Hydration Number of Sodium Ions Determined by Sodium Magnetic Resonance[1]

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Abstract: The hydration of sodium ions which occurs when a solution of sodium tetraphenylborate in tetrahydrofuran is titrated with water can be followed by the chemical shift of the sodium magnetic resonance, as well as by the electrical conductivity. As the THF in contact with the sodium ion is replaced by H_2O, a downfield shift of ultimately 7.2 ppm occurs. From the titration curves, a hydration number of 3–4 is obtained, and the equilibrium constant for the replacement of a particular THF by H_2O is 10. No contact ion pairs are formed. Further addition of water has no effect, and the chemical shift is the same in the completely aqueous solution, regardless of concentration. The results are consistent with the ion $Na(H_2O)_4^+$ in aqueous solution at sodium concentrations of 0–0.7 M (22–26°). Proton magnetic resonance shows that the large anion is unreactive.

We present here a novel method for the determination of primary hydration numbers, that is, the number of water molecules in the first coordination sphere of an ion. The method is especially suitable for small, monovalent ions. The ion, dissolved in a nonaqueous solvent such as tetrahydrofuran (oxacyclopentane) is titrated with water

$$Na^+ + nH_2O \longrightarrow Na(H_2O)_n^+ \qquad (1)$$

and the titration is followed by the chemical shift of the sodium magnetic resonance, or some other suitable probe. From the titration curve, we find a value of 3–4 for the hydration number of sodium and also obtain the equilibrium constant for the hydration.

Previously reported hydration numbers[2–4] for the sodium ion vary from 3 to 21.

By X-ray diffraction studies of concentrated KOH solutions a hydration number of 4 has been obtained[5] for the K^+ ion. However, it is not certain that the hydration number would be the same in dilute solution.

Malinowski, *et al.*,[6] measured the chemical shift of the proton magnetic resonance of aqueous NaCl solutions as a function of temperature and concentration. By assuming that the shift of a proton in the hydration sphere of the ion is independent of temperature, they were able to unravel the many interactions and arrived at a value of 4 for the sodium ion.

In aqueous solutions, many anions can freely penetrate the first coordination sphere of the sodium ion,[7] forming transient contact ion pairs. At very high concentrations, this will result in fewer water molecules in the first coordination sphere, causing a slightly lower primary hydration number, although the coordination number may be the same.

Experimental Part

Chemicals. Sodium tetraphenylborate, reagent grade, water content 0.1%, was weighed into a small volumetric flask and dissolved in reagent grade tetrahydrofuran, water content 0.02%. The flask was filled to the mark at 25° and weighed: density 0.973 g/ml, molarity 0.750 M, molality 1.047 m. Two aqueous solutions of $NaBPh_4$ (1.049 g/ml (24°), 0.750 M, 0.947 m; and 1.03 g/ml, 0.480 M, 0.555 m) were prepared. The solution in THF was weighed into a series of nmr tubes of 5 mm o.d., and varying amounts of water were added and weighed.

Nmr Experiments. Sodium nmr spectra (absorption mode) were obtained at 15.871 MHz by sweeping the magnetic field. The field sweep is calibrated by sidebands obtained by modulating the magnetic field at 50 Hz. A 3 M NaCl solution gives a symmetrical signal of apparently Lorentzian shape, with signal-to-noise ratio over 150 and a full width at half height $\nu_{1/2} = 10.4$ Hz at $\gamma H_1 T_1 T_2 = 1$, that is, at the value of H_1 giving maximum signal height.[8] At this value of H_1, the line is slightly broadened, and the expected width is $\sqrt{2}/\pi T_2 = 9.4$ sec^{-1}, with[9] $T_1 = T_2 = 0.048$ sec. Thus, the inhomogeneous broadening $\nu_{R/2} = 1$ Hz.

The relaxation time $\sqrt{T_1 T_2}$ is obtained at resonance by adjusting H_1 for maximum signal height,[8] so $\sqrt{T_1 T_2} = 1/\gamma H_1$.

