# Proton Magnetic Resonance Studies of Magnesium(II) in Ethanol. Determination of Solvation Number and Exchange Rate

**T. D. Alger**

*Contribution from the Department of Chemistry, Utah State University, Logan, Utah 84321.* *Received August 14, 1968*

**Abstract:** Separate OH proton magnetic resonance signals for free and bound ethanol molecules have been observed at reduced temperatures for solutions of magnesium perchlorate in ethanol. From relative intensity measurements of these signals below −60°, the solvation number of magnesium was shown to be 6. The $CH_2$ and $CH_3$ signals of the coordinated ethanol, which are hidden behind the bulk $CH_2$ and $CH_3$ peaks, could not be observed after adding cupric ion to the solution. Thus, it is impossible to observe directly whether ligand exchange is *via* whole ethanol molecules or by alcoholic protons. Addition evidence is presented, however, which supports whole ligand exchange. Proof that a single exchange mechanism is operating over the observed temperature range is furnished by a linear Arrhenius plot for the calculated rate constants. If the reaction is assumed to be first order, the rate constant and activation parameters at 25° for the bound to free exchange process are: $k = 2.8 \times 10^6$ sec$^{-1}$, $\Delta H^{\ddagger} = 17.7$ kcal/mole, and $\Delta S^{\ddagger} = 30$ eu. Comparisons of activation parameters indicate that ligand exchange in several metal, water, methanol, or ethanol systems is SN1.

This paper reports a follow-up investigation of a comment in a paper by Nakamura and Meiboom.[1] They reported that solutions of magnesium perchlorate in ethanol exhibited separate OH proton magnetic resonance (pmr) signals for solvation shell and bulk solvent molecules.[2] This paper centers on accurate measurements of the solvation number and rate of ligand exchange for magnesium in ethanol, but comparisons between this system and systems involving various metal ions in water and methanol are also made.[1,3-8]

Nakamura and Meiboom[1] used a technique introduced by Jackson, Lemons, and Taube[4] to demonstrate that it is methanol molecules and not alcoholic protons which exchange in Mg(II)–methanol systems. The $CH_3$ pmr signals of the solvated and bulk methanol so nearly coincided that they could not be observed separately. However, addition of cupric ion to the solution selectively broadened the bulk $CH_3$ peak, thereby allowing observation of the solvation-sphere $CH_3$ peak. By observing that the $CH_3$ and OH solvation-sphere signals had identical temperature dependence, it was determined that ligand exchange was by the methanol molecule.[1] A similar attempt to determine the nature of the exchanging ligand in the magnesium–ethanol system is reported in this paper.

Considerable work utilizing relaxation methods[3,] has been done by Eigen on the rate of substitution of water molecules in the first solvation shell of metal ions by various anions. The independence of these rates relative to the nature of the incoming anion has been interpreted as indicating that the substitution rate corresponds to the exchange rate of the coordinated water molecules. Although this is subject to further substantiation, it has strong supporting evidence since ligand-exchange rates obtained from $O^{17}$ nmr measurements in aqueous solutions of paramagnetic metal ions agree well with the ultrasonic rate determinations.[3,5,8] These facts seem to support an SN1 mechanism for the ligand exchange in metal–water systems. From structural similarities within the series water, methanol, and ethanol, one might speculate that exchange mechanisms would be similar for the three ligands.

## Experimental Section

**Materials.** Anhydrous magnesium perchlorate and anhydrous cupric perchlorate solution in ethanol were prepared essentially by the methods described by Nakamura and Meiboom.[1]

Anhydrous ethanol was prepared by treatment of absolute ethanol with magnesium turnings using iodine to initiate the reaction.[9,10] The water content of these solutions was always less than 0.05% (less than 0.02 *M*).

A stock solution of perchloric acid in ethanol was prepared by mixing 76.3% perchloric acid in anhydrous ethanol.[11]

All starting materials and other chemicals were of reagent grade quality.

Solutions for pmr measurements were prepared by weighing anhydrous magnesium perchlorate in stoppered vessels, and then adding anhydrous ethanol and other anhydrous stock solutions as needed.[11] The samples were sealed in standard pmr tubes following freeze–thaw degassing and stored in a Dry Ice–2-propanol mixture when not in use. Samples used for measurements were always less than 1 week old. Samples used for solvation number determinations were about 0.5 *M* in Mg(II), while those used for rate determinations were approximately 0.25 *M*.

