aromatic ring while the second is delocalized into a molecular orbital containing the two beryllium atoms, S can be considered as $^1/_2$; F is then a weighting factor estimating the spin density centered on the p orbitals of carbon of the coordinated solvent. Calculating F from these data gives 0.012% for the spin density on aromatic ring carbon atoms where $S = {}^1/_2$. This value seems qualitatively reasonable, being consistent with the low intensity of the esr spectrum and with other reported contact shift ranges. Figure 1 demonstrates that the shift is linear with $1/T$ as required by the equation but also implies (as does Figure 3) that there is a zero activation energy to form the diradical. This may be quite the opposite effect, however, and means that the activation energy is so large that there is no significant change in F in the range of temperatures studied. The presence of the methyl resonance of complexed toluene on the *low*-field side of the free solvent signal is also consistent with paramagnetic contact-shift phenomena since Q for methyl groups is of opposite sign.

The line widths of the nmr and esr signals are quite compatible. In order to observe contact shifted resonances, electronic relaxation times must be short, whereas electronic relaxation times must be relatively long to observe sharp esr signals. As noted above, the nmr contact shifted peak begins to broaden at lower temperatures (−50°) while the esr spectrum is unresolvable until the temperature is about −120°.

Further confirmation of complexation to form stabilized triplet states or diradicals was obtained from the phosphorescence emission study. Small amounts of $(C_5H_5)_2Be$ in benzene caused the lifetime of the triplet state of benzene to increase markedly. The lifetime is even longer in more dilute solutions, indicating that concentration quenching is decreasing. This may also be the reason for the anomalous and lower intensity ratios in the nmr spectra of saturated solutions. The shift of the phosphorescence maximum from 440 to 470 mμ upon addition of $(C_5H_5)_2Be$ to benzene indicates, further, that the triplet state is arrived at more easily *via* complex formation.

Finally, vapor pressure measurements over toluene solutions of $(C_5H_5)_2Be$ indicate that this interaction is strong enough to manifest itself as apparent association in solution.

Magnesium(II) in Aqueous Acetone and the Kinetics of Proton Exchange

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio. *Received October 17, 1967*

Abstract: Magnesium nitrate and magnesium perchlorate solutions in aqueous acetone were prepared, and the proton magnetic resonance spectra were recorded between *ca.* −40 and *ca.* −90°. Below *ca.* −60° the water resonance signal is resolved into two components, one from bulk water and one from water in the primary hydration spheres of magnesium ions. These doublets were treated by a complete line-shape analysis technique based on the Bloch equations, and the values of τ_A, the average lifetime of a given proton in the primary hydration sphere of Mg^{2+}, were obtained as a function of temperature. Spectra obtained above *ca.* −60° were also analyzed by a somewhat different technique to obtain values of τ_A between *ca.* −60 and *ca.* −40°. The value of τ_A at a given temperature is a function of the concentration of added $HClO_4$ and HNO_3, indicating that the acid-catalyzed proton-transfer reaction observed previously for paramagnetic metal ions in aqueous solution is also operable for diamagnetic nontransition metal ions in aqueous acetone.

Considerable effort has been devoted in recent years to the study of the solvation of simple metallic cations in pure and mixed solvents,[2] principally through the application of magnetic resonance techniques. These cations may be separated into two distinct classes for a given solvent system, namely those ions for which a separate resonance signal (or signals) is observable (at least in theory) for those solvent molecules in the cationic primary solvation sphere in solution and those ions for which all observables such as line widths and chemical shifts are inseparable averages of the respective parameters for primary sphere solvent and bulk solvent.

The differentiation between these two classes arises from the wide variation between various ion–solvent systems of the rate constant for solvent exchange between the cationic primary solvation sphere and the bulk. For an ion such as Al^{3+}, the exchange rate may be made sufficiently slow in any of a variety of solvents[3,4] so that a separate resonance signal is readily observable for primary sphere solvent molecules, and Al^{3+} clearly belongs in the first of the two classes for these solvents.

At the opposite extreme is Na^+, an ion for which the solvent exchange rate is extremely rapid in all solvents for which measurements have been attempted.

In any such array there must obviously be borderline cases, and one of particular interest in this

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[1] Author to whom inquiries should be addressed.

[2] J. F. Hinton and E. S. Amis, *Chem. Rev.*, **67**, 367 (1967).

