Spectroscopic Studies of Ionic Solvation. XI. Sodium Magnetic Resonance in Basic Solvents

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Abstract: Chemical shifts of sodium-23 nucleus in sodium iodide and tetraphenylborate solutions were studied, as a function of concentration, in strongly basic solvents, liquid ammonia, ethylenediamine, ethylamine, isopropylamine, *tert*-butylamine, hydrazine, and 1,1,3,3-tetramethylguanidine. The chemical shifts, measured with reference to an aqueous, saturated, sodium chloride solution, were downfield from the reference, indicating strong solvating ability of the above solvents. The results indicate that in dilute sodium iodide solutions (≤ 1 *M*) the cation is completely solvated by ammonia, ethylenediamine, and hydrazine, while in other solvents, contact ion pairs are formed to some extent. No evidence for contact ion pairs was found for the sodium tetraphenylborate solutions in the 0.1–0.5 *M* concentration range. Gutmann's donor numbers of the above solvents were estimated.

Studies of ionic solutions in liquid ammonia by a variety of classical experimental techniques date back to the days of Franklin and Kraus.[1] More recently, such solutions have been studied by spectroscopic techniques, in particular by nuclear magnetic resonance and by infrared spectroscopy. It has been shown that the nmr measurements can be used for the determination of the primary solvation number of metal ions,[2,3] while the infrared studies have been used to elucidate the structures of alkali and alkaline earth salt solutions in this solvent.[4,5] It has been postulated that at high concentrations (>1.0 *M*) alkali metal halides form solvent-shared ion pairs, while in potassium amide solutions the salt forms contact ion pairs. Recently it has been shown by uv and visible spectroscopy that the fluorenyl cation ion pair is also solvent shared.[6]

It was of interest to us to study the nature of ionic species in liquid ammonia by ^{23}Na magnetic resonance. Recent results obtained in this laboratory showed that this technique is a very sensitive probe of the environment of sodium ions in solutions.[7,8] The study was also extended to other basic solvents.

Experimental Part

Reagents. Liquid ammonia was purified by a previously described technique.[9] Hydrazine was purified by the method of Audrieth and Penneman.[10,11] Aqueous hydrazine solution was treated with sodium hydroxide. The upper layer of the two-phase system, containing ~95% hydrazine, was separated, and the product was further purified by several fractional crystallizations. Ethylenediamine was distilled according to the procedure of Creamer and Chambers[12] and then fractionally recrystallized three times. Ethylamine (Eastman), *tert*-butylamine (Eastman), isopropylamine (Matheson), sodium iodide (Matheson), and sodium tetraphenylborate (J. T. Baker) were used without further purification. The purification of 1,1,3,3-tetramethylguanidine has been previously described.[13,14]

Samples. Except for hydrazine and ethylenediamine, solutions were prepared on a vacuum line and sealed in 12-mm tubes. The tubes were inserted into a 15-mm test tube, and the reference solution (saturated aqueous sodium chloride solution) was placed between the two tubes.

Hydrazine and ethylenediamine solutions were placed in 15-mm tubes and the reference solution, in a standard 8-mm nmr tube, was inserted coaxially with the sample tube.

Spectrometer. The nmr spectrometer and the mode of operation were described in a previous publication.[7]

Results and Discussion

Measurements were carried out on solutions of sodium iodide and sodium tetraphenylborate. The extent of ion association of the first salt has been previously studied in ammonia, ethylenediamine, and pyridine by conductance measurements. The respective pK_d values[15] (K_d = ion-pair dissociation constant) are 2.5 (−33°), 3.15 (25°), and 3.45 (25°). Since, in general, pK_d values decrease with increasing temperature, we can expect that the pK_d value for liquid ammonia at the probe temperature (~30°) would be ~2, which implies that in 0.1 *M* solutions the ion-pair dissociation is essentially complete.

Information on ion-pair dissociation constants of sodium tetraphenylborate in the above solvents is not available in the literature. Nevertheless, being given the large size of the anion, we would expect that the extent of ion-pair dissociation would be somewhat larger than for the sodium iodide. Previous work on ^{23}Na resonance of sodium tetraphenylborate solutions in solvents of low dielectric constant such as tetrahydrofuran (D = 7.4) and pyridine (D = 12.3) indicates that the ion pairs are of the solvent-separated or solvent-shared types rather than the contact pairs.

