Canadian Journal of Chemistry

Published by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 46 NOVEMBER 15, 1968 NUMBER 22

Solvation of sodium ions studied by ^{23}Na nuclear magnetic resonance

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Received May 31, 1968

The ^{23}Na chemical shifts, extrapolated to infinite dilution, of solutions containing sodium iodide dissolved in 14 different oxygen or nitrogen donor organic solvents have been determined. The observed range of chemical shifts can be successfully related to changes in the paramagnetic term of the general nuclear screening equation. A fair correlation between the magnitude of the paramagnetic term and the Lewis basicity of the solvent has been drawn. Those solvents showing anomalous behavior are the ones for which large magnetic anisotropies are to be expected. The ^{23}Na chemical shifts for two mixed solvent systems containing sodium iodide have been obtained, and these support the conclusion that preferential solvation of the sodium ion occurs.

Canadian Journal of Chemistry, 46, 3425 (1968)

Introduction

In recent years, the nuclear magnetic resonance (n.m.r.) technique has yielded a great deal of information about concentrated solutions of electrolytes. Most of these results have been obtained from studies of the proton magnetic resonance of the solvent water (1–5). Comparatively few results have been obtained by observing the resonance of a nucleus within the electrolyte (6). The purpose of this investigation was to obtain a detailed description of the ion–solvent interactions in nonaqueous solutions of sodium iodide using the ^{23}Na nucleus as a probe.

In spite of the rather favorable characteristics possessed by the ^{23}Na nucleus for the observance of its magnetic resonance, very little has been achieved from measurements on this nucleus. Previous studies on aqueous (2, 7, 8) and nonaqueous (8) solutions of various sodium salts failed to show any dependence of the position of the ^{23}Na resonance on the salt concentration. However, in 1966, Deverell and Richards (6) reported a linear dependence of the chemical shift on the concentrations of the sodium halides and sodium nitrate in water. The chemical shifts covered a total range of 5 p.p.m. They also found that the shielding of the sodium ion depended on the anion present, the order of increasing shielding being $I^- < Br^- < Cl^- < F^- < H_2O < NO_3^-$.

Maciel *et al.* (9) have studied the ^{7}Li resonances of lithium perchlorate and lithium bromide in various organic solvents and found that the chemical shifts of these resonances cover a range of 6 p.p.m. depending on the solvent. Since Jameson and Gutowsky (10) have noted that the chemical shifts in different compounds increase with increasing atomic number for a particular group, it is thus expected that a larger range of chemical shifts will be found for ^{23}Na salts than for ^{7}Li salts in various solvents, thus allowing any trends to be more readily discernible.

Experimental

Materials

The sodium iodide was B.D.H. laboratory reagent grade. This powder was recrystallized from water, washed with ether, and dried under reduced pressure. The resulting powder was then recrystallized from ethanol, washed with ether, and dried at 150–200 °C for 3 days at a pressure of 0.02 mm. The acetic anhydride, acetone, ethyl acetoacetate, benzaldehyde, ethyl acetate, pyridine, and anhydrous ethylenediamine were Fisher certified reagent grade. The acetonitrile, acetyl-acetone, N,N-dimethylformamide, and dimethyl sulfoxide (DMSO) were B.D.H. laboratory reagent grade. The

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[1] Holder of National Research Council of Canada Studentships during 1966–68.

tetrahydrofuran and pyrrolidine were from Eastman Organic Chemicals and the glacial acetic acid was C.I.L. C.P. reagent grade. All of these solvents, except pyridine, were dried over molecular sieves (Linde 4A). The pyridine was dried over KOH pellets. All preparation and transfer operations were carried out under the dry nitrogen atmosphere of a glove box.

^{23}Na Magnetic Resonance Measurements

The ^{23}Na n.m.r. spectra were obtained from a standard Varian HR-60 spectrometer operating at a frequency of 15.083 MHz. A spherical sample container fitted with a concentric spherical insert for the reference solution was used. The sample tube had a maximum inner diameter of 14 mm and that of the insert was 3 mm. Corrections due to differences in bulk susceptibilities between samples were not applied to the chemical shifts. These would arise from any imperfections in the geometry of the cell and would be expected to be small. Each spectrum was calibrated by means of side bands generated by a General Radio variable frequency oscillator, type 1310A. The audio frequencies employed were in the range 150 Hz (for smallest chemical shifts) to 350 Hz (for largest chemical shifts) and were measured by a Hewlett-Packard 5245L electronic counter. A sweep rate of about 5 Hz/s was used and each sample was swept at least four times in both increasing and decreasing field directions. A positive δ corresponds to an upfield chemical shift and represents increased screening of the ^{23}Na nucleus.

