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# Nitrogen-14 Magnetic Resonance Studies of the Effect of Pressure on the Exchange of Ammonia in Aqueous Nickel(II)-Ammonia Solutions

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The effect of temperature and pressure on the rate of exchange of $NH_3$ with $Ni(NH_3)_6^{2+}$ in 15 M aqueous $NH_3$ was measured by $^{14}NH_3$ NMR line broadening and shift. The pseudo-first-order rate constant for departure for a particular $NH_3$ from the inner sphere of $Ni(NH_3)_6^{2+}$ was found to be $k_1(25\ ^\circ C) = 7.0 \times 10^4\ s^{-1}$ with $\Delta H^* = 13.7$ kcal mol$^{-1}$, $\Delta S^* = +9.6$ cal mol$^{-1}$ K$^{-1}$ and $\Delta V^* = +5.9$ cm$^3$ mol$^{-1}$. The contact coupling constant $(A/h)$ for $^{14}NH_3$ was 15.1 MHz. A dissociative-interchange mechanism is suggested by the results. A similarity in the transverse relaxation of $^{14}NH_3(aq)$ and $^{17}OH_2$ was observed and ascribed to similar hydrogen bond breaking and formation rates as the mechanism for relaxation.

## Introduction

Swaddle[1] has described a high-pressure $^{14}N$ NMR study of acetonitrile in neat acetonitrile–Ni(II) solutions. Also Merbach and co-workers[2] have done several pioneering studies at high pressure using $^1H$ NMR for nonaqueous systems including nitrogen-donor ligands and solvents.

The system Ni(II)–aqueous ammonia is of interest in comparing the neat solvent work with that for a mixed solvent. Solvation and/or outer-sphere effects should be different than in pure solvents, and some insight may be gained concerning these effects.

An early study[3] was made on the Ni(II)–ammonia system using $^{14}N$ NMR in aqueous and liquid ammonia in our laboratories, and it has seemed worthwhile to apply our newest techniques to this system. The main objective of the high-pressure studies is, of course, to obtain mechanistic information, as le Noble,[4] Stranks,[5] Swaddle,[6] and others have emphasized, by obtaining $\Delta V^*$ values.

## Experimental Section

**Materials.** Baker Analyzed reagent ammonia (15 M) was used as well as their ammonium nitrate and zinc nitrate. The nickel nitrate was Mallinckrodt Analytical reagent grade.

**NMR Measurements.** These were made at 6.505 MHz with a field-locked spectrometer and procedures developed in these laboratories.[7] Atmospheric-pressure samples were run in sealed 12-mm Pyrex tubes. The reference solutions for shifts and line broadenings were either zinc–ammonia solutions or aqueous $NH_3$ alone. No measurable differences were seen at the concentrations used. Spectra were taken with a frequency-swept, frequency-modulated marginal oscillator. Previously used magnetic modulation was impractical in the presence of a thick-wall pressure vessel, so frequency modulation was used. A modulation frequency of 5 kHz was used with phase-sensitive detection, phased to give the center sideband. Frequency modulation was produced with a varactor in the tank circuit, and amplitude modulation was canceled by a varactor in the feedback circuit. This allowed sweeps of 10 kHz with a reasonably flat base line.

For the high-pressure measurements the tank coil and a copper–constantan thermocouple were placed inside a 1-in. o.d. by $^1/_2$-in. i.d. pressure vessel fabricated from Ti6Al-4V alloy. The electrical leads were brought out through a self-sealing plug at the bottom of the vessel. Connection to the pressurizing pump was made through the top of the vessel via a sample interchange device, which permitted interchange of the nickel-containing sample and a blank while under pressure. The interchange was accomplished by a solenoid acting on an iron armature inside the pressure system. The interchange device made possible the measurement of the width and frequency of the sample and blank under identical conditions. This makes accurate shift measurements possible and provides cancellation of field inhomogeneity contributions to line width. Measurements on samples with narrow lines indicated field inhomogeneities of 3–5 Hz inside the pressure vessel. Tellus oil was used in the system, and pressures were generated with a Pressure Products Industries Model 102-60 hand pump. Pressures accurate to ±0.4 MPa were read from a 16-in. Heise Pressure Gauge gauge attached to the system. The pressure vessel was immersed in silicone oil circulated from a thermostat.

Sample temperatures were known to about ±0.1 K. The sample container for the high-pressure work was a thin-wall polyethylene tube 0.2-in. o.d. by 1 in. long. The center portion contained a fused-in solid polyethylene plug, and the ends were sealed with fused-on polyethylene disks. The sample was put in one end through a fine polyethylene tube, which was then heat sealed. The blank was placed in the opposite end. A movement of $^3/_4$ in. was sufficient to interchange the sample and blank in the rf coil.