Chemical shifts of ^{23}Na nucleus, with respect to aqueous saturated sodium chloride solutions, are given in Tables I and II. The plots of the chemical shifts

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(1) See references in J. Jander, "Chemistry in Anhydrous Liquid Ammonia," Vol. I, Part I, Interscience, New York, N. Y., 1966.

(2) T. J. Swift and H. H. Lo, *J. Amer. Chem. Soc.*, **89**, 3988 (1967).

(3) L. W. Harrison and T. J. Swift, *ibid.*, **92**, 1963 (1970).

(4) C. Moreau, P. Damay, and G. Lepoutre, *Ann. Chim. (Paris)*, **14**, 309 (1969).

(5) J. Corset, P. V. Huong, and J. Lascombe, *Spectrochim. Acta, Part A*, 24, 1385 (1968).

(6) J. P. Pacault and J. Gole, *J. Chim. Phys. Physicochim. Biol.*, **68**, 442 (1971).

(7) R. H. Erlich, E. Roach, and A. I. Popov, *J. Amer. Chem. Soc.*, **92**, 4989 (1970).

(8) R. H. Erlich and A. I. Popov, *ibid.*, **93**, 5620 (1971).

(9) M. Herlem and A. Thiebault, *Bull. Soc. Chim. Fr.*, 383 (1970).

(10) L. F. Audrieth and B. A. Ogg in "The Chemistry of Hydrazine," New York, N. Y., 1951, p 50.

(11) R. A. Penneman and L. F. Audrieth, *J. Amer. Chem. Soc.*, **71**, 1644 (1949).

(12) R. M. Creamer and D. H. Chambers, *J. Electrochem. Soc.*, **101**, 162 (1954).

(13) J. A. Caruso, Ph.D. Thesis, Michigan State University, 1967.

(14) J. A. Caruso, P. G. Sears, and A. I. Popov, *J. Phys. Chem.*, **71**, 1756 (1967).

(15) G. Charlot and B. Tremillon, "Les Reactions Chimiques dans les Solvants et les sels Fondus," Gauthier Villars, Paris, 1963, pp 276, 286, and 292.

Table I. Chemical Shifts (ppm) of ^{23}Na for Sodium Iodide Solutions

Solvent	0.1	0.125	0.25	0.30	0.50	0.60	1.0	2.0	2.2	2.5	3.0	4.0	5.0	6.7	8.0
Pyridine[a]		−2.4	−2.4		−3.8										
Hydrazine	−5.7				−5.9		−6.1	−6.5			−6.9[b]				
Ammonia	−13.5			−13.6		−13.9	−14.1	−14.4			−14.8	−15.2	−15.5	−16.8	−17.4
Ethylenediamine	−11.1			−11.8		−12.4	−11.9	−12.7							
Ethylamine	−13.2				−13.3		−13.7	−15.0		−15.7					
Isopropylamine				−15.5		−15.5	−15.9	−16.3	−16.5[b]						
tert-Butylamine				−16.8[b]											

[a] Data from ref 7. [b] Saturated solution.

Table II. Chemical Shifts (ppm) of ^{23}Na for Sodium Tetraphenylborate Solutions

Solvent	0.10	0.125	0.20	0.25	0.30	0.50
Pyridine[a]		−0.9		−0.7		−0.7
Hydrazine	−5.4			−5.4		−5.4
Ammonia	−13.1			−13.2		−13.2[b]
Ethylenediamine	−11.1		−11.1		−11.1[b]	
Ethylamine	−11.3		−11.3		−11.2	−11.4[b]
Isopropylamine	−12.4		−12.5		−12.7[b]	
tert-Butylamine			Insoluble			

[a] Data from ref 7. [b] Saturated solution.

as a function of the concentration are shown in Figure 1. In all cases the chemical shifts are downfield from the aqueous NaCl reference and become progressively more so on dilution.