---

[1] S. Nakamura and S. Meiboom, *J. Am. Chem. Soc.*, **89**, 1765 (1967).

[2] It should be pointed out that no separate $CH_3$ or $CH_2$ signals were observed for the coordinated ethanol.[1]

[3] (a) M. Eigen and G. G. Hammes, *J. Am. Chem. Soc.*, **82**, 5951 (1960); (b) M. Eigen, *Z. Electrochem.*, **64**, 115 (1960).

[4] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **32**, 533 (1960).

[5] T. J. Swift and R. E. Connick, *ibid.*, 37, 307 (1962).

[6] (a) J. H. Swinehart and H. Taube, *ibid.*, 37, 1579 (1962); (b) J. H. Swinehart, T. E. Rogers, and H. Taube, *ibid*, **38**, 398 (1963).

[7] Z. Luz and S. Meiboom, *ibid.*, **40**, 1058, 1066, 2686 (1964).

[8] M. Eigen and L. de Maeyer, "Techniques of Organic Chemistry," Vol. VIII, Part II, A. Weissberger, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963.

[9] H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

[10] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., Boston, Mass., 1957, p 287.

[11] The ethanolic solution of perchloric acid was made up in such a fashion that when it was finally added to the ethanol solutions for measurements it was only 0.001 *M* in $HClO_4$. Hence, the $H_2O$ molarity was on the order of 0.002 *M*. Since anhydrous perchloric acid and alcohol solutions form explosive mixtures, this insignificant amount of water was neglected. The complication of water does, however, limit the amount of acid that can be added (thus, only 0.001 *M* $HClO_4$ was used).

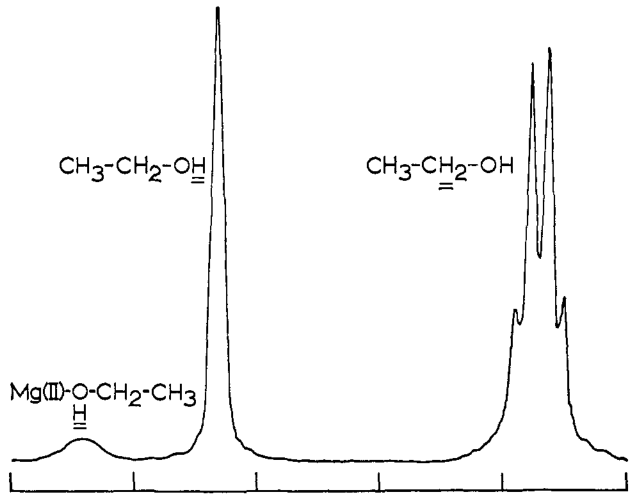

Figure 1. Partial pmr spectrum of a 0.5 $M$ solution of $Mg(ClO_4)_2$ in anhydrous ethanol at −64° (the upfield $CH_3$ peak is omitted). The field increases from left to right. The interpretation of the various peaks is indicated by the underlined protons. Frequency markers are placed every 50 Hz.

**Pmr Measurements.** All measurements were recorded on a Varian A-60 spectrometer equipped with a V-6040 temperature controller. Signal peaks were integrated by both the A-60 and a planimeter.

Ligand-exchange rates were obtained by curve fitting experimental OH slow-passage spectra with computer-calculated spectra for several trial exchange rates. The computer program was based on Kubo's method for many-site exchange.[12,13]

In all solutions used for rate measurements, small quantities of acid were added to suppress the base-catalyzed exchange. The spectra appeared to be independent of the acid added in the range 0.001–0.002 $M$.[11]

Measurements of parameters required for rate calculations[14] were made over a range of −90 to +60°. Such a wide range improves the accuracy of the parameters and provides a check that a single ligand-exchange mechanism is operating throughout.

