Sodium Magnetic Resonance of Aqueous Salt Solutions[1,2]

Gareth J. Templeman[3] and Anthony L. Van Geet*[4]

Contribution from the Department of Chemistry,
State University of New York, Buffalo, New York 14214.
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Abstract: The chemical shift of the magnetic resonance of sodium-23 in aqueous solutions of $NaClO_4$ and NaOH is proportional to the mole fraction X of the salt up to saturation and is respectively $24.0\ X(25°)$ and $-21.7\ X(27°)$ in parts per million relative to the aqueous sodium ion at infinite dilution. The result is interpreted by the formation of short-lived ion pairs with a formation constant close to 1. The shift of $NaBPh_4$ is zero, suggesting that no contact ion pairs are formed with this large anion. Higher temperature displaces the resonance downfield, $-3.65 + 900/T$ for 5.59 m NaCl and $-5.79 + 950/T$ for 8.3 m NaOH relative to infinite dilution. The relaxation rate $1/T_1 = 1/T_2$ increases steadily for $NaClO_4$ solutions but shows an indefinite break for NaOH solutions around $Na/H_2O = 0.10$. When corrected for the viscosity, the break disappears, and $1/\eta T_2$ for NaOH increases steadily. The viscosities at 26° of the solutions are given as a polynomial in c.

The magnetic resonance of the sodium nucleus is a very direct probe for the study of ionic solutions.[5-7] The chemical shift of the resonance is caused by perturbations of the electrons of the sodium atom and is expected to be sensitive only to the immediate environment. From the shift, it should be possible to decide which molecules or ions are in contact with the sodium ion. Additional references are given elsewhere.[1]

The sodium ion is not easily polarized, and the chemical shifts are fairly small, typically a few parts per million. By comparison, cesium ions have very large shifts.[7] The sodium resonance consists of a single, symmetrical peak, which may be as narrow as 6 Hz in spite of the large quadrupole moment. In an asymmetrical environment, the resonance is broadened.[8] This provides additional information, but the interpretation is not as straightforward as the chemical shift.

By comparison, the interpretation of the proton[9,10] chemical shift of the solvent is more complex. Usually the average resonance of solvating and bulk solvent molecules is observed. It is also affected by proton exchange and hydrogen bonding.

While ^{17}O resonance[11,12] is also sensitive to hydrogen bonding, it should be more sensitive to the solvation of cations then anions.

Experimental Part

Apparatus. The measurements were made with a Varian HA-60 high-resolution nmr spectrometer at a frequency of 15.871 or 15.085 MHz, using sample tubes with an outside diameter of 5 mm. Since the field was not locked, the magnet was protected from air drafts by a curtain of polyvinyl chloride. A photograph[1] may be obtained from the authors. Over a period of 10 hr, the field drift was constant within 1%. The field was swept in both directions for all measurements. The field homogeneity was adjusted for the proton signal at 60.000 MHz. The sodium resonance is obtained when the frequency is changed to 15.871 MHz, and the homogeneity is excellent (0.5 Hz at 15.871 MHz).

The sensitivity allows detection of an 0.1 M NaCl solution in water with a signal to noise (rms) ratio of 13 to 1, and an 0.01 M solution is detectable. This is almost half of the proton sensitivity.

The absorption mode signal was used, and the signal height was maximized ($v_{\max}$) by varying the radiofrequency power H_1 so

$$\gamma H_{1,\max}\sqrt{T_1T_2} = 1 \tag{1}$$

At this value of γH_1, the full width at half-height, $\nu_{1/2}$, is slightly broadened.[13]

$$\nu_{1/2} = \sqrt{2}/\pi T_2 \tag{2}$$

A change in γH_1 of 1 db changes $\nu_{1/2}$ by 5.8%.

Relative values of $1/\sqrt{T_1T_2}$ were obtained from $\gamma H_{1,\max} = 1/\sqrt{T_1T_2}$. By measuring a few values of the signal height on both sides of the maximum, $\gamma H_{1,\max}$ may be located within 0.2 db. This can be done visually, graphically, or by computer. The latter was the method used.

The sweep rate was calibrated from the side bands obtained by applying a frequency of 100 Hz or higher to the linear sweep coil. To avoid saturation, the modulation was removed while scanning the center signal.