[3] (a) R. E. Connick and D. N. Fiat, *J. Chem. Phys.*, **39**, 1349 (1963); (b) S. Thomas and W. L. Reynolds, *ibid.*, **44**, 3148 (1966).

[4] H. H. Glaeser, H. W. Dodgen, and J. P. Hunt, *J. Am. Chem. Soc.*, **89**, 3065 (1967).

regard is Mg^{2+}. The solvation of this ion is of particular interest because of the biological importance of the ion in solution. Solvent exchange involving Mg^{2+} in aqueous solution is quite rapid, and hence the ion belongs to the second class of ions for this solvent.[5,6] However, in those solvents with considerably lower freezing points than water, such as methanol[7,8] and liquid ammonia,[9] the solvent exchange rate can be made sufficiently small such that Mg^{2+} belongs to the first class of ions with these solvents. Based on the results obtained for these solvents, it is highly likely that Mg^{2+} would belong to the first class for water if the temperature of an aqueous solution could be lowered sufficiently. One way of accomplishing this has been employed by Matwiyoff and coworkers,[10] and it is to adulterate the aqueous solution with a sizable amount of acetone since in this manner reasonably concentrated electrolyte solutions can be prepared having freezing points as low as *ca.* −100°.

The direct observation of a pmr signal from water in the primary solvation sphere of Mg^{2+} would have particular significance and application to the cation protonation studies which have been recently carried out in these laboratories.[11-13] It has been found in these studies that for certain paramagnetic cations such as Cr^{3+}, Ni^{2+}, and VO^{2+} the proton spin–spin relaxation rate in a given temperature range is a distinct function of the concentration of added general acids, increasing with increasing acid concentrations. This phenomenon has been interpreted as reflecting protonation[11,12] of the aquated cations and, more generally,[13] as the coordinated water molecules serving as catalysts in the transfer of protons from general acids to bulk water.

In view of the great similarities between the acid-dependent relaxation for Ni^{2+}, VO^{2+}, Cr^{3+}, and $CrCl^{2+}$, this interpretation is certainly a very reasonable one. It would certainly be strengthened considerably, however, if a separate resonance signal could be observed for first coordination sphere protons so that the exchange effect could be observed directly. In addition the case for cation protonation as a general process of wide occurrence requires evidence from the study of diamagnetic nontransition metal ions.

Clearly both of these aims could be served by the low-temperature study of Mg^{2+} in aqueous acetone.

Experimental Section

Magnesium perchlorate hexahydrate was prepared by the recrystallization of Matheson Coleman and Bell anhydrous $Mg(ClO_4)_2$ from aqueous solution followed by drying under vacuum for several days. Magnesium nitrate hexahydrate was also purified by recrystallization from water, and both salts were analyzed for magnesium by titration with EDTA with Eriochrome Black T as the indicator. G. F. Smith lithium perchlorate was used without further treatment.

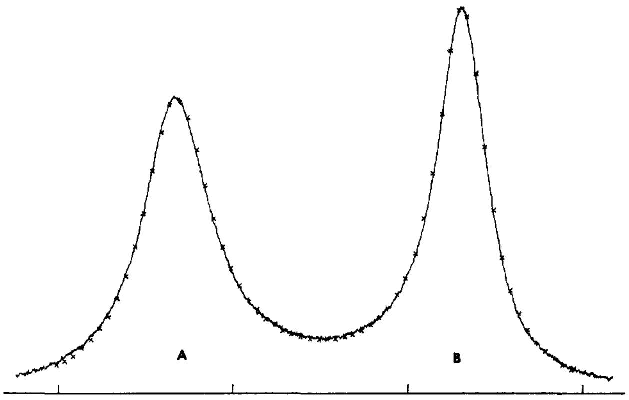

Figure 1. The water portion of the pmr spectrum of a $Mg(ClO_4)_2$–water–acetone solution of mole ratio 1:10.90:20.93, respectively, at a temperature of −70°. Peak A arises from bound water and peak B from bulk water. The continuous line is the experimental spectrum and the ×'s form the computer calculated spectrum. The four markers on the base line are drawn 50 Hz apart.

Solutions were prepared by the addition of weighed quantities of distilled water and Matheson A.R. grade acetone to a weighed amount of either the magnesium perchlorate or nitrate.