## Experimental Results

**General.** Figure 1 shows the partial pmr spectrum of an anhydrous 0.5 $M$ magnesium perchlorate sample in ethanol at −64° ($CH_3$ peak has been excluded). The lines are relatively broad due to the viscosity of the solution at this temperature and the high salt concentration. Note that neither of the underlying triplet structures for the solvation sphere or bulk OH signals is observed. The triplet structure of the solvation shell OH peak is apparently masked by the previously mentioned broadening effects. On the other hand, the triplet structure for the bulk OH peak is not only masked by broadening effects but also "averaged out" by rapid proton exchange in the acidified solutions used.

Separate OH solvation shell signals are observed only below −40° in acidified solutions.[15] The line widths of the solvation shell and bulk OH signals are minimal at about −70 and −60°, respectively. Below these temperatures viscosity broadens the lines, while above these temperatures the lines are exchange broadened. At about −35°, the lines coalesce to a single "averaged-out" peak which narrows as the temperature is raised.

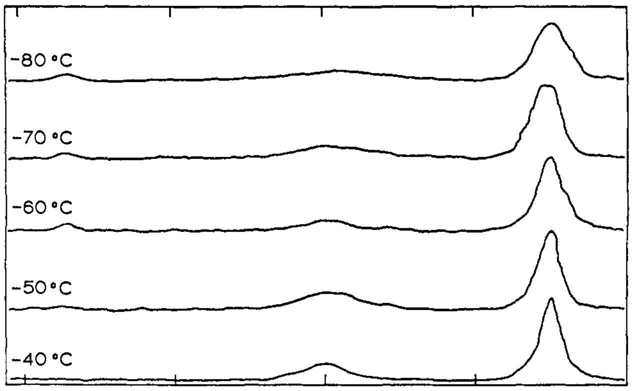

Figure 2. Spectra of 0.25 $M$ $Mg(ClO_4)_2$ solutions in ethanol with 0.006 $M$ Cu(II) ion added. The lower field peak (to left) is the solvation shell OH signal (disappears around −40 to −50°). The midfield and upfield peaks are respectively the broadened $CH_2$ and $CH_3$ signals. Note that separate solvation shell $CH_2$ and $CH_3$ signals are not observed (neither is the bulk OH signal which is apparently too broadened).

**Solutions Containing $Cu^{+2}$.** Separate pmr signals were not observed for the $CH_2$ and $CH_3$ protons of the coordinated ethanol (Figure 1) since these peaks positions are very little shifted from the positions of the corresponding peaks in the bulk ethanol. Unfortunately, their presence could not be observed even by addition of cupric ion to the solution (Figure 2). Apparently, viscosity effects selectively broaden the solvation-shell $CH_2$ and $CH_3$ signals nullifying the selective broadening effects of the $Cu^{+2}$ upon the bulk peaks. The inability to observe the temperature dependence of the solvation shell OH, $CH_2$, and $CH_3$ peaks makes it impossible to determine directly the nature of the exchanging ligand.

**Solvation Number.** The solvation number of Mg(II) in anhydrous ethanol was determined between −60 and −90° from molar ratios of $Mg(ClO_4)_2$ and ethanol, and the relative areas under the OH signals.[16] At the temperatures investigated, the $CH_2$ peak was also broadened sufficiently for area measurements. The area of the $CH_2$ peak agreed reasonably well with the total areas of the two OH signals and thus provided a check on the accuracy of area measurments.

All calculations, including two concentrations and five temperature changes, indicate that the solvation number is 6 (Table I). A noninteger solvation number has been rejected since this seems incompatible with the relatively slow ligand-exchange rate at these temperatures.[17]

A solvation number of 6 for magnesium indicates that there is no penetration of the perchlorate into the solvation sphere of Mg(II). Thus, no "close association" is observed between Mg(II) and $ClO_4^-$ even at relatively high salt concentrations ([Mg(II)] = 0.5 $M$, [$ClO_4^-$] = 1.0 $M$).

---

(12) C. S. Johnson, "Advances in Magnetic Resonance," Vol. I, Part II, J. S. Waugh, Ed., Academic Press, New York, N. Y., 1965.

(13) The program was graciously made available to the author by Dr. M. Saunders of Yale University.

(14) The temperature dependence of the following parameters must be determined for accurate rate calculations: chemical shift between solvation shell and bulk OH signals, and line widths of solvation shell and bulk OH peaks.

