bulkiness of the substituent: the inner sphere does not include the substituent to cyano group and its size does not depend on the bulkiness of the nitrile. In fact the $\Delta V^{\ne}$ value is positive and varies little from solvent to solvent. Therefore both V_a and V_d are

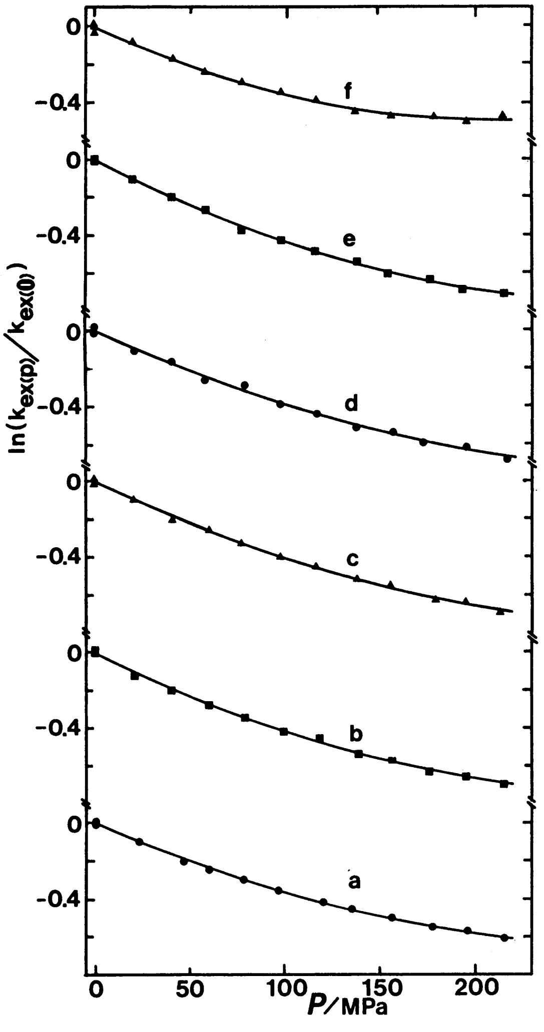

Fig. 6. Pressure dependences of $k_{ex(p)}/k_{ex(0)}$ for solvent exchange at Ni^{2+} in nitriles.
a, acetonitrile solution ($P_M=1.76\times10^{-2}$); b, propionitrile solution ($P_M=2.07\times10^{-2}$); c, butyronitrile solution ($P_M=2.39\times10^{-2}$); d, isobutyronitrile solution ($P_M=2.02\times10^{-2}$); e, valeronitrile solution ($P_M=3.02\times10^{-2}$); f, benzonitrile solution ($P_M=4.05\times10^{-2}$).

expected to be almost the same for all the studied nitriles. After all, the mechanism of the nitrile exchange at the nickel(II) ion is of the similar dissociative character for different nitriles of different bulkiness.

There is no parallel relation between $\Delta S^{\neq}$ and $\Delta V_0^{\neq}$ in the present systems (Table 2). The activation volume reflects the difference in nuclear positions between reactants and transition state, while the alternative concept of activation entropy seems to reflect the difference in both nuclear positions and energy.[24] Thus the solvent-solvent interaction may contribute considerably to values of $\Delta S^{\neq}$.[25] In the present system, acetonitrile liquid is highly structured due to strong dipole-dipole interactions, and the coordination sphere of the central nickel(II) ion has a definite octahedral structure. There should be the less ordered secondary sphere between the coordination sphere and the bulk solvent (B region according to the Frank-Wen model).[26] Therefore the leaving acetonitrile molecule in the activation process may strongly interact with the solvent molecules in the secondary sphere, and then the entropy of activation should become largely negative. Thus we anticipate a trend that the solvent interaction in the transition state should become smaller, and accordingly $\Delta S^{\neq}$ values may become larger with increasing size of solvent molecules. We notice such a trend for values of $\Delta S^{\neq}$ in Table 2. In conclusion, the sign of $\Delta V^{\neq}$ is useful for diagnosing the mechanism, whereas the interpretation of $\Delta S^{\neq}$ in terms of mechanism is likely to be complicated by the solvent-solvent interactions.

This work was supported by a Grant-in-Aid for Scientific Research (No. 62470041) from the Ministry of Education, Science and Culture. We thank Professor Jiri Jonas (University of Illinois) for his useful advice and Mr. Sadao Kanbe (JEOL) for his technical assistance on the construction of our high-pressure NMR probe.