Solutions were also prepared which contained added $HClO_4$, HNO_3, or $LiClO_4$. In each case this was done by the addition of a weighed amount of the salt or a weighed amount of a standardized concentrated aqueous acid solution to the magnesium salt before the water and acetone were added. The solution containing added perchloric acid was prepared at *ca.* −50° to avoid the decomposition of the acetone which proceeds quite rapidly at room temperature in this solution.

Proton magnetic resonance spectra were recorded on a Varian A-60A high-resolution spectrometer equipped with a V-6040 temperature-control unit.

Results

The pmr spectrum of a $Mg(ClO_4)_2$ solution in water–acetone consists of two well-resolved singlets (one for water and one for $(CH_3)_2CO$) at temperatures above *ca.* −60°. Below this temperature the water proton signal is resolved into two components, and a typical water proton spectrum is shown in Figure 1 with the particular concentrations and temperature given in the figure caption. Upon the addition of small concentrations of $Cu(NO_3)_2$, peak B broadens considerably and is indistinguishable at a Cu^{2+} concentration of *ca.* 3×10^{-3} *M*. Under these same conditions peak A is only slightly broadened. These results indicate the assignment of peak A to primary sphere water and peak B to bulk water.

No peak was observed for bound acetone at any temperature for this solution.

The behavior of the coalesced water proton spectra for the solution of Figure 1 is shown in the plot of half-line width at half-maximum intensity *vs.* reciprocal temperature given in Figure 2. The three open circles in this plot represent data obtained after allowing the solutions to stand for 10 days. The other experimental points were obtained within 24 hr after solution preparation, and such was also the case with the remaining spectral data reported in this paper.

The spectra (both doublets and singlets) were analyzed by line-shape methods based on the Bloch equations. The Bloch equations for a two-species system were solved in a manner analogous to that of Gutowsky

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[5] J. A. Jackson, J. F. Lemons, and H. Taube, *J. Chem. Phys.*, **32**, 553 (1960).

[6] T. J. Swift and W. G. Sayre, *ibid.*, **44**, 3567 (1966).

[7] J. H. Swinehart and H. Taube, *ibid.*, **37**, 1579 (1962).

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

[9] T. J. Swift and H. H. Lo, *ibid.*, **89**, 3988 (1967).

[10] N. A. Matwiyoff, private communication.

[11] T. J. Swift and T. A. Stephenson, *Inorg. Chem.*, **5**, 1100 (1966).

[12] T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

[13] T. A. Stephenson, J. B. Spencer, and T. J. Swift, *ibid.*, in press.

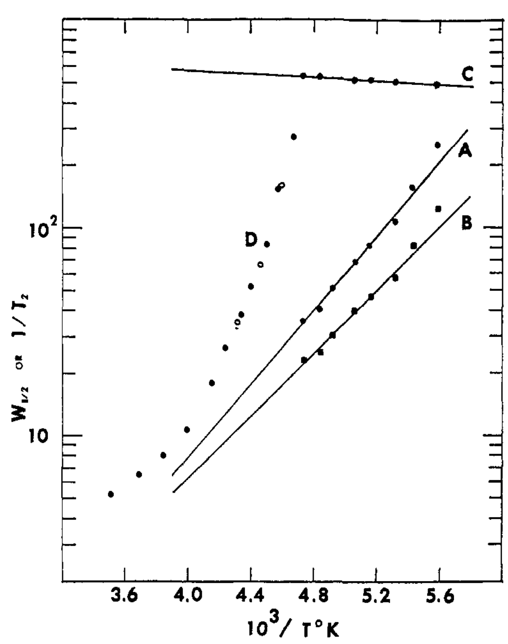

Figure 2. A plot of four quantities obtained from pmr spectra for the solution of Figure 1 as functions of temperature: (A) the relaxation rate T_{2A}^{-1} for bound protons; (B) the relaxation rate T_{2B}^{-1} for bulk protons; (C) the line-separation parameter, δ; (D) the half-widths ($W^1/_2$) of collapsed spectra at half-maximum amplitude.

and Holm[14] and Rogers and Woodbrey.[15] The following set of parameters was used: P_A = mole fraction of "bound" protons = $\tau_A/(\tau_A + \tau_B)$; P_B = mole fraction of bulk protons = $\tau_B/(\tau_A + \tau_B)$; τ_A = average lifetime of a given proton in the bound state; τ_B = average lifetime of a given proton in the bulk state; $\delta\omega$ = chemical-shift difference between A and B protons in the absence of exchange; T_{2A}^{-1} = proton spin-spin relaxation time in the bound state in the absence of exchange; T_{2B}^{-1} = proton spin-spin relaxation time in the bulk state in the absence of exchange.