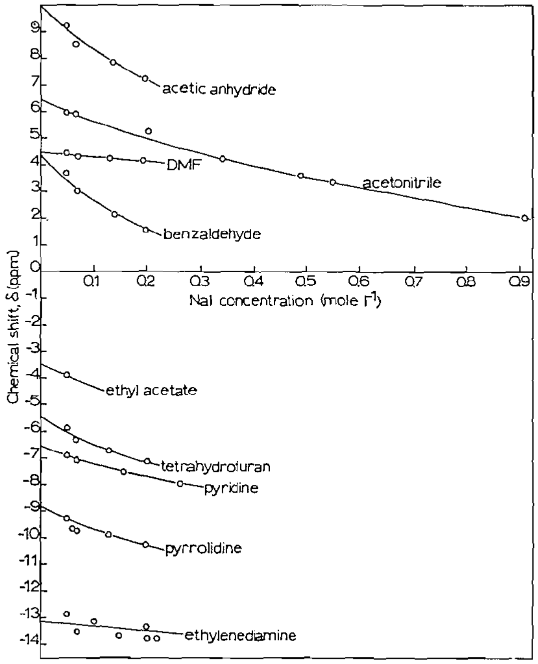

FIG. 1. ^{23}Na chemical shifts of sodium iodide in various solvents as a function of concentration.

Results

The chemical shifts with respect to an aqueous solution of sodium iodide (22.8% NaI) were determined for a minimum of four concentrations of sodium iodide in each of the solvents except DMSO and ethyl acetate (see below). The shift of the 22.8% aqueous sodium iodide reference solution from infinitely dilute aqueous sodium iodide ($\delta_{22.8\%} = -0.41$ p.p.m.) was determined from Fig. 1 of ref. 6. The chemical shifts of the nonaqueous solutions of sodium iodide relative to an infinitely dilute aqueous sodium iodide solution are given by

$$[1] \qquad \delta = \delta_{\text{obs}} + \delta_{22.8\%}$$

where δ_{obs} is the observed shift relative to the 22.8% aqueous sodium iodide external reference. The chemical shifts for each solvent were extrapolated to infinite dilution as in Fig. 1. The chemical shifts at infinite dilution, δ_0, for all the solvents studied are listed in Table I.

TABLE I

^{23}Na chemical shifts of sodium iodide at infinite dilution in various solvents

Solvent	δ_0 (p.p.m.)*	pK_a†
Acetic anhydride	9.9	
Acetonitrile	6.4	−10.13
Acetone	5.8	−7.2
Acetic acid	5.4	−6.1
Ethyl acetoacetate	5.2	
Acetyl-acetone	4.8	
Acetyl-acetone (diketone)		−6.2
Acetyl-acetone (enol)		−5.1
N,N-Dimethylformamide	4.5	−0.01
Benzaldehyde	4.3	−7.1
Water	0.0	
Dimethyl sulfoxide	~0	0
Ethyl acetate	−3.5	−6.5
Tetrahydrofuran	−5.5	−2.08
Pyridine	−6.6	5.29
Pyrrolidine	−8.9	11.27
Ethylenediamine	−13.1	

*Chemical shifts relative to infinitely dilute aqueous NaI.
†Values obtained from ref. 16.

The plots of the chemical shifts versus molar concentration of NaI in acetone, ethyl acetoacetate, and acetyl-acetone all had similar slopes to that for the NaI–benzaldehyde solutions. No concentration dependence of the ^{23}Na resonance was detectable for the solutions of sodium iodide in acetic acid in the concentration range studied for this solvent (up to 0.41 *M*). The chemical shift for only one concentration of sodium iodide in ethyl acetate was obtained because of the low solubility of NaI in this solvent. Its chemical shift at infinite dilution was obtained by analogy with the other curves. Owing to the overlapping of the ^{23}Na resonance in the DMSO solution with the external reference signal, no direct chemical shift measurement was possible. However, the peak due to ^{23}Na in DMSO was 0.68 p.p.m. wide at half-height, thus the chemical shift would be in the range ±0.34 p.p.m. The standard deviations of all the other chemical shifts recorded were not in excess of ±2% of the value of the shift.