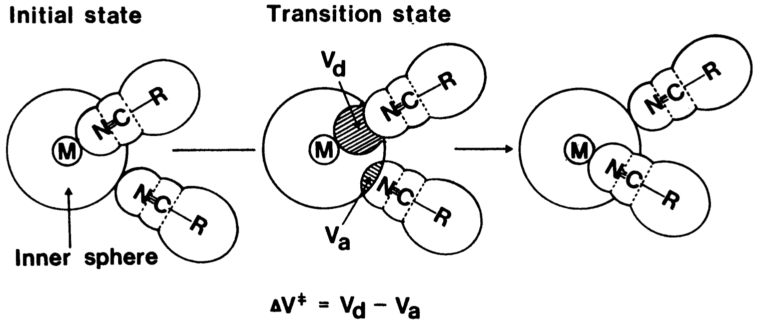

Fig. 7. Illustration for solvent exchange at a metal ion. The non-exchanging solvent molecules are omitted for simplicity; V_d, the volume that the leaving solvent molecule loses from the inner sphere in the activation process; V_a, the volume that the entering solvent molecule gets in the inner sphere in the activation process. The activation volume $\Delta V^{\neq}$ is represented as $\Delta V^{\neq}=V_d-V_a$.

References

1) A. E. Merbach, *Pure Appl. Chem.*, **54**, 1479 (1982).

2) T. W. Swaddle, *Adv. Inorg. Bioinorg. Mech.*, **2**, 95 (1983).

3) A. E. Merbach, *Pure Appl. Chem.*, **59**, 161 (1987).

4) "Inorganic High Pressure Chemistry : Kinetics and Mechanisms" ed by R. van Eldik, Elsevier, Amsterdam (1986).

5) P. Arthur, W. M. Haynes, and L. P. Varga, *Anal. Chem.*, **38**, 1630 (1966).

6) Y. Yano, M. T. Fairhurst, and T. W. Swaddle, *Inorg. Chem.*, **19**, 3267 (1980).

7) T. Ishizuki, H. Wada, and G. Nakagawa, *Bunseki Kagaku*, **28**, 535 (1979).

8) M. Ishii, S. Funahashi, and M. Tanaka, *Inorg. Chem.*, **27**, 3192 (1988).

9) I. Leban, D. Gantar, B. Frlec, D. R. Russell, and J. H. Holloway, *Acta Crystallogr., Sect. C. Cryst. Struct. Commun.*, **34**, 1888 (1987).

10) R. Bougon, P. Charpin, K. O. Christe, J. Isabey, M. Lance, M. Nierlich, J. Vigner, and W. W. Wilson, *Inorg. Chem.*, **27**, 1389 (1988).

11) B. J. Hathaway and D. G. Holah, *J. Chem. Soc.*, **1964**, 2400.

12) K. E. Newman, F. K. Meyer, and A. E. Merbach, *J. Am. Chem. Soc.*, **101**, 1470 (1979).

13) S. Chopra, R. E. D. McClung, and R. B. Jordan, *J. Magn. Reson.*, **59**, 361 (1984).

14) W. B. Moniz and H. S. Gustowsky, *J. Chem. Phys.*, **38**, 1155 (1963).

15) T. E. Bull and J. Jonas, *J.Chem. Phys.*, **53**, 3315 (1970).

16) T. T. Bopp, *J. Chem. Phys.*, **47**, 3621 (1967).

17) P. A. Casabella and P. J. Bray, *J. Chem. Phys.*, **29**, 1105 (1958).

18) H. Negita and P. J. Bray, *J. Chem. Phys.*, **33**, 1876 (1960).

19) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

20) Z. Luz and S. J. Meiboom, *J. Chem. Phys.*, **40**, 1058 (1964).

21) L. L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **15**, 709 (1976).

22) A. Hioki, S. Funahashi, and M. Tanaka, *J. Phys. Chem.*, **89**, 5057 (1985).

23) F. K. Meyer, K. E. Newman, and A. E. Merbach, *Inorg. Chem.*, **18**, 2142 (1979).

24) S. Funahashi, K. Ishihara, and M. Tanaka, *Inorg. Chem.*, **22**, 2070 (1983).

25) E. F. Caldin and H. P. Bennetto, *J. Solution Chem.*, **2**, 217 (1973); H. P. Bennetto and E. F. Caldin, *J. Chem. Soc. A*, **1971**, 2198.

26) H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).