(15) No attempt was made to study ligand exchange in neutral or basic solutions.

(16) At temperatures higher than these, exchange broadening coupled with a relatively small chemical shift difference between bulk and solvated OH signals (60 Hz) causes too much overlap between the two OH peaks for accurate area measurements to be made.

(17) At higher temperatures the exchange rates increase substantially, and the possibility of a noninteger solvation number also increases. Since the author had no way of testing for such a possibility at higher temperatures, he used the solvation number of 6 throughout.

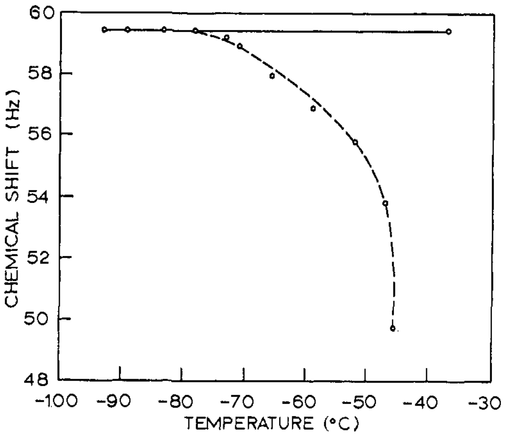

Figure 3. Relative chemical shift ($\delta_{OH}$) between the bulk and solvation shell OH signals as a function of temperature. The graph is for anhydrous ethanol containing 0.25 $M$ $Mg(ClO_4)_2$.

**Measurements of Parameters for Rate Calculations.** The chemical shift difference between bulk and solvation shell OH signals will be denoted by $\delta_{OH}$. Between −78 and −93°, no change was apparent in the value of $\delta_{OH}$ (59.5 Hz, Figure 3). Above −78°, exchange processes begin to decrease the apparent separation of the signals. The high-temperature value of $\delta_{OH}$ was found at the coalescence temperature (−39°) by a method described by Nakamura and Meiboom[1] and will be discussed in the Calculations and Discussion section.

**Table I.** Determination of Solvation Number

| Temp, °C | Molar ratio,[b] $E/M$ | Area under peaks[a] Solvation OH $A_s$ | Bulk OH $A_b$ | $CH_2$ $A_m$ | $2(A_s + A_b)$ | Solvation no.[c] $N$ | $N'$ |
|---|---|---|---|---|---|---|---|
| −59.5 | 35.70 | 1.96 | 11.58 | 28.32 | 27.08 | 5.2 | 6.5 |
| −64.0 | 35.70 | 2.14 | 11.36 | 27.34 | 27.00 | 5.7 | 6.0 |
| −68.0 | 37.63 | 2.20 | 12.90 | ... | ... | 5.5 | ... |
| −68.0 | 37.63 | 2.30 | 11.70 | ... | ... | 6.2 | ... |
| −75.6 | 35.70 | 2.10 | 11.02 | 26.40 | 26.24 | 5.7 | 5.9 |
| −87.0 | 37.63 | 2.10 | 10.16 | ... | ... | 6.4 | ... |

[a] The areas are given in aribtrary units and should be compared within each row only. [b] $E$ is the number of moles of ethanol and $M$ the number of moles of magnesium perchlorate in the solution. [c] $N$ is calculated from the OH peaks: $N = (E/M)[A_s/(A_s + A_b)]$; while $N'$ is calculated from the $CH_2$ peak (which accounts for both bulk and solvation shell ethanol) and the bulk OH peak: $N' = (E/M)[(A_m - 2A_b)/A_m]$. The average solvation number from above is 5.9 ± 0.4.