The relaxation time T_2 follows from the line width by subtracting the estimated inhomogeneous broadening of 1 Hz and correcting[8] for saturation broadening γH_1

$$1/T_2^2 = \pi^2(\nu_{1/2} - \nu_{R/2})^2 - \gamma^2 H_1^2 \qquad (2)$$

For all samples, $T_1 = T_2$.

Chemical shifts are measured relative to 3.00 M NaCl (3.19 m), which has a downfield shift[7] of 0.40 ppm relative to the aqueous sodium ion at infinite dilution. To obtain the chemical shift between two samples, the magnetic field is adjusted to the center of resonance of the first sample. The sample tube is replaced, and the field is swept through the resonance of the second sample.

Conductance. An impedance bridge (Electroscientific Industries, Portland, Ore. 97229, Model 250DE) was used at 1000 Hz. To obtain a perfect bridge balance, it was necessary to add capacitors varying from 2.4 μF at the start to 0.03 μF at the end of a titration.

The solutions are titrated with water from a micrometer type buret of 2 ml (Roger Gilmont Instruments, Great Neck, N. Y. 11021, Model S1200A), which could be read to 0.001 ml. After each addition of water, the solution is stirred manually by moving the conductance electrode up and down (Figure 1). The electrode fits in the cell by means of a rubber sleeve, so no air can enter. The cell needs only 4 ml of solution and can hold more than 30 ml. Constant temperature is maintained with a water bath. The arrangement is very convenient and satisfactory.

The conductance electrodes are platinized, cell constant 0.100 cm^{-1}, determined with 0.0500 M KCl (16°), $\kappa = 5.532 \times 10^{-3}$

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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 1971, Abstract No. ANAL 34.

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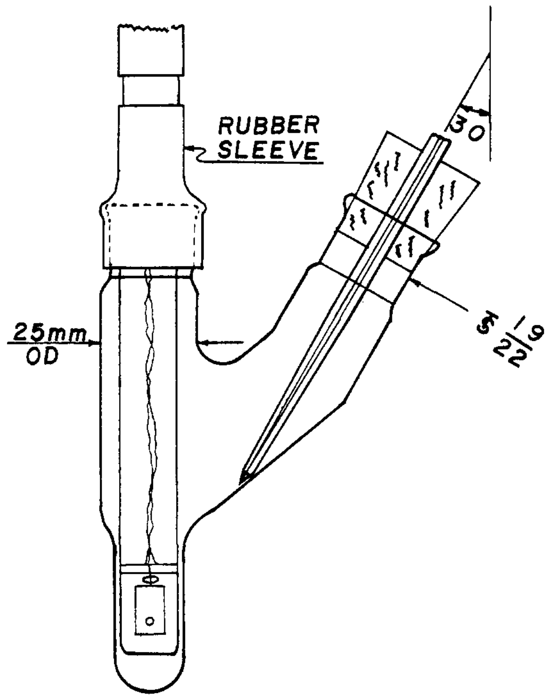

Figure 1. Conductance cell. The electrode can slide up and down through the rubber sleeve on top to stir the solution.

$ohm^{-1} cm^{-1}$ at 16°. The KCl solution was prepared from reagent grade KCl dried for 24 hr at 525°.

The water from the buret dilutes the solution, and the concentration is calculated assuming negligible volume change upon mixing of the water with the tetrahydrofuran solution.

Method

Theory. A salt containing a very large ion, such as sodium tetraphenylborate, is dissolved in a nonaqueous solvent. Ethers are very suitable, and we have used oxacyclopentane (tetrahydrofuran). Sodium tetraphenylborate is very soluble (0.76 *M*) in this, and heat is evolved upon solution. The interaction is attributed to the sodium ion, which forms a solvate.

$$Na^+ + m\text{THF} \longrightarrow Na(\text{THF})_m^+ \qquad (3)$$

By comparison, the solubility of $NaBPh_4$ in diethyl ether is small. Apparently the mobile chain of this ether does not fit around the Na^+ as well as the cyclic tetrahydrofuran.

When water is added, some of the THF will be displaced.

$$Na(\text{THF})_m^+ + H_2O \rightleftharpoons Na(\text{THF})_{m-1}H_2O^+ + \text{THF} \quad (K_1) \qquad (4)$$

Eventually, $Na(H_2O)_n^+$ is formed. If the equilibrium constant for this reaction is sufficiently large, a fair break will occur in the titration curve, and the value of *n* can be obtained.