To obtain the chemical shift of the sodium hydroxide solutions, an external reference of 5 M NaCl was used. A coaxial sample cell (Wilmad Glass Co.) was used, and the reference solution was placed in the inner tube, which was sealed with Dow Corning Silastic clear silicon rubber. Although the tubes were spun, the heavy wall inner reference tube caused an increase of the field inhomogeneity by 20 Hz. The results were corrected to a reference of an infinitely dilute solution of sodium ions by subtracting 0.75 ppm from the measurements.

For sodium perchlorate, some of the measurements were made without the external reference by simply sweeping the field. The center of resonance of 3 M NaCl was used as the starting position. The tube with sodium chloride was then replaced by a tube with sodium perchlorate solution, and the field was swept through the resonance. This method was much more convenient and equally accurate. To correct to infinite dilution, 0.45 ppm was subtracted from the measurements.

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(1) Abstracted in part from the Ph.D. dissertation of G. J. Templeman, State University of New York at Buffalo, 1970; *Diss. Abstr. Int. B*, 31, 5301 (1971). A Xeox copy ($10) may be obtained from University Microfilms, Dissertation Copies, Ann Arbor, Mich. 48106, Order No. 71-6122.

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(3) The Pillsbury Co., Research and Development Laboratory, Minneapolis, Minn. 55414.

(4) Department of Chemistry, State University College, Oswego, N. Y. 13126.

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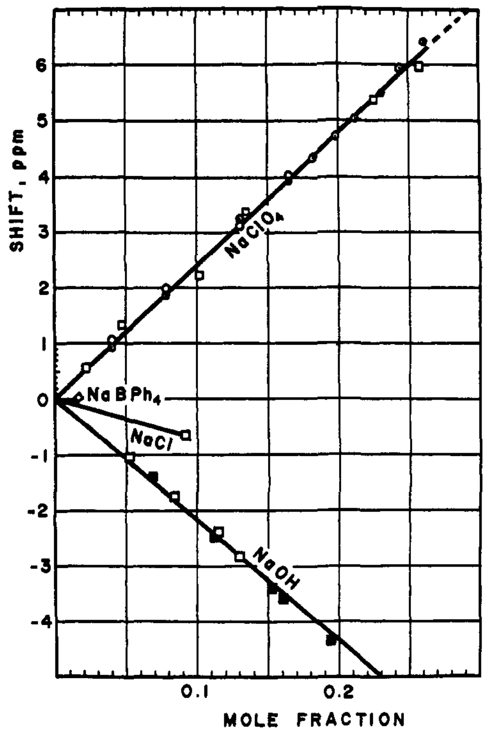

Figure 1. ^{23}Na chemical shift of aqueous solutions of $NaClO_4$ (26°), NaCl (27°), and NaOH (27°). The shift of $NaClO_4$ is upfield: (⊙, □) 15.871 MHz; (■) 15.085 MHz; (○, ◇) referenced by tube substitution; (□, ■) coaxial tube.

No correction for magnetic susceptibility differences was made. For 12 *M* NaOH the correction is calculated[1,14] as +0.06 ppm, for 5.00 *M* NaCl ($X = 0.092$) as +0.11 ppm, and for 9.65 *M* $NaClO_4$ it is estimated as +0.08 ppm. In this, the correction for water (infinite dilution) is taken as 0.00 ppm. These values are to be added to the observed shifts.

The temperature of the solutions was measured in the region of the radiofrequency coils of the spectrometer with a static Teflon thermistor probe[15] connected to an Atkins Model 3F01 thermometer.

Materials. A nearly saturated solution of sodium perchlorate was prepared at about 40° and allowed to stand overnight at 24°. The crystals which had formed were filtered off: apparent density in air at 25°, 1.675 g/cm^3. *Anal.* 70.5% $NaClO_4$ by weight, molarity 9.65 *M*, molality 19.6 *m*, mole fraction $X = 0.261$, mole ratio $NaClO_4/H_2O = 0.353$, as determined from the signal height v_{max} of the sodium magnetic resonance relative to 3.00 *M* NaCl and the density of diluted solutions.[16] The two methods of analysis agreed within 1%. The 3.00 *M* (26°) NaCl solution had a density of 1.114 g/cm^3 (26°), molality 3.19 *m*, $X = 0.0544$, $NaCl/H_2O = 0.0575$, viscosity 1.152 cP (25°).