Some of the parameters are conveniently combined to yield the following new parameters: $1/\tau$ = reduced rate constant for exchange = $(\tau_A + \tau_B)/\tau_A\tau_B$; $\alpha = T_{2A}\delta\omega/2$; $\beta = T_{2B}\delta\omega/2$; $\delta = \tau\delta\omega/2$.

The independent variable is x which is defined as $2\Delta\omega/\delta\omega$, and $\Delta\omega$ is measured from the "center of gravity" of the spectrum, namely that frequency for which $P_A\Delta\omega_A = P_B\Delta\omega_B$.

The expression for v, the absorption mode signal, is

$$v = \frac{C\delta^2 + D\delta + E}{F\delta^2 + G\delta + H} \qquad (1)$$

where

$$C = P_B\beta + P_A\alpha + P_A\alpha\beta^2 + P_B\alpha^2\beta + x(\alpha^2\beta - \alpha\beta^2 - P_A\alpha^2\beta - P_A\alpha\beta^2 + P_B\alpha\beta^2 + P_B\alpha^2\beta) + x^2(\alpha\beta^2 + \alpha^2\beta - P_B\alpha\beta^2 - P_A\alpha^2\beta)$$

$$D = \alpha^2\beta^2 + \alpha\beta + P_A{}^2\alpha\beta + P_B{}^2\alpha\beta + P_AP_B\alpha^2 + P_AP_B\beta^2 - P_A{}^2\alpha^2\beta^2 - P_B{}^2\alpha^2\beta^2 + 2P_AP_B\alpha^2\beta^2$$

$$E = P_B\alpha^2\beta + P_A\alpha\beta^2$$

$$F = 1 + \alpha^2\beta^2 + \alpha^2 + \beta^2 + x(2\alpha^2 - 2\beta^2) + x^2(\alpha^2 + \beta^2 + 2\alpha^2\beta^2) + \alpha^2\beta^2x^4$$

$$G = 2P_B\alpha + 2P_A\beta + 2P_A\alpha^2\beta + 2P_B\alpha\beta^2 + x(2\alpha^2\beta - 2\alpha\beta^2 + 2P_a\alpha\beta^2 - 2P_B\alpha\beta^2 + 2P_A\alpha^2\beta - 2P_B\alpha^2\beta) + x^2(2\alpha\beta^2 + 2\alpha^2\beta - 2P_A\alpha\beta^2 - 2P_B\alpha^2\beta)$$

$$H = P_B{}^2\alpha^2 + P_A{}^2\beta^2 + 2P_AP_B\alpha\beta + P_A{}^2\alpha^2\beta^2 + P_B{}^2\alpha^2\beta^2 - 2P_AP_B\alpha^2\beta^2 + x(2P_A\alpha^2\beta^2 - 2P_B\alpha^2\beta^2) + \alpha^2\beta^2x^2$$

For doublets this equation for v was used in a complete line-shape analysis technique involving use of a Univac 1107 computer. Values of the previously defined parameters were systematically varied, and values of v as a function of $\Delta\omega$ were calculated until the calculated and experimental spectra were essentially identical within experimental error. An example of such a calculated spectrum is given as the X's of Figure 1.

From the fitting of the doublets, precise values were obtained for T_{2A}, T_{2B}, P_A, P_B, and $\delta\omega$. These values were then plotted, and extrapolation to higher temperatures yielded the values of these parameters used in the analysis of the singlet spectra.

A second computer program was used to obtain τ values from the Lorentzian singlet spectra obtained at higher temperatures. Values of τ were obtained from the polynomial resulting from substitution of the expressions for $v(0)$ and $v(\overline{\Delta\omega})$ into eq 2, where $v(0)$ is

$$v(0) = 2v(\overline{\Delta\omega}) \qquad (2)$$

obtained from eq 1 by setting $x = 0$ (x is taken to be zero at the maximum of the singlet) and $\overline{\Delta\omega}$ then indicates from eq 2 the value of $\Delta\omega$ at half-intensity. The solution of the resulting polynomial was obtained