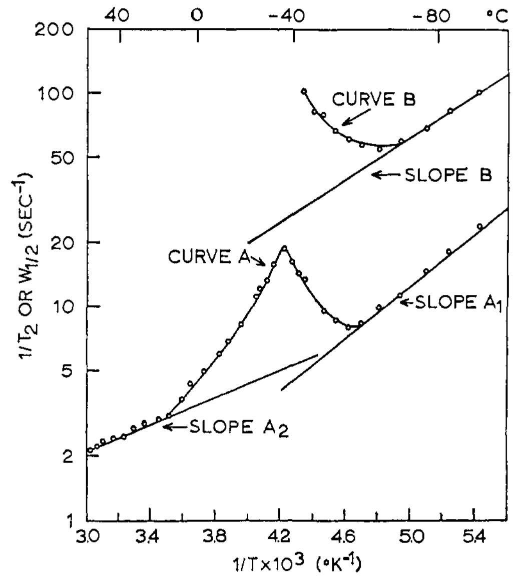

Figure 4. Line widths (radians sec) of the bulk OH (curve A) and the solvation shell signals (curve B) as a function of temperature. At high temperatures curve A represents the coalesced signal. Hence, slopes $A_1$, $A_2$, and $B$ are respectively the natural line widths for the bulk, coalesced, and solvation sphere OH signals. The concentration is approximately 0.25 $M$ $Mg(ClO_4)_2$. $W_{1/2}$ is the half-line width at half-intensity. It is used here, rather than $1/T_2$, because at intermediate exchange rates the lines are not Lorentzian and $T_2$ is not strictly defined. At both low and fast rates $W_{1/2}$ (in units of radians sec) is identical with $1/T_2$.

Figure 4 depicts the results of line-width measurements from −90 to +60°. Curves A and B represent respectively the bulk and solvation shell OH signals. Exchange reactions do not affect the line widths below −70°. Thus, from −70 to −90°, the temperature dependence of the natural line widths (line widths in the absence of exchange) can be determined. We were also able to obtain the line widths for the coalesced signal in the region where exchange narrowing is completed (high-temperature region of curve A). The accuracy of the measurements of natural line widths was checked by comparing coalesced line-width values with bulk and solvation shell line-width values $[(1/T_{2A_2}) = (P_A/T_{2A_1}) + (P_B/T_{2B})]$.[18]

**Order of Mg(II) Concentration.** Line-width measurements at various magnesium perchlorate concentrations were made to determine the order of magnesium in the ligand exchange. The measurements were made at −48° since this temperature is still in the range where lifetime broadening of the OH peak is a good approximation. Thus, the exchange rate can be obtained directly from excess line width[12,18] since

$$\frac{1}{\tau_A} = \frac{P_B}{P_A}\frac{1}{\tau_B} = \left(\frac{1}{T_{2A'}} - \frac{1}{T_{2A}}\right) \qquad (1)$$

where $\tau_A$ and $\tau_B$ are respectively the mean lifetimes of ethanol in the bulk and solvation sphere between exchanges, $1/T_{2A}$ and $1/T_{2B}$ are respectively the observed and natural line widths for the bulk OH peak (Figure 4), and $P_B$ and $P_A$ are respectively the ethanol mole fractions in the bulk and solvation sphere. Measurements indicate $(1/\tau_A)[(1/T'_{2A}) - (1/T_{2A})]$ is proportional to $P_B/P_A$, and it follows from eq 1 that $1/\tau_B$ is constant. It can, therefore, be concluded that the exchange rate is first order with respect to Mg(II) concentration and is independent of ionic strength.

## Calculations and Discussion

**Rate Constant Calculation.** Since only single peaks were observed for the solvation shell and bulk OH signals, a simple two-site case could be used for the analysis. Rate calculations were simplified by using slow- and fast-exchange approximations. The first three points of Table II are averages of $1/\tau_B$ calculations

---

[18] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Co., Inc., New York, N. Y., 1959, pp 220–222.