Sodium hydroxide and sodium chloride solutions were prepared using reagent grade chemicals. Boiled water was used to dissolve the former, and an effort was made to exclude carbon dioxide from the air. The density of the solutions was determined and compared with tabulated values[17] to determine the concentration. Two concentrated solutions: NaOH, density 1.377 g/cm^3 (23°), 12.0 *M* (25°), 13.4 *m*, $X = 0.193$, $NaOH/H_2O = 0.241$, viscosity 17.6 cP (25°); NaCl, density 1.184 g/cm^3 (26°), 4.99 *M* (26°), 5.59 *m*, $X = 0.0914$, $NaCl/H_2O = 0.1006$ (nearly saturated).

The density of the solutions was determined by weighing in a closed weighing bottle the amount of solution delivered by a 10.0-ml pipet.

Viscosities were determined with an Oswald-Cannon-Fenski series 25 viscometer (Cannon Instrument Co., State College, Pa. 16801) at 25° in a water bath. The viscometer was calibrated periodically with water, viscosity 0.8937 cP.[18]

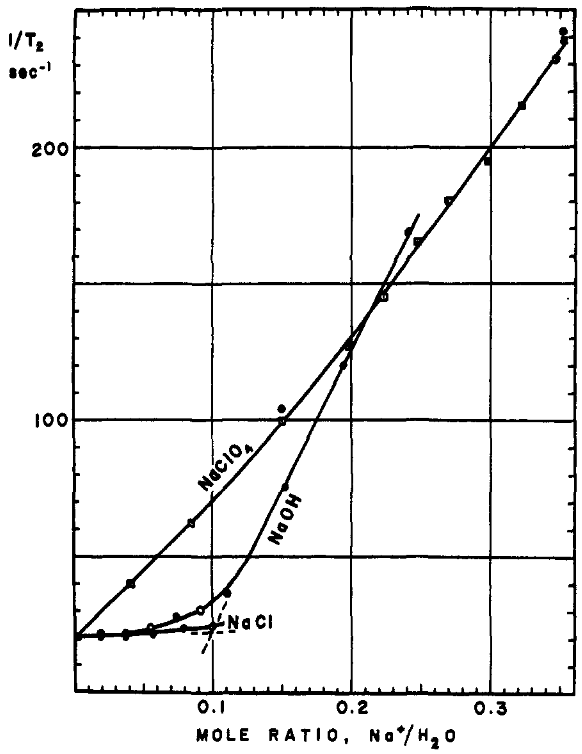

Figure 2. ^{23}Na relaxation in aqueous solutions of $NaClO_4$ (26°), NaCl (25°), and NaOH (25°): (⊙, ⊡) 15.871 MHz; (●) 15.085 MHz; (⊙, ●) $1/T_2$ from line width, corrected for inhomogeneity by subtracting 0.3 Hz (⊙) or 2.0 Hz (●) or 1.0 Hz (⊙, $NaClO_4$); (⊡) $1/\sqrt{T_1T_2}$ from $\gamma H_{1,\max}$.

Results

From Figure 1, it is apparent that the chemical shift δ is proportional to the mole fraction *X* of the salt

$$\delta = X\delta_Z \qquad (3)$$

For $NaClO_4$, δ_Z = 24.0 ppm (26°), and for NaOH, −21.7 ppm (27°). A table of the data is given elsewhere.[1]

The shift of solutions of sodium tetraphenylborate, $NaBPh_4$, is zero within experimental error. For a nearly saturated solution ($X = 0.0168$, density 1.049 g/cm^3 at 24°, 0.750 *M*, 0.947 *m*), the shift was $\delta = 0.10 \pm 0.10$ ppm, and for a more dilute solution ($X = 0.0099$, 0.48 *M*, 0.555 *m*) it was $\delta = 0.04 \pm 0.10$ ppm. The last number is the estimated rms error. Thus, $\delta_Z = 0 \pm 6$ ppm for $NaBPh_4$. The relaxation times are given in Figure 2.