All spectra were collected in a signal averager, transferred to the memory of a microprocessor-based computer, and fitted with a digitally computed Lorentzian line shape to yield widths and center frequencies. Measurements were made at several rf levels, and widths were extrapolated to zero rf level.

## Data Treatment and Results

The line width and frequency of $^{14}NH_3$ in 15 M $NH_3$ was measured as a function of temperature and pressure. The results are shown in Figure 1 as a plot of ln $T_2$ vs. $1/T$ at 1 atm along with ln $T_2$ vs. pressure at 30.3 and 14.6 °C. A linear least-squares fit of the pressure data with the equation $\ln T_2 = -P\Delta V^*/RT + \ln T_{20}$, where $\Delta V^*$ is the volume of activation for relaxation of the $^{14}N$ nucleus, gave $\Delta V^* = 1.5 \pm 0.2$ and $+1.9 \pm 0.4$ cm$^3$ mol$^{-1}$ at the two temperatures, respectively. The line width of $^{14}NH_3$ increased with increasing pressure as observed[1] for $CH_3CN$, which had a larger $\Delta V^*$ of 6.3 cm$^3$ mol$^{-1}$, and was opposite to the results of $^{17}OH_2$, which shows[2] a small decrease in line width as pressure increases.

The $^{14}NH_3$ resonance frequency increases about 0.09 Hz MPa$^{-1}$ at the two temperatures.

The temperature dependence of $T_2$ for $^{14}NH_3(aq)$ is remarkably similar to that[11] of $T_1$ for $^{17}OH_2$ (we assume $T_1 = T_2$ for $^{14}NH_3(aq)$). The solid line in Figure 1 gives the $T_1$ values for $^{17}OH_2$ displaced downward by 1.16 units, i.e., a factor of 3.2 in $T_1$. The apparent activation energy for $T_2$ ranges from ~3 to ~5 kcal mol$^{-1}$ from 100 to 0 °C and is clearly virtually identical with that of $T_1$ for $^{17}OH_2$ over the same temperature range. For comparison a line in Figure 1 gives $T_2$ for $CH_3CN$, and its activation energy[1] is 1.8 kcal mol$^{-1}$.

The atmospheric-pressure temperature dependence of line widths and shifts for Ni(II)–$NH_3$ solutions was measured in detail and with care. The data were treated by essentially the same method as used for the aquo–nickel system.[7] The quantities $T_{2p}^*$ and $Q$ are plotted vs. $1/T$ on a semilog scale in Figure 2. As before, we define $T_{2p}^* \equiv [Ni]/\pi(\Delta\nu)[NH_3]$ and $Q \equiv TS[NH_3]/[Ni]$, where $\Delta\nu$ is the increase in the full

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

(2) Meyer, F. K.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1979**, *18*, 2754.

(3) Glaeser, H. H.; Lo, G. A.; Dodgen, H. W.; Hunt, J. P. *Inorg. Chem.* **1965**, *4*, 206.

(4) Asano, T.; le Noble, W. T. *Chem. Rev.* **1978**, *78*, 407.

(5) Stranks, D. R. *Pure Appl. Chem.* **1974**, *3*, 303.

(6) Swaddle, T. W. *Coord. Chem. Rev.* **1974**, *14*, 217.

(7) Bechtold, D. B.; Liu, G.; Dodgen, H. W.; Hunt, J. P. *J. Phys. Chem.* **1978**, *82*, 333.

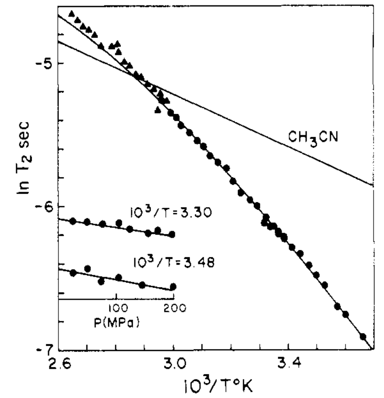

**Figure 1.** ln $T_2$ vs. $1/T$ for $^{14}NH_3$: (●) 15 M $NH_3$; (▲) 0.1 M $Zn(NO_3)_2$ in 15 M $NH_3$. The insert at the left shows the effect of pressure.