The influence of water on the ^{23}Na chemical shifts of NaI in acetonitrile and ethylenediamine is shown in Fig. 2. The molar concentration of sodium iodide was approximately constant in each of these solutions, while the mole ratio of water in the solvent was varied. Figure 3 represents the results of a similar study of different sodium iodide concentrations in ethylenediamine–water solvent mixtures. The curves in Figs. 2 and 3 have been extrapolated to the chemical shift values expected (6) for aqueous solutions of sodium iodide of these concentrations (i.e. approximately zero).

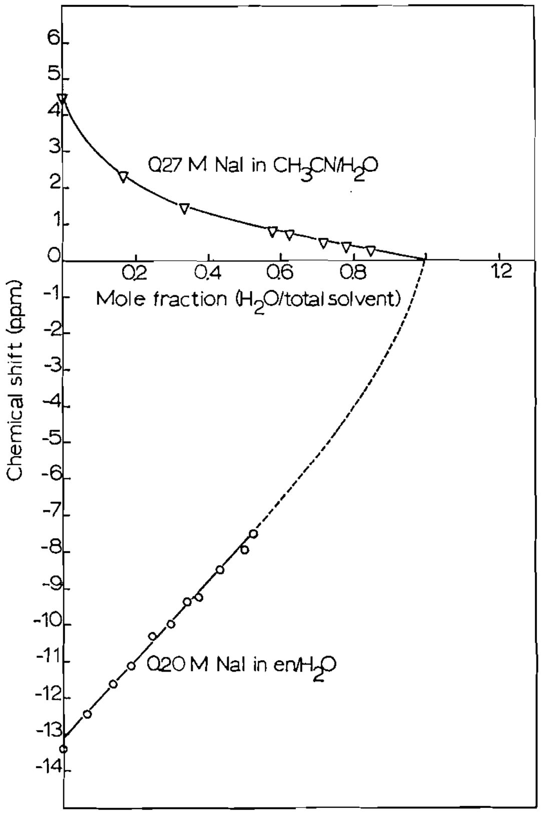

FIG. 2. Influence of water on the ^{23}Na chemical shifts of sodium iodide in acetonitrile and ethylenediamine.

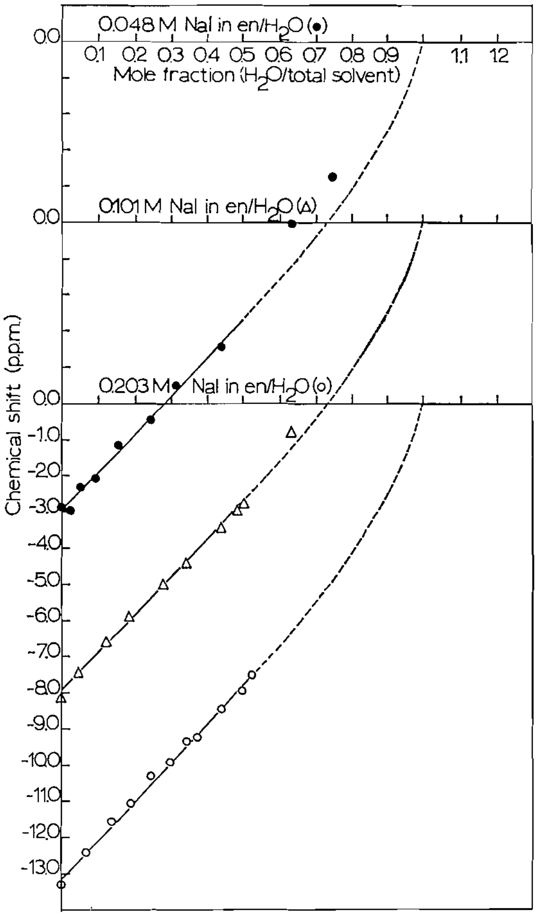

FIG. 3. Influence of water on ^{23}Na chemical shifts of sodium iodide in ethylenediamine.

Interpretation of Chemical Shifts

The position of a nuclear magnetic resonance signal is determined by the total shielding that the nucleus under investigation receives from various sources. This shielding is expressed by the screening constant, σ. A general formula for σ has been developed by Ramsey (11) but its applicability to all but the simplest systems is limited. Saika and Slichter (12) have put the calculation of screening constants on a practical basis by dividing the screening constant into three independent contributions represented by

$$[2] \qquad \sigma = \sigma_d + \sigma_p + \sigma_o$$

The σ_d term arises from the local diamagnetic currents in the molecule and is expressed by the Lamb formula,

$$[3] \qquad \sigma_d = \frac{e}{3mc^2} \sum_i \left\langle \Psi_0 \left| \frac{1}{r_i} \right| \Psi_0 \right\rangle$$