Effect of Temperature. The chemical shift in parts per million of 5.00 *M* NaCl ($X = 0.0914$) relative to 1.00 *M* NaCl ($X = 0.0184$) was measured between 275 and 366°K at 15.87 MHz.

$$\delta(5\ M) - \delta(1\ M) = -2.92 + 720/T \pm 0.19 \qquad (4)$$

The last term is the rms error. Assuming that the shift is linear with mole fraction at all temperatures, the result may be extrapolated to infinite dilution.

$$\delta(5\ M) = -3.65 + 900/T \qquad (5)$$

The agreement with the results of Deverell and Richards[7] is perfect.

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The chemical shift of 7.89 M NaOH ($X = 0.130$) relative to 5 M NaCl was measured over the same temperature range

$$\delta - \delta(5\ M\ \text{NaCl}) = -2.14 + 50/T \pm 0.04 \quad (6)$$

By adding eq 5, the shift relative to infinite dilution is obtained.

$$\delta = -5.79 + 950/T \quad (7)$$

A graph as well as a table of the measurements is available.[1]

The temperature-dependent terms for NaCl and NaOH in eq 5 and 7 are the same within experimental error, suggesting that the shift is caused by the interaction $Na^+–H_2O$ rather than $Na^+–Z^-$.

Viscosities. The viscosities of aqueous solutions were measured at 25° up to saturation. The concentrated NaOH solutions were more viscous than $NaClO_4$ solutions of the same concentration, presumably because OH^- forms part of the hydrogen bonded structure of water. The results in centipoise (10^{-3} N sec/m^2) were fitted to a polynomial

$$\text{NaCl} \quad \eta = 0.896 - 0.097c + 0.098c^2 - 0.011c^3 \pm 0.008 \quad (8)$$

$$\text{NaClO}_4 \quad \eta = 0.895 + 0.076c - 0.020c^2 + 0.007c^3 \pm 0.008 \quad (9)$$

$$\text{NaOH} \quad \eta = 0.900 + 0.193c + 0.004c^2 + 0.008c^3 \pm 0.072 \quad (10)$$

where c is the concentration in moles per liter at 26, 26, and 25°, respectively, and the last term is the rms error. The densities were also measured, and the results are given elsewhere.[1] A graph of the viscosities is also available.[1]

Discussion

Contact Ion Pairs. From Figure 1, it is apparent that the chemical shift is linear with the mole fraction of the salt. Deverell and Richards[7] measured the shift of aqueous solutions of $NaNO_3$, NaCl, NaBr, and NaI. When their results are plotted against mole fraction, straight lines are obtained[1] also, except for $NaNO_3$. The values of δ_Z in parts per million are: NaCl, −7.0; NaBr, −9.6; NaI, −13.4; $NaNO_3$, +19.

The shift can be interpreted by either or possibly both of the following hypotheses. (a) The Na^+ and ClO_4^- form transient contact ion pairs. (b) Ion pairs, if formed, remain solvent separated, and the Na^+ is directly surrounded only by H_2O molecules. The shift reflects a change in the bond between Na^+ and H_2O as the salt concentration increases. While we strongly favor a, we will discuss both of these hypotheses.

(a) The chemical shift observed is large and comparable to the shift observed in nonaqueous solutions.[5,6,19] For example, the chemical shift of sodium tetraphenylborate dissolved in tetrahydrofuran (THF) is +7.5 ppm, independent of concentration.[5,6] A change of the bond between Na^+ and H_2O as the salt concentration increases would be expected to have a less drastic effect.

The solubility of $NaClO_4$ in water exceeds the mole fraction 0.25. Thus, for every two ions in the solution, less than three molecules of water are available. At least some of the Na^+ must be in direct contact with ClO_4^-, as not enough water is available. One might suppose that contact ion pairs only form at very high concentration. If so, the shift would not be linear however. It is concluded that at least some contact ion pairs are present at all concentrations.