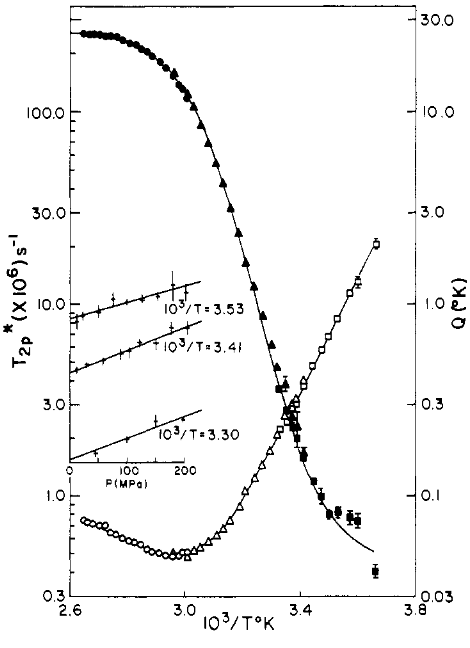

**Figure 2.** $T_{2p}$* and $Q$ vs. $1/T$ for the aqueous Ni(II)–$NH_3$ system (open symbols denote the blank solutions): (● and ○) 0.01 M Ni(II) in 15 M $NH_3$, 15 M $NH_3$ blank; (▲ and △) 0.01 M Ni(II) in 15 M $NH_3$, 0.1 M Zn(II) in 15 M $NH_3$ blank; (■ and □) 0.1 M Ni(II) in 15 M $NH_3$, 0.1 M Zn(II) in 15 M $NH_3$ blank; (+) 0.05 M Ni(II) and 1 M $NH_4NO_3$ in 15 M $NH_3$, 0.1 M Zn(II) and 1 M $NH_4NO_3$ in 15 M $NH_3$ blank (only $T_{2p}$ shown). The small insert at the left shows pressure effects on $T_{2p}$*.

line width over the blank and $S$ is the relative shift, $\Delta\omega/\omega_0$, where $\omega_0$ is the reference frequency. The $T_{2p}$* and $Q$ data were fitted to a complete Swift–Connick equation[7] with use of a nonlinear least-squares program with $n = 6$, i.e., assuming $Ni(NH_3)_6^{2+}$ as the only species present. The parameters from the fitting are $k_1(25\ °C) = (6.96 \pm 0.05) \times 10^4\ s^{-1}$, $\Delta H^* = 13.70 \pm 0.07$ kcal mol$^{-1}$, $\Delta S^* = +9.6 \pm 0.2$ cal mol$^{-1}$ K$^{-1}$, $T_{2M}(72\ °C) = (3.81 \pm 0.04) \times 10^{-6}$ s, and $E_a = -1.8 \pm 0.1$ kcal mol$^{-1}$ for $T_{2M}$. The errors given are estimates of standard deviations given by the fitting program. Also $Q$(lim) = 26.5 ± 0.07 K and $Q$(outer sphere) = 0.057 ± 0.004 K, which yield an inner-sphere contact interaction, $A/h = 15.11 \pm 0.05$ MHz, with a spin-only value assumed for the magnetic moment of $Ni(NH_3)_6^{2+}$.

The flat region for $Q$ at high temperature suggests that no temperature-dependent equilibria are seriously involved, as, for example, $Ni(NH_3)_6^{2+} + H_2O \rightleftarrows Ni(H_2O)(NH_3)_5^{2+} + NH_3$, which would be expected to produce a temperature-dependent $Q$ in the fast- (high-temperature) exchange region and invalidate the assumption of $n = 6$. Further support for the absence of any stoichiometrically significant amount of $Ni(H_2O)(NH_3)_5^{2+}$ was obtained by measuring the shift and broadening of the $^{17}OH_2$ resonance line at natural abundance at 30.3 and 51.3 °C. The results were $T_{2p}^* = (3.1 \pm 0.9) \times 10^{-5}$ s, $Q = 0.36 \pm 0.01$ K and $T_{2p}^* = (5 \pm 2) \times 10^{-5}$ s, $Q = 0.49 \pm 0.01$ K at the respective temperatures. We assume that water would be in the fast-exchange limit[14] in $Ni(H_2O)(NH_3)_5^{2+}$ and conclude there is <0.1 $H_2O$ bound per Ni in 15 M $NH_3$ from the observed $Q$ values since one would expect $Q > 0.4$ K for 0.1 bound $H_2O$.[7] A more precise value cannot be determined because of uncertainties in outer-sphere shifts for $^{17}OH_2$. The $T_{2p}$* values for $^{17}OH_2$ are not inconsistent with the above conclusions but cannot be used to set limits on bound $H_2O$'s because $T_{2M}$ for $^{17}OH_2$ is unknown in this case.