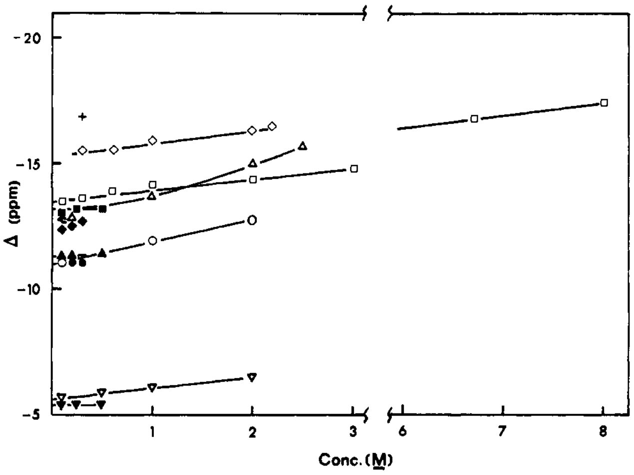

Figure 1. Variation in the ^{23}Na chemical shifts with concentration in basic solvents: (+) NaI in *tert*-butylamine, (◇) NaI in isopropylamine, (◆) $NaPh_4B$ in isopropylamine, (□) NaI in ammonia, (■) $NaPh_4B$ in ammonia, (△) NaI in ethylamine, (▲) $NaPh_4B$ in ethylamine, (○) NaI in ethylenediamine, (●) $NaPh_4B$ in ethylenediamine, (▽) NaI in hydrazine, (▼) $NaPh_4B$ in hydrazine.

In the case of hydrazine, ammonia, and ethylenediamine solutions, the chemical shifts are approximately the same for the two salts, at least for solutions of lower concentrations. It seems reasonable to conclude that in these cases we do not have anions in the sodium ion solvation shell but have either a solvent-separated ion pair or free solvated cations. This conclusion would be especially applicable to the hydrazine solutions in view of the large dielectric constant of this solvent.

In ethylamine and isopropylamine solutions, there is a marked difference in the chemical shifts between sodium iodide and sodium tetraphenylborate. It should be noted that the chemical shift of the tetraphenylborate is essentially the same in the two solvents. On the other hand, the chemical shifts of the sodium iodide solutions are much less negative than those of sodium tetraphenylborate. It seems likely that in the former case contact ion pairs are formed even in the 0.1 *M* solutions. It would be interesting to determine the chemical shifts for more dilute solutions but, at the present time, the sensitivity of our instrument is not adequate for such studies.

In the case of *tert*-butylamine solutions, the measurements could not be carried out for sodium tetraphenylborate because of its insolubility in this solvent. Sodium iodide was only slightly more soluble, and a chemical shift was determined for the saturated solution (~0.3 *M*).

It is interesting to note that in liquid ammonia, at low concentrations, the ^{23}Na resonance line is extremely narrow and for 0.1 *M* the line width of 6 Hz is approximately one-half of the corresponding line width (at half-height) of that in aqueous solution. In contrast to the aqueous solutions, the line begins to broaden as the concentration increases (Figure 2). It was observed, however, that the concentrated solutions of sodium iodide in liquid ammonia became quite viscous, and it seems reasonable to assume that the broadening of the signal is due to the increase in the viscosity.[16,17]

An attempt was made to measure chemical shifts in basic ammonia solutions. Two solutions were prepared containing 0.5 and 1 *M* solutions of sodium amide, respectively, but the sodium-23 resonance could not be detected in these solutions. Similarly,

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(16) S. Kikuchi, *J. Soc. Chem. Ind. Jap.*, 47, 305 (1944).
(17) S. Kikuchi and S. Kudo, *ibid.*, 47, 448 (1944).