The titration is followed with a probe sensitive to the immediate environment of the Na^+. The chemical shift of the sodium magnetic resonance is such a probe. The shift is caused by the slight distortion of the sodium ion which occurs when it is in contact with other molecules or ions.[7,10,11] Water is a stronger electron donor than THF and causes a larger downfield shift. Other suitable probes are conductance and perhaps ion-selective electrodes, by which the chemical potential of the sodium ion is obtained quite directly. Thermometric titration is less direct, as it responds also to H_2O–THF interactions. The same applies also to proton magnetic resonance.

The break which occurs upon titration with water is indistinct but still allows the determination of *n*. To analyze the titration curve, it is necessary to make two simplifying assumptions. *First*, the probability of replacing a *particular* THF molecule by H_2O is assumed to be the same, regardless of whether 0, 1, 2, or 3 waters are present in the complex.

$$\text{Na-THF} + H_2O \rightleftharpoons \text{Na-}H_2O + \text{THF} \quad (K) \qquad (5)$$

The first assumption can be stated in a different manner. The sodium ion has *n* independent sites available for coordination, and the sites on one sodium ion do not interact. Thus, Na–THF and Na–H_2O in eq 5 represent interaction sites.

The concentration of the solvent, tetrahydrofuran, varies only slightly during the titration. Thus, the THF may be taken out of the equilibrium constant *K*.

$$\text{Na} + H_2O \rightleftharpoons \text{Na-}H_2O \quad (K_S) \qquad (6)$$

Instead of sodium, other metal ions (M) may be used, and instead of water, other ligands (L). Each metal ion had *n* interaction sites S. Thus, eq 6 is generalized to

$$S + L \rightleftharpoons SL \quad (K_S) \qquad (7)$$

The total number of available sites in 1 l. is

$$c_S = nc_M \qquad (8)$$

where c_M is the *formal* metal ion concentration. The total number of sites is also the sum of "empty" sites S, and occupied sites SL.

$$c_S = [S] + [SL] \qquad (9)$$

Similarly, the formal ligand concentration is the sum of free ligand L and bound ligand SL.

$$c_L = [L] + [SL] \qquad (10)$$

The fraction of occupied sites is

$$p = [SL]/c_S \qquad (11)$$

Thus, *p* varies from 0 at the beginning to 1 at completion of a titration. By means of eq 9, 10, and 11, [S], [SL], and [L] may be eliminated from K_S.

$$K_S = [SL]/[S][L] = \frac{p}{(1-p)}\frac{1}{(c_L - pc_S)} \qquad (12)$$

The actual value of *p* during the titration may be obtained from the chemical shift. The chemical shift results from overlapping of the oxygen orbitals of the water with the outer sodium orbitals.[7] In order to treat the chemical shift data, it is necessary to make a *second* assumption, similar to the previous one. When a water molecule (L) is added to the ion M^+, or ML^+, or ML_j^+, the chemical shift increases by $\Delta\delta$, regardless of the value of *j*. Thus, the coordinated waters do not interact. The second assumption is consistent with the work of Stengle, Pan, and Langford,[12] who studied the ultraviolet absorption and the chemical shift of

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[12] T. R. Stengle, E. Y. C. Pan, and C. H. Langford, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, Abstract No. PHYS 154.

$^{35}Cl^-$ in mixed solvents, and with theoretical considerations.[10] Going from M^+ to ML_n^+, the shift is $\delta_n - \delta_0 = n\Delta\delta$. Similarly, going from M^+ to ML_j^+, the shift is $\delta - \delta_0 = j\Delta\delta$. Thus, the observed shift δ gives the average value of j at a particular water concentration, and the fraction p of occupied sites is

$$p = j/n = (\delta - \delta_0)/(\delta_n - \delta_0) \qquad (13)$$

In this, δ_0 and δ_n are the shifts before and after the titration, respectively.