**Table II.** Rate Constants ($P_B$ = 0.0850)

| Point no. | Temp, °C | $k = 1/\tau_B$,[a] sec$^{-1}$ | Method of rate calculation |
|---|---|---|---|
| 1 | −66.0 | 4.7 | Broadening of solvation shell and bulk OH peaks (slow-exchange approximation) |
| 2 | −61.0 | $1.3 \times 10^1$ | |
| 3 | −57.0 | $2.0 \times 10^1$ | |
| 4 | −53.0 | $6.3 \times 10^1$ | Bulk or coalesced OH signal (complete solution of Block equations) |
| 5 | −50.0 | $1.3 \times 10^2$ | |
| 6 | −47.0 | $1.6 \times 10^2$ | |
| 7 | −43.0 | $2.8 \times 10^2$ | |
| 8 | −42.0 | $3.8 \times 10^2$ | |
| 9 | −39.0 | $4.4 \times 10^2$ | |
| 10 | −37.0 | $7.9 \times 10^2$ | |
| 11 | −33.0 | $2.5 \times 10^3$ | |
| 12 | −30.0 | $3.8 \times 10^3$ | |
| 13 | −28.0 | $4.4 \times 10^3$ | |
| 14 | −27.0 | $5.0 \times 10^3$ | |
| 15 | −20.0 | $7.9 \times 10^3$ | |
| 16 | −16.0 | $3.1 \times 10^4$ | Coalesced OH signal (fast-exchange approximation) |
| 17 | −11.0 | $4.7 \times 10^4$ | |
| 18 | −6.0 | $6.3 \times 10^4$ | |
| 19 | 1.0 | $1.3 \times 10^5$ | |
| 20 | 5.0 | $2.5 \times 10^5$ | |

[a] Relative errors in rate constant calculations may be as large as ±20% (more likely ±15%).

utilizing the slow-exchange approximation on both the bulk and solvation shell OH signals (Figure 4). On the other hand, points 16–20 were calculated using the fast-exchange approximation on the coalesced OH signal. At points where neither the slow- nor fast-exchange approximation could be used, equations for complete line-shape analysis had to be substituted. The computer program discussed in the Experimental Section was used to calculate such points (Table II).

As mentioned in the Experimental Section, the high-temperature value of $\delta_{OH}$ was found by analysis of the coalesence point (−39°). The following procedure, as devised by Nakamura and Meiboom,[1] was used. For a trial value of $\delta_{OH}$, the line width of the bulk peak was computed for a number of rates, $1/\tau_B$, and its maximum value determined graphically. The maximum line width was then plotted as a function of the assumed $\delta_{OH}$, and that value of $\delta_{OH}$ adopted for which the calculated and observed maximum width agreed.

Figure 5 is an Arrhenius plot of Table II. Although there is some scatter, the plot is essentially linear, giving assurance that only one dominant exchange mechanism operates over the temperature range studied. Thus, the first-order rate constant, $k$, can be assigned to either of the following processes

$$\mathrm{Mg^{II}(EtOH)_5(Et^*OH^*)} + \text{bulk EtOH} \xrightarrow{k} \mathrm{Mg^{II}(EtOH)_6} + \mathrm{Et^*OH^*} \quad (2)$$

or

$$\mathrm{Mg^{II}(EtOH)_5(Et^*OH^*)} + \text{bulk EtOH} \xrightarrow{k} \mathrm{Mg^{II}(EtOH)_5(Et^*OH)} + \text{bulk EtOH}^*, \quad (3)$$

although the mode of participation of the incoming ligand in the transition state (SN1 or SN2) is not clear from the results. The rate constant and activation parameters at 25° are $k = 2.8 \times 10^6$ sec$^{-1}$, $\Delta H^{\ddagger}$ = 17.7 kcal mole$^{-1}$, and $\Delta S^{\ddagger}$ = 30 eu.

**Discussion.** Direct attempts to delineate the nature of the exchanging ligand in this study have been indeterminate. Nevertheless, relative comparisons between the acidities of methanol and ethanol indicate exchange in the latter should *also* occur by whole ligands[1] (eq 2). For example, since methanol is 3.5 times as acidic as ethanol,[19] the latter is less likely to undergo proton exchange than is methanol. On the other hand, the relative acidities of the ligands are most likely modified by solvation to the magnesium ion. Such bonding generally increases the acidity of the alcoholic protons. However, since methanol is about 4.0 times as basic as ethanol,[20,21] the more strongly bound methanol should still be relatively more acidic than the bound ethanol. Since methanol exchanges by whole molecules,[11] it appears that eq 2 best represents the process in Mg(II)–ethanol systems. This assumption will be used in further development of this paper.