Table I. Kinetic Parameters for Solvent Exchange on Ni(II)

| solvent | $k_1$(298 K), s$^{-1}$ | $\Delta H^\ddagger$, kcal mol$^{-1}$ | $\Delta S^\ddagger$, cal mol$^{-1}$ K$^{-1}$ | $\Delta V^\ddagger$, cm$^3$ mol$^{-1}$ | ref |
|---|---|---|---|---|---|
| $NH_3$(aq) | 7.0 × 10$^4$ | 13.7 | 9.6 | 6 | this work |
| $H_2O$ | 3.14 × 10$^4$ | 13.6 | 7.7 | 7.2 | 7, 9 |
| DMF | 3.8 × 10$^3$ | 15.0 | 8.0 | 9.1 | 2 |
| $CH_3CN$ | 3.1 × 10$^3$ | 14.5 | 6.2 | 7.3 | 1 |
| $CH_3OH$ | 1.0 × 10$^3$ | 15.8 | 8.0 | 11.4 | 2 |
| $NH_3$(aq)$^a$ | 6.5 × 10$^3$ | 10 | −6 | 6.0 | 10 |

$^a$ Substitution on $Ni(H_2O)_6^{2+}$ by $NH_3$(aq) at 303 K. Units of $k$ are M$^{-1}$ s$^{-1}$.

The pressure study was done at 30.0, 20.2, and 10.0 °C on solutions containing 1 M $NH_4NO_3$ and 15 N $NH_3$. The $T_{2p}$* values vs. $P$ are plotted in Figure 2. The blank in this case contained 1 M $NH_4NO_3$ and showed a $\Delta V^* = 3.0 \pm 0.3$ cm$^3$ mol$^{-1}$ for $T_2$ of $^{14}NH_3$ and a frequency change with pressure of 0.11 Hz MPa$^{-1}$ at the above temperatures. These values are slightly different from those in the absence of $NH_4NO_3$ and may represent an effect of the salt on the solution structure. Previous work[3] has shown that $NH_4NO_3$ has a negligible effect on the $Ni(NH_3)_6^{2+}$–$NH_3$ exchange rate, and this is confirmed by the satisfactory agreement between $T_{2p}$* extrapolated to 1 atm from the pressure measurements and the $T_{2p}$* at the corresponding temperature obtained in the 1-atm measurements on solutions that contained no $NH_4NO_3$. Since the pressure measurements were made in the Arrhenius region where $T_{2p}^* = \tau_M/n = (k_1n)^{-1}$, a linear least-squares fit of the pressure data was made to the equation $\ln T_{2p}^* = P\Delta V^*/RT + \ln T_{(2p)_0}^*$, where $\Delta V^* = 6.6 \pm 1$, $6.6 \pm 0.6$, and $4.7 \pm 0.7$ cm$^3$ mol$^{-1}$ at the respective temperatures above. The $\Delta V^*$ values seem to be reasonably independent of pressure and temperature, and the weighted average of the above values is 5.9 ± 0.4 cm$^3$ mol$^{-1}$.

The effect of pressure on the shift was small and difficult to measure. Appoximate values are $dQ/dP = -1 \times 10^{-3}$ K MPa$^{-1}$ at 30.0 °C and $-2 \times 10^{-4}$ K MPa$^{-1}$ at 20.2 and 10.0 °C. The larger value at 30.0 °C is expected since a small inner-sphere contribution to $Q$ is present and it would decrease with pressure since the rate of exchange decreases with increasing pressure. The values at 10.0 and 20.2 °C represent the effect of pressure on the outer-sphere contribution to $Q$.

## Discussion

Parameters for the present and related systems involving ligand exchange are collected in Table I. The $\Delta H^*$ value for the Ni(II)–$NH_3$(aq) system (13.7 kcal mol$^{-1}$) is near the value predicted by Jordan[8] (14.8 kcal mol$^{-1}$) for the Ni(II)–$NH_3$(l)

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(8) Rusnak, L. L.; Yang, E. S.; Jordan, R. B. *Inorg. Chem.* **1978**, *17*, 1810.
(9) Ducommun, Y.; Newman, K. E.; Merbach, A. E. *Inorg. Chem.* **1980**, *19*, 3696.