The resulting values of p as obtained from eq 13 may be fitted to K_S (eq 12). To do so, eq 12 is rearranged by solving for c_L, and eliminating c_S by eq 8

$$\frac{c_L}{pc_M} = \frac{1}{K_Sc_M}\frac{1}{(1-p)} + n \qquad (14)$$

By plotting $1/(1 - p)$ *vs.* c_L/pc_M a straight line should result. Its intercept with the c_L/pc_M axis gives n, and K_S follows from the slope.

The apparent equilibrium constant K_S (eq 6 or 7) obtained this way treats the metal ion as if it were intially free and uncoordinated. It is also possible to calculate the competitive equilibrium constant K as defined by eq 5, which expresses the competition between H_2O and THF for sites on the metal ion. To do so, it is necessary to know the coordination number m of the complex $Na(THF)_m^+$. In the absence of any information, we assume $m = n$. Comparing eq 5 and 6, the two equilibrium constants are seen to be related by

$$K_S \cdot [THF] = K \qquad (15)$$

where [THF] is the concentration of *free* THF, that is, not solvated to the metal ion. A material balance for the THF requires that

$$c_{THF} = [THF] + mc_M \qquad (16)$$

where c_{THF} is the formal concentration.

It is also possible to calculate the equilibrium constants K_1, K_2, and K_n for the successive replacement of THF by H_2O (eq 4). According to our *first* assumption, the probability or rate constant k_f for the replacement of a *particular* THF by H_2O is assumed to be the same regardless of the composition of the complex. The same holds for the reverse reaction, and hence for $K = k_f/k_b$. As a result, the rate constant K_1 is related to K by a simple statistical factor.[13] For example, if $m = n = 4$, the forward reaction of eq 4 will take place if any of four THF molecules is replaced, while the backward reaction will only take place if the single H_2O is replaced. Statistically, the forward reaction is favored by a factor 4 over the backward reaction.

Similarly

$$K_1 = 4K \qquad (17)$$

$$K_2 = {}^3/_2K \qquad (18)$$

$$K_3 = {}^2/_3K \qquad (19)$$

$$K_4 = {}^1/_4K \qquad (20)$$

Applicability and Limitations. By eq 14, the hydration number is obtained graphically as the intercept with the axis c_L/pc_M. The intercept can be located reasonably accurately if the slope c_MK_S is sufficiently high.

$$c_MK_S > 0.5 \qquad (21)$$

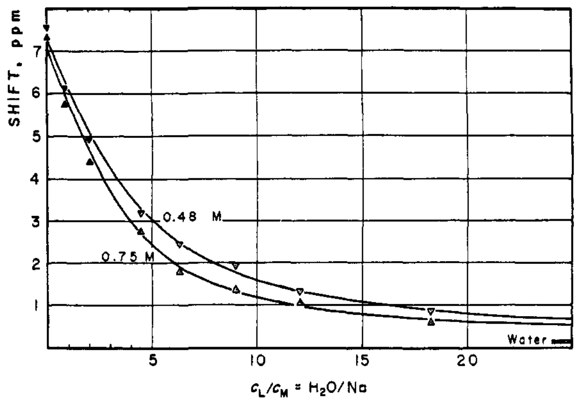

Figure 2. Effect of water addition on the sodium magnetic resonance at 15.871 MHz of sodium tetraphenylborate dissolved in tetrahydrofuran. The shifts are relative to the aqueous sodium ion at infinite dilution and are upfield. The short lines marked "Water" indicate the chemical shift of the aqueous solutions of the same concentrations. To correct for magnetic susceptibility, subtract 0.19 ppm from the shift in tetrahydrofuran.

For the sodium ion, the interaction Na^+–H_2O is largely electrostatic. This ion–dipole dipole energy is $-ep_e/r^2$. For smaller ions, ep_e/r^2 will be higher, resulting in higher values of K_S, and sharper breaks will occur. Larger ions, such as K^+, have a low ion–dipole energy, and the hydration energy is low. As a result, $KBPh_4$ is nearly insoluble in water and tetrahydrofuran. A still larger anion is tetrabutylaluminate.[14,15] The lattice energy of $NaAlBu_4$ is very small, and the salt is even soluble in cyclohexane. No doubt, $KAlBu_4$ is soluble also. Unfortunately, the anion is decomposed by water. Potassium hexafluoroarsenate, $KAsF_6$, is very soluble[16] in many organic solvents and can be recrystallized from water without decomposition.[16]

Contact ion pairs interfere with the determination of the hydration number by this method. In the ion pair M^+Z^-, one site S of the ion is occupied by Z^-. Upon the addition of water, or L, the ion pair may dissociate.

$$SZ^- + L \rightleftharpoons SL + Z^- \qquad (22)$$

This reaction competes with eq 7, causing a more complex titration curve. Contact ion pairs contribute to the chemical shift but not to the conductance of the solution. Dissociation of the pairs according to eq 22 will lead to a strong increase in the conductance of the solution.