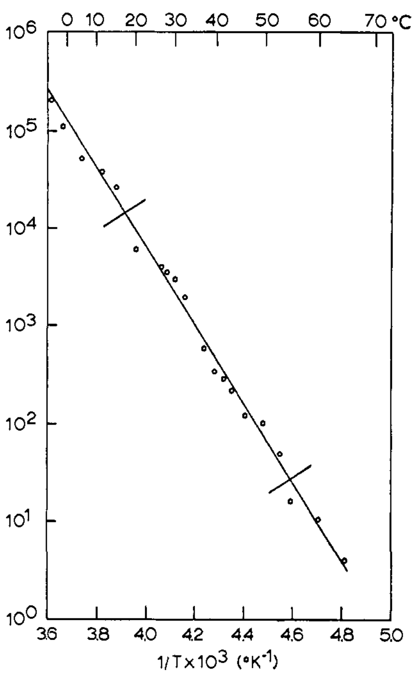

Figure 5. Arrhenius plot of the rate of ligand exchange between free and bound ethanol molecules. The quantity $\tau_B$ is the average lifetime between exchanges of ethanol molecules in the solvation sphere.

In the Mg(II)–methanol system, Nakamura and Meiboom[1] observed that addition of water produced variations in the multiplet structure of the solvation shell OH signal as well as differences in $\delta_{OH}$. They also noted that exchange rates in the monohydrate system (Mg(II)–$(CH_3OH)_5 \cdot H_2O$) were larger by a factor of 10–50[1] than those for the anhydrous system (Mg(II)–$(CH_3OH)_6$). Similar results were also observed for paramagnetic metal–methanol solutions containing water.[7] Since the multiplet structure of the solvation shell OH signal is masked by broadening effects, only chemical shift and line-width variations are observed in solutions to which 0.30 and 0.65 *M* water concentrations were added. Nevertheless, the presence of water in Mg(II)–ethanol systems apparently also causes the hydrated species to predominate, thereby altering the exchange rate. The dominance of the hydrated

---

(19) J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(20) J. Kolthoff, *J. Phys. Chem.*, **35**, 2732 (1931).

(21) H. Goldschmidt and P. Dahll, *Z. Physik. Chem.*, **108**, 121 (1924).

species is in agreement with work which indicates that water is, respectively, 400 and 100 times as basic as ethanol and methanol.[20,21]

Justification of the assumed SN1 mechanism in eq 2 and 3 is difficult, because no data using Eigen's relaxation methods[3,8] are available for ethanol solutions. However, support can be obtained by comparing observed activation parameters for hexacoordinate water, methanol, and ethanol solvation systems (Table III) with those expected from hypothetical SN1 and SN2 mechanisms. The respective SN1 and SN2 modes are represented in eq 4 and 5 for reference purposes.

**Table III.** Comparisons of Rate Constants and Activation Parameters for Water- and Alcohol-Metal Solvation Systems at 25°

| System[a] | $k$, sec$^{-1}$ (bound to free) | $\Delta H^\ddagger$, kcal/mol | $\Delta S^\ddagger$, eu | $r^b$ ionic |
|---|---|---|---|---|
| Mn(II)-$H_2O$[c] | $3.1 \times 10^7$ | 8.1 | 2.9 | 0.80 |
| Mn(II)-$CH_3OH$[d] | $9.5 \times 10^5$ | 8.0 | −4.6 | |
| Co(II)-$H_2O$[c] | $1.1 \times 10^6$ | 8.0 | −4.1 | 0.78 |
| Co(II)-$CH_3OH$[e] | $1.8 \times 10^4$ | 13.8 | 7.2 | |
| Ni(II)-$H_2O$[c] | $2.7 \times 10^4$ | 11.6 | 0.6 | 0.68 |
| Ni(II)-$CH_3OH$[e] | $1.0 \times 10^3$ | 15.8 | 8.0 | |
| Mg(II)-$H_2O$[f,g] | $1.0 \times 10^5$ | 13.0 | 6.0 | 0.65 |
| Mg(II)-$CH_3OH$[h] | $4.7 \times 10^3$ | 16.7 | 14.0 | |
| Mg(II)-$C_2H_5OH$ | $2.8 \times 10^6$ | 17.7 | 30.0 | |

[a] All systems are hexacoordinated. [b] Ionic radii for divalent cations were taken from E. S. Gould, "Inorganic Reactions and Structure," Henry Holt and Co., New York, N. Y., 1955, p 452. [c] Reference 5. [d] H. Levanon and Z. Luz, *J. Chem. Phys.*, **49**, 2031 (1968). [e] Reference 7. [f] Values for activation parameters are estimated from comparisons of rates, etc., in the Co(II) and Ni(II)-water and -methanol systems. The comparisons were extended to the Mg(II)-water and -methanol systems. [g] It is assumed that the value found by Eigen,[3b] for the rate-determining step of incorporation of anion in the Mg(II) solvation sphere is the rate for water exchange. [h] Reference 1.