Contributions from other atoms to the shielding of the resonant nucleus are contained in σ_o. These contributions are due to anisotropies in the magnetic susceptibilities of the distant atoms and vary as the inverse cube of their distance from the resonant nucleus. These effects are generally minor on nuclei other than protons. σ_p is the paramagnetic term and is usually the dominant shielding term. It represents the contribution due to the net orbital angular momentum of electrons in the valence orbitals of the nucleus under investigation and it makes a negative contribution to the screening. Thus only electrons in p, d, f, . . . orbitals make a first-order contribution to σ_p. Electrons in s-orbitals contribute to σ_p only to the extent that they influence the effective nuclear charge of the atom and thus the inverse cube radius of the other electrons, $\langle 1/r^3 \rangle_{n,l}$, which affects σ_p.

The addition of an electron to any orbital of Na^+ will increase the diamagnetic shielding. This change in σ_d can be approximated by the following expression (13):

$$[4] \quad \sigma_d = \frac{e^2}{3mc^2} \cdot \frac{Z_{\text{eff}}}{\alpha_0 n^2} = 17.8 \times 10^{-6} \frac{Z_{\text{eff}}}{n^2}$$

where α_0 is the Bohr radius, n is the principle quantum number of the orbital to which the electron is added, and Z_{eff} is the "effective nuclear charge". The effective nuclear charge which determines the radial portion of Slater-type atomic orbitals is given by $Z_0 = Z - S$, where Z is the real nuclear charge and S is a screening constant evaluated using Slater's rules (14). It is generally recognized that for all but the lightest atoms, Slater atomic orbitals give values for the average orbital radius $\langle r \rangle$ which are too large, indicating that the strict application of Slater's rules gives a value of Z_0 which is too low. In estimating the magnitude of σ in their "atom in a molecule" model, Schneider and Buckingham have used $(Z_0 Z)^{1/2}$ for the effective nuclear charge, presumably to allow for this factor. For sodium, $Z = 11$, $Z_0 = 2.20$, and $\sigma_d = 9.7$ p.p.m. for the addition of one electron to any orbital with $n = 3$. Thus, on progressing from purely ionic sodium to atomic sodium, the changes in the diamagnetic shielding of the nuclei would result in a total chemical shift of approximately 10 p.p.m. Since neither of these two extreme cases would be expected to be encountered in a solution of sodium iodide, the actual range of chemical shifts caused by variations in the diamagnetic shielding would be much less than 10 p.p.m.

The range of chemical shifts possible from changes in the paramagnetic shielding can be approximated by the following expression for σ_p using Schneider and Buckingham's "atom in a molecule" model (13):

$$[5] \quad \sigma_p = -\frac{e^2 \hbar^2 L(L+1)}{3m^2c^2 \Delta E} \left\langle \frac{1}{r^3} \right\rangle_{n,l}$$

$$= -7.67 \times 10^{-16} \frac{(Z_0 Z)^{3/2} L(L+1)}{n^3 l(l+1)(l+\frac{1}{2}) \Delta E}$$

where $\hbar^2 L(L+1)$ is the square of the total orbital angular momenta of the valence electrons and ΔE is taken as the first ionization potential of the sodium atom, i.e. $\Delta E = 8.22 \times 10^{-12}$ ergs (15). For Na^+ with an electron donated by the solvent to a 3p orbital, $L = l = 1$. Thus $\sigma_p = -270$ p.p.m.

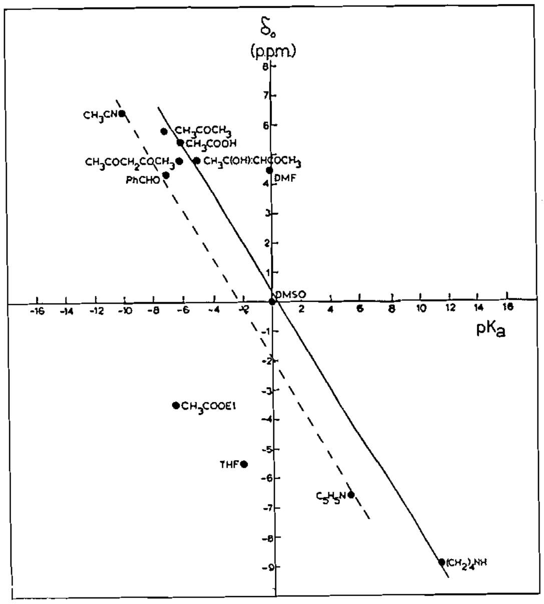

FIG. 4. Correlation of the chemical shifts at infinite dilution with the pK_a values of the solvent.