In the preceding, it has been assumed that the large anion is not hydrated. If it is, the value of n is really the sum of the hydration numbers of cation and anion. The proton nmr spectrum of the anion will provide information about possible hydration.

So far, only hydration of metal ions has been considered. The method, however, is equally applicable to anions, and we are presently studying the fluoride ion.

Results and Discussion

Chemical Shift. The chemical shifts are given in Figure 2. The shift in dry THF is independent of concentration, suggesting that no contact ion pairs are

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(14) E. Schaschel and M. C. Day, *J. Amer. Chem. Soc.*, **90**, 503 (1968).

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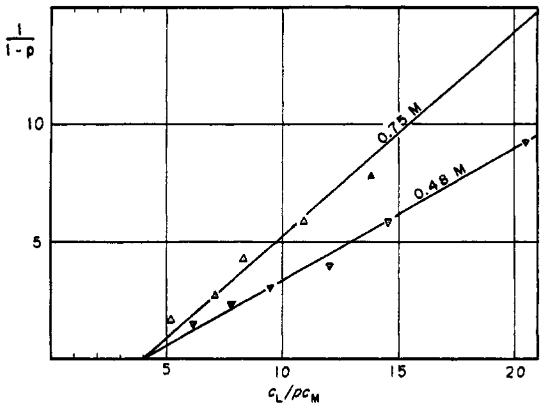

Figure 3. Replotting of the data of Figure 1. The intersect with the c_L/pc_M axis gives the hydration number, and the slope is K_Sc_M. $(1-p)$ is the relative chemical shift.

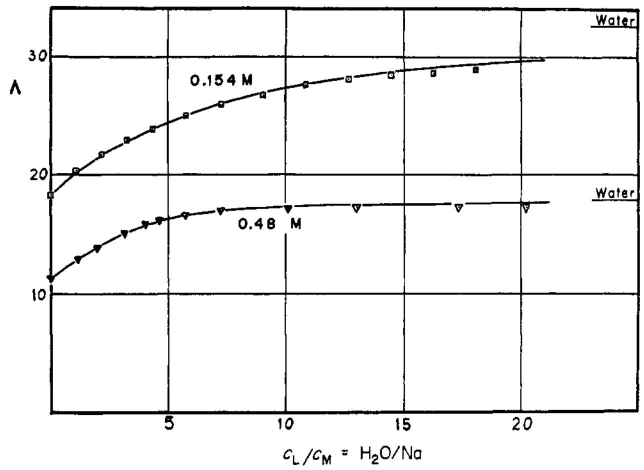

Figure 4. Effect of water addition on the equivalent conductance (ohm^{-1} cm^2 mol^{-1}) of sodium tetraphenylborate dissolved in tetrahydrofuran. The short lines at right marked "Water" indicate the extrapolated conductance of $Na(H_2O)_4^+$.

formed.[7] Erlich and Popov[17] obtain the same result but report their shifts with saturated NaCl as a reference, which has a shift of −0.69 ppm relative to infinite dilution.[7] In aqueous solution, the fraction of sites filled with H_2O (eq 11) is $p = 1$. The shift in aqueous solution (Figure 2) is zero within experimental error. Most likely, no contact ion pairs are formed in aqueous solution also,[7] at least not in noticeable amounts.

The shift plotted according to eq 14 (Figure 3) fits a hydration number of 4, and $K_S = 1.2$ l./mol (eq 7). However, Figure 3 could be fitted reasonably well to $n = 3$ also, but not to $n = 5$ or $n = 6$. If the fit is made by least squares, the intercept is $n = 3.0$ and 3.7, respectively, for the 0.75 and 0.48 M solutions. The value of the competitive equilibrium constant K of eq 5 and 15 is given in Table I. From this, K_1–K_4 follow by eq 17–20.