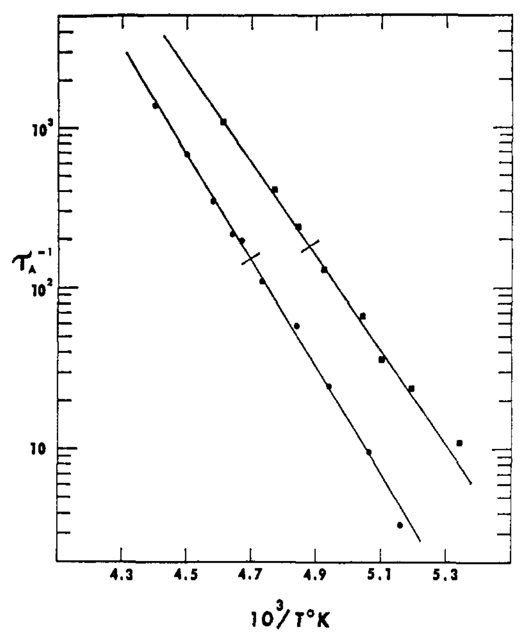

Figure 3. Arrhenius plot of τ_A^{-1} as a function of temperature for the $Mg(ClO_4)_2$-water-acetone solution of Figures 1 and 2 and for a $Mg(NO_3)_2$-water-acetone solution of similar concentration ratios.

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[14] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[15] M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962).

through use of the Newton–Raphson iterative procedure on a Univac 1107 digital computer.

As was mentioned above, the values of P_A, P_B, T_{2A}, T_{2B}, and $\delta\omega$ needed for the analysis of the singlet spectra were obtained by extrapolation of the values obtained for doublet spectra. The T_{2A}, T_{2B}, and $\delta\omega$ values with the extrapolation are shown in Figure 2. The magnesium ion solvation number is simply related to P_A values and the solvation numbers obtained for the doublet spectra were approximately 6 at all temperatures, in essential agreement with the results of an extensive investigation of the primary hydration number of Mg(II) in aqueous acetone by Matwiyoff and coworkers.[10]

The Arrhenius plot of $-\log \tau_A$ *vs.* T^{-1} for the $Mg(ClO_4)_2$ solution of Figure 1 and for a $Mg(NO_3)_2$ solution containing the Mg^{2+}–H_2O–acetone ratio of 1:11.40:21.4 is given in Figure 3.

The points to the low-temperature side of the small line drawn normal to the line drawn through the experimental points correspond to results obtained from doublets, while the points at higher temperature were obtained from singlets.

The values of the average lifetime of a given proton in the bound state at 25° and the activation parameters, ΔH^* and ΔS^*, are 2.6×10^{-7} sec, 14.5 kcal, and +19.8 eu, respectively, for the perchlorate system and 2.0×10^{-7} sec, 12.7 kcal, and +14.3 eu for the nitrate system.

There is a quite distinct difference between the proton exchange rates for the perchlorate and nitrate solutions. This difference was investigated further through the addition of other electrolytes. The effect of added $HClO_4$, HNO_3, and $LiClO_4$ on the rate of proton exchange is shown in the data of Table I. Lithium perchlorate (and hence by inference, perchlorate ion) appears to have little effect on τ_A. However, a marked decrease in τ_A is noted for both $HClO_4$ and HNO_3. Addition of $HClO_4$ also has the effect of greatly lowering the apparent solvation number of magnesium, with HNO_3 having the same effect but to a lesser extent, and $LiClO_4$ appears to have no effect at all on the measured number.

Discussion

For the unacidified solutions studied here, τ_A^{-1} is *ca.* 4–5 $\times 10^6$ sec^{-1} at 25°. This number may be compared with the rate constant for the last step (rate-determining step) in the formation of some magnesium complexes in aqueous solution,[16] and this rate constant typically has the value of *ca.* 1×10^5 sec^{-1} at 25°. The discrepancy between this value and the value of τ_A^{-1} given above is quite significant in light of the rather good agreement between the values of the two quantities for other ions such as Mn^{2+}, Fe^{2+}, Ni^{2+}, etc., in pure aqueous solution.[17] This result for Mg^{2+} tends to indicate that the kinetic behavior of the hydrated ion is altered significantly in going from water to aqueous acetone. This conclusion is not a particularly surprising one in view of the number of possible factors involved, and the result would provide the basis for an interesting series of studies on mixed solvents. However, the principal purpose of this investigation is the study of the acid dependence of τ_A for the hydrated Mg(II) ion.