SN1

$$M^{n+}(L)_5(L^*) \xrightarrow{\text{slow}} M^{n+}(L_5) + L^*$$

$$M^{n+}(L)_5 + \text{bulk L} \xrightarrow{\text{fast}} M^{n+}(L)_6 \tag{4}$$

SN2

$$M^{n+}(L)_5(L^*) + \text{bulk L} \xrightarrow{\text{slow}} M^{n+}(L)_6(L^*)$$

$$M^{n+}(L)_6(L^*) \xrightarrow{\text{fast}} M^{n+}(L)_6 + L^* \tag{5}$$

In all but one of the four metal ion systems of Table III, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ increase directly with the size of the ligand. Furthermore, with few exceptions $\Delta H^\ddagger$ and $\Delta S^\ddagger$ increase as the radius of the metal ion decreases. Such behavior indicates that steric interference due to ligand size is a major contributor to the activation barrier and entropy of activation in these metal-ligand systems. In agreement with this, both eq 4 and 5 predict increases in $\Delta H^\ddagger$ with increasing L/M$^{n+}$ size ratios since removal or addition of ligands is hampered by other solvated ligands. Unfortunately, such agreement offers little help in distinguishing the mode of attack of the incoming ligand.[22] On the other hand, $\Delta S^\ddagger$ comparisons lend support to the SN1 mechanism. For example, the intermediate in eq 4 has had a ligand removed while that in eq 5 has added one. Thus, $\Delta S^\ddagger$ for the SN1 mode should be positive, while that of the SN2 mode would be negative. The SN1 mechanism also predicts an increase in $\Delta S^\ddagger$ with increasing $L/M^{n+}$ size ratios, while that for SN2 modes would decrease. Such comparative arguments indicate that ligand exchange in the metal-water, -methanol, or -ethanol systems of Table III are best described by an SN1 mechanism.[23] Since there is additional evidence that water exchanges by an SN1 mechanism,[3,5,8] the above argument is strengthened.

Little can be said concerning the geometry of the hexacoordination in the Mg(II)-ethanol system. Nakamura and Meiboom[1] indicated that the Mg(II)-methanol system most likely formed a regular octahedral arrangement. The additional steric requirements of ethanol, however, could force the system to a distorted octahedron. Such a difference between ethanol and methanol geometries is supported by increased ethanol exchange rates (10-1000 times methanol rates), decreased magnitude and temperature dependence of $\delta_{OH}$ (60 Hz constant compared to 110-140 Hz), and distortion of the solvation sphere ethanol OH signal (failure to observe the triplet structure).[1] All of the above, however, can be adequately explained by other arguments.

**Acknowledgments.** The author wishes to thank both Dr. M. Saunders (Yale University) and Dr. M. Cocivera (Bell Laboratories) for making computer programs available as well as for valuable discussions on the subject. The research was supported by grants from the National Science Foundation (GU2532 and GP-8255).

---

(22) Larger effects upon $\Delta H^\ddagger$ are predicted by the SN2 mechanism (eq 5), because steric interference should increase with addition of a seventh ligand. Since differences in $\Delta H^\ddagger$ are smaller between methanol and ethanol systems than for methanol and water systems, one is tempted to state that the former ligand pair also exchange by SN1 mechanisms. However, without a reference which compares magnitudes in changes of $\Delta H^\ddagger$ between known SN1 and SN2 systems, such comparisons are weak.

(23) It is recognized that errors in determinations of $\Delta H^\ddagger$ can be as large as ±1 kcal (or larger if studies are over a narrow temperature range) resulting in errors of $\Delta S^\ddagger$ as large as ±4 eu. Thus, the absolute values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for each system have not been taken as literal as have their over-all trends with increasing ligand-to-metal size ratios.