Table I. Competitive Equilibrium Constant (Eq 5)

c_M, M	c_M, m	Density, g/ml	c_{THF}, M	K (26°), nmr	K (22°), cond
0.154[a]	0.181[b]	0.903 (23°)	11.8[c]		16.7
0.481	0.617	0.942 (23°)	10.8	10.4	31
0.750	1.047	0.973 (25°)	10.0	8.2	

[a] Concentration of $NaBPh_4$ in moles per liter. [b] Same, molality. [c] Formal THF concentration.

As a final check, the calculation procedure was reversed, calculating the titration curve (Figure 2) from the straight line (Figure 3). The result is the solid line in Figure 2. The line fits the experimental points well, supporting the first and second assumption, which stated respectively that the sites on the sodium ion are independent and that the chemical shift is additive.

Of course, one would like to know whether alternative interpretations could explain the data. One such assumption is

$$K' = [ML_n^+]/[M^+][L]^n \tag{23}$$

This leads to a very strong dependence upon the water concentration c_L and does not fit the data.

It has been assumed that the large anion is not hydrated. The proton nmr spectrum of the tetraphenylborate was taken at three different water concentrations, and no chemical shift or spectral change was observed. Thus, the evidence for the hydration of the anion is negative.

While the results virtually demonstrate that the weak complex $Na(H_2O)_4^+$ or $Na(H_2O)_3^+$ is formed when a small amount of water is added to the solution in tetrahydrofuran, one wonders whether the first coordination sphere will gradually pick up additional waters as the THF in the solution is progressively replaced by water. If so, the chemical shift should decrease further. This is not observed, and there is no indication for a hydration number higher than 4 in an aqueous solution of sodium tetraphenylborate with a concentration around 0.5 M.

Conductance. The bulky solvate $Na(THF)_m^+$ has a lower conductance than $Na(H_2O)_4^+$, and the conductance increases during the titration (Figure 4). The titration curves are very similar to the previous ones (Figure 2), except that following the initial fast rise the equivalent conductance $\Lambda = \kappa/c_M$ eventually starts to decrease slowly, probably because water has a higher viscosity than tetrahydrofuran. As a result, it is not clear how the conductance should be extrapolated to $p = 1$. The extrapolated values are marked "Water" in Figure 4 and were chosen to give the best straight line in Figure 5. The solid lines in Figure 4 were calculated from the straight line in Figure 5 as before.

As before, the conductance fits a hydration number of 3 or 4 equally well. A least-squares fit gives $n = 3.7$ for the 0.48 M solution.

In the concentrated solutions, solvent-separated ion pairs appear to be formed, and a maximum of the conductance, κ, occurs near 0.54 M. The value of K near this concentration is anomalous (Table I). The ion pairs do not contribute to the conductance. As water is added, they dissociate, leading to a sharper break and a higher value of K. The chemical shift does not show this effect, as all sodium atoms contribute equally.

Relaxation Times. One might expect that the relaxation rates could also be used to determine hydration numbers. In Figure 6, it is seen that the relaxation curve is more complex than the chemical shift. In the absence of a detailed, quantitative understanding of the

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[17] R. H. Erlich and A. I. Popov, *J. Amer. Chem. Soc.*, 93, 5620 (1971).

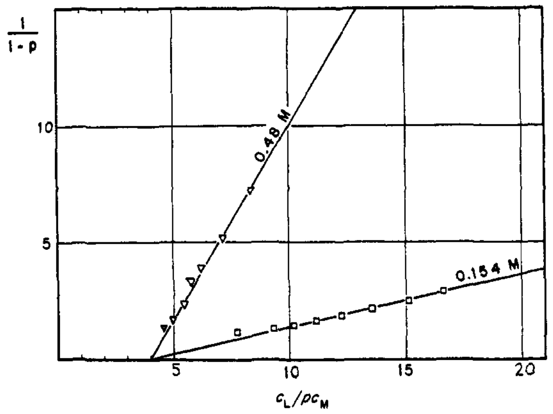

Figure 5. Replotting of the data of Figure 4. The intersect with the c_L/pc_M axis gives the hydration number.

relaxation, it is unreliable for the determination of hydration numbers.