From the doublet spectra obtained for acidified Mg(II) solutions in aqueous acetone, it was clear that the average lifetime of a proton in the Mg(II) primary hydration sphere is significantly decreased upon the addition of HNO_3 or $HClO_4$, and the τ_A^{-1} values are given

Table I. Values of τ_A^{-1} for $Mg(NO_3)_2$ and $Mg(ClO_4)_2$ in Acetone–Water and for $Mg(ClO_4)_2$ with Added $HClO_4$ and $LiClO_4$ and Also $Mg(NO_3)_2$ with Added HNO_3

Added electrolyte[a]	Mole ratios[b]	Temp, °C	τ_A^{-1}, sec^{-1}
	$Mg(ClO_4)_2$		
None	1:10.90:20.93:0	−37.5	4.75×10^3
	1:10.90:20.93:0	−43.0	2.29×10^3
	1:10.90:20.93:0	−46.0	1.41×10^3
	1:10.90:20.93:0	−51.0	6.75×10^2
	1:10.90:20.93:0	−55.0	343
	1:10.90:20.93:0	−58.0	213
	1:10.90:20.93:0	−59.0	193
	1:10.90:20.93:0	−62.0	109
	1:10.90:20.93:0	−66.5	58
	1:10.90:20.93.0	−70.0	24.6
	1:10.90:20.93:0	−76.0	9.6
	1:10.90:20.93:0	−79.5	3.3
$HClO_4$	1:11.73:23.2:1.19	−70.0	118
	1:11.73:23.2:1.19	−77.0	37
	1:11.73:23.2:1.19	−86.0	21.6
	1:12.27:25.9:1.95	−70.0	159
	1:12.27:25.9:1.95	−77.0	37.8
	1:12.27:25.9:1.95	−86.0	14.3
	1:12.75:27.7:2.79	−70.0	190
	1:12.75:27.7:2.79	−77.0	60.6
	1:12.75:27.7:2.79	−86.0	6.3
	1:13.95:29.7:4.36	−70.0	216
	1:13.95:29.7:4.36	−77.0	46
	1:13.95:29.7:4.36	−86.0	11.7
$LiClO_4$	1:11.66:31.2:0.685	−62.0	65
	1:11.66:31.2:0.685	−69.0	28.5
	1:11.66:31.2:0.685	−76.0	12.3
	1:12.59:24.6:1.29	−66.5	43.5
	1:12.59:24.6:1.29	−71.0	28.6
	1:12.59:24.6:1.29	−74.5	6.9
	1:12.59:24.6:1.29	−78.0	7.4
	$Mg(NO_3)_2$		
None	1:11.40:21.4:0	−56.5	1.06×10^3
	1:11.40:21.4:0	−62.5	412
	1:11.40:21.4:0	−66.5	240
	1:11.40:21.4:0	−70.0	128
	1:11.40:21.4:0	−75.0	67
	1:11.40:21.4:0	−77.0	35.8
	1:11.40:21.4:0	−80.5	23.8
	1:11.40:21.4:0	−86.5	11
HNO_3	1:10.56:24.9:1.53	−77.0	95.8
	1:10.56:24.9:1.53	−87.5	35.3
	1:10.56:24.9:1.53	−90.0	23.4
	1:10.60:26.4:2.06	−77.0	97.7
	1:10.60:26.4:2.06	−81.5	47.5
	1:10.60:26.4:2.06	−87.5	22.6
	1:10.60:26.4:2.06	−90.0	20.2
	1:10.55:28.38:2.79	−77.0	127
	1:10.55:28.28:2.79	−81.5	71.2
	1:10.55:28.38:2.79	−87.5	50.2
	1:10.55:28.38:2.79	−90.0	38

[a] Added electrolyte corresponds to addition of $HClO_4$ or $LiClO_4$ to the $Mg(ClO_4)_2$ solution or HNO_3 to the $Mg(NO_3)_2$ solution. [b] Mole ratios. Represents the mole ratio of components normalized to the magnesium ion concentration. The ratios correspond to Mg^{2+}:H_2O:acetone:added electrolyte.

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(16) M. Eigen and L. DeMaeyer in "Techniques of Organic Chemistry," Vol. VIII, 2nd ed, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(17) R. G. Wilkins and M. Eigen in "Mechanisms of Inorganic Reactions," Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965.

in Table I. Acid-catalyzed proton transfer from a cationic primary hydration sphere to bulk definitely does occur, and the occurrence is not restricted to paramagnetic transition metal ions, but is quite likely a phenomenon to be expected for hydrated ions in general.