(b) In support of the second hypothesis, it is noted that salt solutions have a negative excess volume. The interionic attraction leads to compression which may cause the shifts. Indeed, increasing pressure on crystals of alkali halides leads to downfield shifts.[20]

While a strong downfield shift indeed occurs in sodium hydroxide solutions, the shift is *upfield* for sodium perchlorate and sodium nitrate. This cannot be explained by compression. The still larger anion BPh_4^- shows no shift at all.

Alternatively, the shift might be long range, as in a solvent-separated ion pair. This would be analogous to proton chemical shifts in organic compounds. Since the shift would have to be transmitted through at least three bonds, it should be fairly small. However, localized hydrolysis[21] of the H_2O separating the ions would lead to species of the type $Na^+OH^{\delta-}\cdots H^{\delta+}Z^-$, and an appreciable downfield shift might occur. An *upfield* shift, as caused by ClO_4^- or NO_3^-, cannot be explained in this way though.

For these reasons, we favor hypothesis a and suppose that the shift is caused mostly by very short range interactions, so only molecules in direct contact with the sodium contribute significantly.

At any one time, the sodium ions in a solution will not all be in the same environment. The observed shift is the average over all sodium ions. In the absence of contradicting information, we furthermore suppose[22] that the chemical shift of a *particular* sodium ion is essentially *additive*. Thus, if the ion is in contact with four molecules, each one causes a shift δ_i, and the total shift is $\delta_1 + \delta_2 + \delta_3 + \delta_4$. The only experimental evidence for this is the shift of solutions of sodium tetraphenylborate in a mixture of tetrahydrofuran and water, which may be interpreted on the basis of four independent "sites" around the ion.[5]

The linearity of the chemical shift with the mole fraction of any of the ions is surprising when compared with the shift of Na^+ in solvent mixtures.[5,19] When the shifts in water[7] are extrapolated to pure salt, the result appears to agree with the chemical shift of crystalline halides.[20,23,24] With high-resolution nmr, we were only able to detect the resonance of crystalline NaCl. Though very broad, we conclude that it occurs between 0 and −7 ppm.

Thus, it is supposed that δ_Z as given by eq 3 is just the chemical shift of the crystalline salt NaZ. It should be emphasized that the experimental evidence for this is meager. In solution, the sodium ion is surrounded by Z^- and H_2O molecules in proportion to the mole

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fraction of each: $X = NaZ/(NaZ + H_2O) = Z^-/(Z^- + H_2O)$, resulting in eq 3. According to this interpretation, the sodium ion has no preference for H_2O over Z^-, or vice versa. Z^- ions freely penetrate the solvation sphere, forming transient contact ion pairs. This situation appears to occur for $NaClO_4$, NaOH, NaBr, NaI, $NaNO_3$, and NaCl but probably not for $NaBPh_4$. Most likely, the large BPh_4^- ion does not penetrate the solvation sphere of the sodium ion, and no significant shift occurs. If it had penetrated, one might have expected a shift still larger than $NaClO_4$.

The equilibrium constant K for the replacement of solvated water by the ion Z^-

$$Na^+\text{-}H_2O + Z^- \rightleftharpoons Na^+\text{-}Z^- + H_2O \qquad (11)$$

is essentially equal to 1 according to our interpretation. If it were not, the chemical shift would not be linear with mole fraction. For rubidium and especially cesium salts, the shift is not linear with mole fraction,[7] suggesting that $K > 1$ for these ions. Apparently these large cations prefer Z^- ions over water in their solvation sphere, because the absolute value of the electrostatic ion–ion energy $-e^2/r$ is larger than the ion-dipole energy $-ep/r^2$ as r becomes larger. Extrapolation of these curves[7] to $X = 1$ agrees with the shift of the crystalline salts.[23,24] Our interpretation of the chemical shift is not inconsistent with the conductivity of these solutions.[1,21]

The shift caused by the perchlorate is upfield because the $Na^+\text{-}ClO_4^-$ interaction is weaker than the $Na^+\text{-}H_2O$ interaction, as explained in the next section. The overlap between the orbitals of Na^+ and ClO_4^- is very small. The Raman spectrum[25] of ClO_4^- in a saturated solution of $NaClO_4$ shows no evidence of $Na^+\text{-}ClO_4^-$ interaction. Raman spectra of NaCl solutions[26,27] suggest that the ion pairs in this solution are solvent separated.