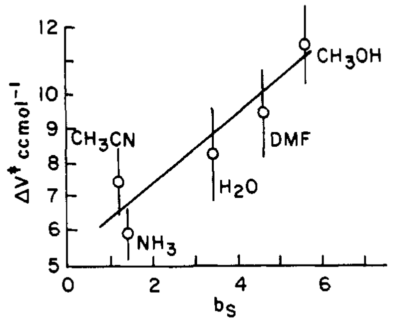

**Figure 3.** Volume of activation for solvent molecules leaving the inner sphere of Ni(II) vs. the solvent parameter $b_s$.

system using a correlation, which works very well, involving crystal field and solvent effects. We had previously found that the Ni(II)–$NH_3$ system was quite insensitive to the amount of water present and indeed to various added salts.

The data in Table I show a remarkable similarity in view of the varied ligand properties such as size, basicity, shape, donor atom, and the mixed solvent. The $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values correlate very well considering the likely errors of ca. ±1–2 units in each, all suggesting dissociative interchange as the proper description for the exchange processes. Swaddle[1] has pointed out that no correlation at all exists with molar volumes of the solvent ligands. Merbach[2] suggests that the faster (at 25 °C) exchanges give smaller positive $\Delta V^{\ddagger}$'s, which appears to be so on the face of it, although consideration of realistic errors weakens this conclusion. A plot of $\Delta V^{\ddagger}$ vs. $b_s$ is shown in Figure 3. The parameter $b_s$, a solvent characteristic, was derived by Jordan et al.[8] in fitting $\Delta H^{\ddagger}$ to $Dq$ for several metal–solvent pairs. The usefulness and physical meaning of $b_s$ will only be known after more systems have been studied.

The low $Q$(outer sphere) (0.06 K) is interesting in comparison with that number found for $Ni(H_2O)_6^{2+}$ in water (it ranges from 0.2 to 0.5 K). The inner-sphere $^{14}N$ $Q$(lim) of 26 K is very similar to the value 24 K found for $^{17}OH_2$ in $Ni(H_2O)_6^{2+}$; thus no special effects due to changing from $NH_3$ to $H_2O$ on Ni(II) seem to be present here. On the basis of the Eigen formulation for substitution mechanisms one calculates a $K_{os}$ (outer-sphere $NH_3$ complexation constant) of 0.22, which would lead to the presence of substantial $NH_3$ in the "outer sphere". The low $Q$(outer sphere), however, suggests that $NH_3$ is farther from the Ni(II) on the average than $H_2O$ molecules or that $K_{os}$ is considerably smaller than ca. 0.2 or both.

The almost identical temperature dependence of $T_2$ for $^{14}NH_3$ relaxation and $T_1$ for $^{17}OH_2$ relaxation strongly suggests that the correlation time (or times) $\tau_q$ controlling the relaxation process is the same in the two cases. For $^{17}OH_2$ and $^{14}NH_3$ quadrupolar relaxation should dominate and the fast modulation limit where $T_1 = T_2$ should exist. Using the usual equation for quadrupolar relaxation, and the quadrupole coupling constants and symmetry parameters for ice[12] and solid[13] $NH_3$, assuming $\tau_q$ is the same for $^{17}OH_2$ and $^{14}NH_3$, one calculates $T_1(^{17}OH_2)/T_2(^{14}NH_3) = 2.7$, which may be compared with 3.2 used in Figure 1. When one remembers that we compared $^{14}NH_3$ in 15 M $NH_3$ with $^{17}OH_2$ in pure $H_2O$, the similarity of these numbers is satisfactory and supports the idea that the mechanism for modulation of the field gradient tensor is the same for the two molecules. It has been suggested[11] that the mechanism involves breaking and forming hydrogen bonds at low temperatures and then approaches rotational diffusion at high temperatures. The small $\Delta V^{\ddagger}$ for $NH_3$ and $H_2O$ as compared to that for $CH_3CN$ is probably due to the smaller sizes of the former molecules and the open hydrogen-bonded structure of $NH_3$ and $H_2O$ which would permit rotation of the molecules with little local volume change once hydrogen bonds are broken.

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**Registry No.** $NH_3$, 7664-41-7; $Ni(NH_3)_6^{2+}$, 15365-74-9.

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(10) Caldin, E. F.; Grant, M. W.; Hasinoff, B. B. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2247.

(11) Hindman, J. C.; Svirmickas, A.; Wood, M. *J. Phys. Chem.* **1970**, *74*, 1266.

(12) Spiess, H. W.; Garrett, B. B. Sheline, R. K.; Rabideau, S. W. *J. Chem. Phys.* **1969**, *51*, 1201.

(13) Lehrer, S. S.; O'Konski, C. T. *J. Chem. Phys.* **1965**, *43*, 1941.

(14) Desai, A. G.; Dodgen, H. W.; Hunt, J. P. *J. Am. Chem. Soc.* **1970**, *92*, 798.