The subject of acid-catalyzed proton transfer from hydrated cations in aqueous mixed solvents is one for which significantly more data are needed before valid comparisons can be made with the mechanistic conclusions reached in studies of pure aqueous solutions and such studies are currently in progress.

Acknowledgment. We wish to express our sincere appreciation to Professor N. A. Matwiyoff of The Pennsylvania State University for making his data available to us and for many discussions. In addition we wish to acknowledge the financial support of the National Science Foundation and of the Public Health Service in the form of research grants to T. J. S.

Direct Determination of the Solvation Number of the Magnesium(II) Ion in Water, Aqueous Acetone, and Methanolic Acetone Solutions

N. A. Matwiyoff and H. Taube

Contribution from the Departments of Chemistry, The Pennsylvania State University, University Park, Pennsylvania, and Stanford University, Palo Alto, California.

Received November 8, 1967

Abstract: At temperatures below -60° the proton magnetic resonance (pmr) signals of the solvent molecules within the primary coordination sphere of the Mg^{2+} ion in aqueous acetone, methanolic acetone, and concentrated aqueous solutions can be distinguished from those of the bulk solvent. From a comparison of the areas of the pmr lines of the solvent in the free and coordinated sites, the composition of the primary solvation sphere of the Mg^{2+} ion in these solvents was found to be $Mg(CH_3OH)_6{}^{2+}$ in methanolic acetone and $Mg(OH_2)_6{}^{2+}$ in aqueous acetone and water. The relative coalescence temperatures of the coordinated and free solvent pmr signals indicate that the order of increasing lability of the complex ions is $Mg(CH_3OH)_6{}^{2+} < Mg(OH_2)_6{}^{2+}$ in aqueous acetone $< Mg(OH_2)_6{}^{2+}$ in water.

A study of the Mg^{2+} ion–water complexes using direct techniques is of importance not only with respect to the difficult task of elucidating the solution chemistry of the coordination compounds of the representative elements, but also because the complexes are implicated in a number of enzyme-catalyzed reactions.[1–3] Direct techniques such as isotope dilution (ID), which provides a kinetic distinction between the solvent molecules within and those outside the first coordination sphere of the metal ion, and proton magnetic resonance (pmr) spectroscopy, which provides a magnetic distinction, have been applied successfully to the characterization of several labile complexes of the Mg^{2+} ion at low temperatures: $Mg(CH_3OH)_{6-n}(OH_2)_n{}^{2+}$ in aqueous methanol (ID and pmr);[4,5] $Mg(CH_3OH)_6{}^{2+}$ in methanol (pmr);[6] and $Mg(NH_3)_5{}^{2+}$ in liquid ammonia (pmr).[7]

Although the rate of exchange of the water molecules from the first coordination sphere of Mg^{2+} has been evaluated using sonic relaxation and temperature-jump techniques,[8–10] the lability of the complex $Mg(OH_2)_n{}^{2+}$ precludes the direct determination of the coordination number, n, in dilute aqueous solutions. However, we have been able to distinguish the pmr signals of the $Mg(OH_2)_6{}^{2+}$ ion from those of the bulk solvent at low temperatures ($<-70^\circ$) in concentrated aqueous solutions of $Mg(NO_3)_2$ and $Mg(ClO_4)_2$. In addition, we have been able to show that the $Mg(OH_2)_6{}^{2+}$ ion exists in aqueous acetone solutions over a much wider range of temperatures and molar ratios, $[Mg(ClO_4)_2]$:$[H_2O]$. The use of acetone as a diluent is advantageous because it not only decreases the rate of exchange between H_2O and $Mg(OH_2)_6{}^{2+}$ but it also magnifies the chemical shift difference between the two species. Since acetone is a weak donor molecule[11] to which the Mg^{2+} ion can coordinate, we also include in this report the results of a series of control experiments in which the complex, $Mg(CH_3OH)_6{}^{2+}$, was characterized in anhydrous methanolic acetone solutions of $Mg(ClO_4)_2$.

Experimental Section

1. Materials. The hexahydrate of $Mg(ClO_4)_2$[12] was prepared by dissolving MgO (Fisher Certified Reagent) in an excess of 30%

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(1) E. L. Smith, *Advan. Enzymol.*, 12, 191 (1951).

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