Chemical Shift. To explain the observed values of the extrapolated chemical shift δ_Z, it is necessary to consider the origin of these shifts.

If an atom or molecule is exposed to a magnetic field, its electrons will rotate about the direction of the field. This rotation causes a smaller secondary magnetic field, opposing the original field. Thus, the resultant field at the nucleus is smaller than the original applied field. In nuclear magnetic resonance, this screening effect is compensated for by increasing the applied magnetic field and corresponds to an upfield chemical shift. The screening effect is also the cause of diamagnetism.

The electron cloud will rotate freely if it has spherical symmetry. If it has axial symmetry, as in the case of a p_z or σ_z orbital, it will rotate freely about its axis of symmetry (z axis), but rotation about the x or y axis is inhibited, and the diamagnetic screening is reduced. This reduction is called the paramagnetic term and leads to a downfield shift. In this way, Saika and Slichter[28] calculate the screening constant (chemical shift) of fluorine and find that the resonance should occur at low field, in good agreement with experiment. Electrons in a p or d orbital have angular momentum. The magnetic field caused by the angular momentum tends to be in the same direction as the applied field, contributing to the paramagnetic term.

An isolated sodium ion has filled shells with perfect spherical symmetry. In a molecule of NaCl, the symmetry is no longer perfect. Under the influence of the electrostatic attraction force $-e^2/r^2$ some overlap between the orbitals of the two ions occurs, leading to an equal opposing force. As a result of the overlap, the sodium ion acquires an extra electron or fraction of an electron, which can only be accommodated in a higher orbital. The partial filling of the 3p orbital causes a downfield chemical shift. Kondo and Yamashita[22] calculate the charge overlap in crystals of rubidium and cesium halides, MZ, and obtain reasonable agreement with experimental values of the chemical shift. In this calculation, the shift is proportional to the number of nearest neighbors and is simply the sum of the individual $M^+\text{-}Z^-$ interactions. Thus, the chemical shift is *additive*, as supposed in the preceding section. Pressure increases the overlap, and the chemical shift becomes more negative.[20]

The overlap, or occupancy of the 3p orbital of the sodium, will be largest when Z^- is an electron-donating ion or molecule. Thus, $\delta_Z = -13.4$ ppm for I^-, and[7] only -7.0 ppm for Cl^-.

The oxygen atoms of NO_3^- and ClO_4^- are poor donors: $\delta_Z = +19$ and 24 ppm, respectively. Also, the electrostatic energy $-e^2/r$ is low because of the larger size of these ions.

Overlap will also occur with the solvent molecules.[19] The electrostatic ion–dipole energy is $-ep/r^2$. In pyridine, which is an excellent electron donor, $\delta = -6.6$ ppm. On the other hand, oxygen-containing solvents such as ethers, ketones, and esters are fairly poor donors, and $\delta \approx +6\text{–}9$ ppm. Water is intermediate with 0.0 ppm. Erlich and Popov[6] relate the chemical shift to the basicity of the solvent as expressed by Gutman's donor[29] numbers and obtain a very good correlation.

The OH^- ion, being negatively charged, interacts more strongly than H_2O and $\delta_Z = -22$ ppm.

Summarizing, the chemical shift is increasingly negative in the order

$$ClO_4^-, NO_3^-, \text{THF}, H_2O, Cl^-, Br^-, I^-, OH^- \qquad (12)$$

This order is a result of the electron-donating ability or basicity of the anion or solvent molecule.

Relaxation Times. The relaxation of ^{23}Na in dilute aqueous solutions of NaCl and $NaClO_4$ has been measured.[7,30–32] A few data in nonaqueous solutions are also available.[5,8] The relaxation of ^7Li in aqueous and nonaqueous solutions of $LiClO_4$, LiCl, and LiBr has also been studied.[33,34] The formation of weak sodium complexes in water leads to an increase[8,35] in the line width of ^{23}Na.

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Our results (Figure 2) are in excellent agreement with the accurate measurements of Eisenstadt and Friedman.[30,31] Since relaxation is caused by molecular motion, it is less easy to interpret than the chemical shift. At modest concentration, $1/T_2$ is essentially constant for NaCl and NaOH, as is the viscosity of the solutions. This would be easy to explain if the ion pairs were solvent separated. However, this can hardly be the case for NaOH.