The features of Figure 6 can be explained qualitatively. The relaxation is caused by fluctuating electric field gradients acting on the electric quadrupole of the sodium nucleus.[7] The fluctuations are caused by the motion of nearby electric charges or dipoles, as well as rotation of the complex. For the complex $Na(H_2O)_4^+$, the fluctuations are dominated by the water molecules in the first coordination sphere. As a result, the relaxation rate at the right hand side of Figure 6 is independent of the concentration of $NaBPh_4$.

The complex $Na(THF)_m^+$ is similar to $Na(H_2O)_4^+$, but the bulky complex rotates more slowly. Thus, the correlation time of this motion is longer, and $1/T_2$ is larger for the dry THF solutions at the left in Figure 6. The viscosities of these solutions are 0.0014 and 0.0035 N sec/m^2, respectively,[18-20] for the 0.48 and 0.75 *M* solutions at 26°. The greater viscosity of the more concentrated solution is caused by solvent-separated ion pairs, trimers, etc. The presence of the BPh_4^- near the Na^+ increases the electric field gradient at the sodium nucleus. This, as well as the viscosity differences, leads to a higher value of $1/T_2$ for the more concentrated solution.

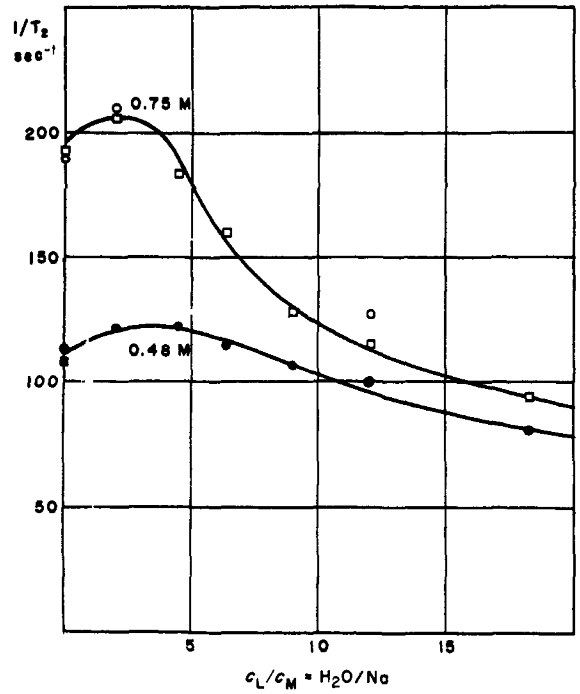

Figure 6. Effect of water addition on the relaxation rates $1/T_2 = 1/T_1$: (□, ■) $1/\sqrt{T_1T_2}$ from γH_1 at maximum signal amplitude; (○, ●) $1/T_2$ from line width (eq 2), accurate only to ±20 sec^{-1}.

The maximum in the curves occurs at $H_2O/Na = 2$–3. From Figure 2, the value of p at the maximum is 0.5, corresponding to the complex $Na(H_2O)_2THF_{m-2}^+$. This unsymmetrical complex has a high field gradient, causing the maximum. However, the maximum is quite flat because the complex is very short lived. In principle, the maximum contains information about the lifetime of the complex. Beyond the maximum, $1/T_2$ drops sharply for the upper curve as the titration and reaction 5 proceeds. This drop is entirely similar to Figure 2.

Conclusion

The chemical shift of the magnetic resonance of the ion is an ideal probe to follow the titration with water. The conductance is suitable also, but the extrapolation of the titration curve to complete titration ($p = 1$) is ambiguous. Both lead to a hydration number of 3–4 for the sodium ion.

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(18) 1 N sec/m^2 = 10 P.

(19) J. Smid, State University College of Forestry, Syracuse, N. Y. 13210, private communication.

(20) D. N. Bhattacharyya, C. L. Lee, J. Smid, and M. Szwarc, *J Phys. Chem.*, **69**, 608 (1965).