These calculations and the observed range of chemical shifts of the ^{23}Na resonances, viz. 23 p.p.m., indicate that the most important factor affecting these chemical shifts is the orbital angular momentum of electrons occupying the $n = 3$ shell of sodium and its effect upon σ_p. This arises from the overlapping of the outer p orbitals of the central sodium ion with the outer s and p orbitals of the neighboring solvent molecules or ions. Thus it would be expected that the ^{23}Na resonance would be at a lower field when sodium iodide is dissolved in a solvent of appreciable electron-donating ability than when it is dissolved in a less basic solvent. That this is indeed the case is illustrated in Table I and Fig. 4. The pK_a values were obtained (16) in aqueous solutions (except that for ethyl acetate, which was obtained in acetic acid) but these values should also be applicable to sodium iodide solutions since the behavior of these solvents toward the sodium ion would be expected to be similar to their behavior toward the hydrogen ion. Fratiello *et al.* (17) have also found a linear correlation of pK_a values with the abilities of certain solvents to solvate $AlCl_3$, $TiCl_4$, and $CoCl_2$ in aqueous solution mixtures.

The dashed line in Fig. 4 through the points due to the acetonitrile, benzaldehyde, and pyridine solutions is shifted farther downfield (by about 2 p.p.m.) than the solid line through the points due to the other solvents. This could arise from a contribution to the chemical shifts due to the magnetic anisotropies of the triply bonded nitrogen in acetonitrile and pyridine and of the ring system in benzaldehyde (18).

A grouping of all oxygen-coordinating solvents at high fields and of all nitrogen-coordinating solvents at lower fields is observed. The oxygen-coordinating solvents are further divided with those donating electrons through $>$C=O being at higher field strengths than those that coordinate via —O—. These divisions would seem to indicate that the sodium ion is coordinated to the $>$C=O of N,N-dimethylformamide and to the —O—Et group of ethyl acetate. The occurrence of the sodium resonance in acetonitrile at a markedly higher field strength than other nitrogen-containing solvents may indicate that the main solvating influence of this solvent is via interaction of the π-electrons of —C≡N with the solute ions rather than via the exposed sp lobe of the nitrogen atom.

Preferential Solvation of Na$^+$

The correlation of sodium ion chemical shift with solvent basicity has, in the preceding discussion, been attributed to increased strength of interaction between cation and solvent as solvent basicity is increased. The fact that the ^{23}Na paramagnetic shift increases as the solvent is changed from acetonitrile to water to ethylenediamine is a reflection of this effect. Evidence to support the contention that strength of cation–solvent interaction varies in the manner postulated above for the case of the Na$^+$ is presented in Fig. 2. For a 0.27 *M* solution of sodium iodide, the shielding of the Na$^+$ in acetonitrile is 4.5 p.p.m. greater than that of the Na$^+$ in water. If the strength of interaction between cation and solvent were the same for both acetonitrile and water, then in a mixed acetonitrile–water solvent system, the average environment of a Na$^+$ as represented by the ratio of acetonitrile/water molecules present in the first coordination sphere of Na$^+$ would be identical with the solvent composition as represented by the mole fraction of the acetonitrile–water system. Under these circumstances, a plot of ^{23}Na chemical shift versus mole fraction of water in solvent should be linear from 100% acetonitrile to 100% water. Figure 2 shows that this is not the case. Addition of 0.1 mole fraction water to an acetonitrile solution of sodium iodide results in a proportionately larger decrease in the chemical shift towards its value in an aqueous solution. This indicates that the Na$^+$–water interaction is stronger than the Na$^+$–acetonitrile interaction. The opposite effect is observed on adding water to an ethylenediamine solution of sodium iodide. Here the addition of 0.1 mole fraction water causes a proportionately smaller increase of the chemical shift towards its value in an aqueous solution. This increase in chemical shift is linear with a slope of -10.6 p.p.m. until the solvent is approximately equimolar in water and ethylenediamine, at which point the chemical shift increases more rapidly to zero ($\delta \simeq 0$ at 0.20 *M* NaI in H_2O). This preference of the sodium ion to be solvated by ethylenediamine rather than by water is shown by Fig. 3 to be the same at concentrations of sodium iodide equal to 0.05 *M*, 0.10 *M*, and 0.20 *M*.

Acknowledgments

We wish to thank the National Research Council of Canada for financial support of this study in the form of Studentships to E.G.B. and Operating Grants to R.G.K.

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