Relaxation of the sodium ion is dominated by its electric quadrupole moment eQ, which interacts with electric field gradients eq. Molecular motions cause a random fluctuation of the field gradient. The probability of finding the field gradient unchanged during time t supposedly can be represented by $\exp\{-t/\tau\}$, where τ is the correlation time of the molecular motion responsible for relaxation. Since the motions are supposed to be random, the Fourier spectrum of the motions is white; that is, it contains all frequencies at equal intensity up to a cut-off frequency $1/\tau$. Only the spectrum component equal to the Larmor frequency ω of the precessing nucleus interacts with the nucleus, causing relaxation. Usually the molecular motions are fast, and $1/\tau \gg \omega$. In this case the relaxation time is

$$1/T_1 = 1/T_2 = Ke^2qQ\tau \qquad (13)$$

where K is a constant depending only on the quantum number I for the total angular momentum of the nucleus. The condition $T_1 = T_2$ appears to hold for all solutions investigated, although verification for the viscous, concentrated NaOH solutions would be desirable.

The field gradient should be zero for the symmetrical complex $Na(H_2O)_4^+$. Addition of a small amount of NaOH should disturb the symmetry and cause a dramatic increase of the field gradient, causing an increase in $1/T_2$. This is not so. Apparently relaxation of $Na(H_2O)_4^+$ at infinite dilution is caused[30,31] by Brownian motion of the H_2O surrounding the Na^+. In aqueous solutions, the high equivalent conductance of the proton is caused by protons jumping across hydrogen bonds. This process leads to the transient presence of H_3O^+ and OH^- even in pure water, and species like $Na(H_2O)_3OH$ will be present transiently. Localized hydrolysis[21] of solvent separated ion pairs will have the same result. The resulting species will have a high field gradient and may also contribute to the relaxation of the sodium ion. The field gradient of $Na(H_2O)_3OH$ or distorted $Na(H_2O)_4^+$ will change by rotation of the complex as well as by proton jumps or exchange of H_2O or OH^-. The effective correlation time will be

$$1/\tau = (1/\tau_r) + (1/\tau_H) \qquad (14)$$

where τ_r and τ_H are the correlation times of the rotation and the proton jumps, respectively. Usually, τ_r is assumed to be proportional to the viscosity.

Addition of a modest amount of NaOH apparently will not greatly effect the field gradient. The presence of some Cl^- ions, even if occasionally in close contact with Na^+, is not able to dominate the relaxation either. However, when the large ClO_4^- ions are in close contact with the Na^+, the rotation of the complex slows down, and τ_r increases, causing broadening. In eq 14, τ_r apparently dominates, and $\tau \approx \tau_r$. The activation energy for the relaxation of $NaClO_4$ should be only slightly higher than for NaCl and NaOH. While the product $1/\eta T_2$ is approximately constant[1] for NaCl, it is not so for $NaClO_4$. The viscosity cannot compensate for the increase of $1/T_2$. This is expected, as the average size of the rotating complex increases with the addition of ClO_4^-. For NaOH, the viscosity overcompensates, and the product $1/\eta T_2$ decreases somewhat.[1] The reason is not clear, but is no doubt related to the anomalous nature of the OH^- ion.

At very high concentrations, $1/T_2$ for NaOH increases sharply, as does the viscosity. The break occurs when $H_2O/Na^+ = 10$. This appears to coincide with the value of the total hydration number[5] of NaOH, that is, 4 for Na^+ and 6 for[36] OH^-. However, $1/\eta T_2$ does not show a break. Thus, it is doubtful that a change in relaxation mechanism occurs.

For $NaClO_4$, $1/\eta T_2$ increases initially and reaches a maximum at $Na^+/H_2O = 0.12$. Beyond this a slight decrease occurs. In these very concentrated solutions, the rotation of the complex may still dominate the relaxation. However, the model which views the complex as rotating in a liquid without structure can hardly be expected to hold, and it would be too much to expect[37] that τ_r and hence $1/T_2$ are proportional to the viscosity η at these high concentrations.

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