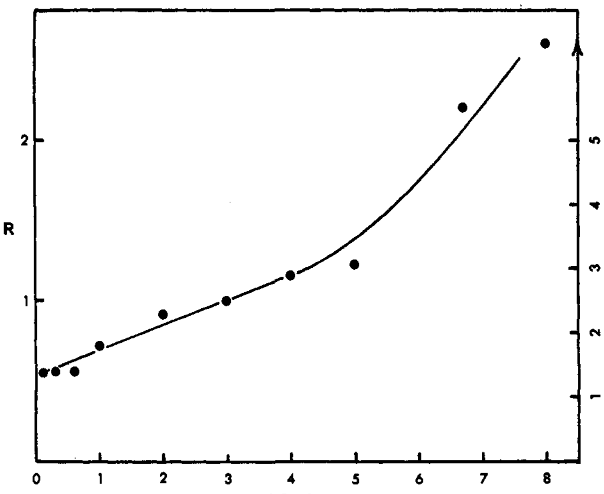

Figure 2. Variation in the ratio R of the half-width of the ^{23}Na signal in liquid ammonia solution of sodium iodide and the half-width of the ^{23}Na signal in a saturated aqueous solution of NaCl as a function of sodium iodide concentration.

negative results were obtained for sodium salt solutions in 1,1,3,3-tetramethylguanidine, aniline, and ethanolamine. It seems that in these cases the ^{23}Na resonance is too broad to be detected.

The influence of traces of water on the chemical shifts was studied in ethylenediamine solutions. Figure 3 shows the variation in the chemical shift as a function of water concentration for a 0.1 M sodium iodide solution.

In the presence of water the resonance shifted upfield, as expected, and the shift was proportional to the concentration of water (Figure 3). The magnitude of the shift, however, is quite small, being only 1 ppm for the 1 M water solution and when the water/NaI mole ratio is equal to 10. It is quite certain that in purified ethylenediamine the water content was <0.1 M and, therefore, should have negligible effect on the chemical shift of the ^{23}Na nucleus.

Table III. Donor Numbers of Some Basic Solvents

Solvent	Dielectric constant	pK_a (H_2O)	Donor no. (Figure 4)
Pyridine	12.3	5.2[b]	33[a]
Hydrazine	51.7	8.0[b]	44
Ethylenediamine	14.2	9.9[b]	55
Ethylamine	6.9	10.6[b]	55.5
Isopropylamine	6	10.6[c]	57.5
tert-Butylamine	6	10.8[c]	57.5
Ammonia	17	9.25[b]	59

[a] Reference 7. [b] Reference 15. [c] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solutions," IUPAC, Butterworths, London, 1965, pp 33 and 36.

In a previous communication we reported that the plot of the chemical shifts of the ^{23}Na resonance *vs.* Gutmann's donor numbers[18] gave a reasonable straight line for the sodium perchlorate and the tetraphenylborate solution. Gutmann's donor numbers vary from 0.1 for sulfuryl chloride to 38 for the strongest donor solvent, hexamethylphosphoramide. Extrapolation of the plot for the sodium tetraphenylborate solutions made it possible to estimate the donor numbers of the basic solvents used in this investigation (Table III and Figure 4). The values obtained by this extrapolation are considerably higher than the donor numbers of the series of solvents investigated by Gutmann. Of course, there is no assurance that the plot maintains its linearity for these large downfield shifts and that the numbers actually represent the respective enthalpies of 1:1 complex formation with antimony pentachloride. Nevertheless, it seems reasonable to assume that, just as donor numbers, the magnitude and the direction of the chemical shifts of ^{23}Na, while they are relative parameters, do *reflect* the donor (or the solvation) ability of the solvents. In view of the well-known complexing abilities, at least of ammonia and of ethylenediamine, the high donor numbers for basic solvents are not surprising. Since these numbers are considerably higher than that of water (~33, ref 7), it is evident that small amounts of the latter will have only a minor influence on the chemical shifts of sodium. Likewise, there is a fairly strong association between water molecules and those of the

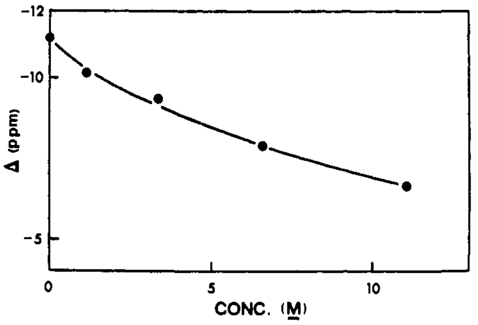

Figure 3. Influence of added water on the variation in the ^{23}Na chemical shift in a 0.1 M solution of NaI in ethylenediamine solutions.

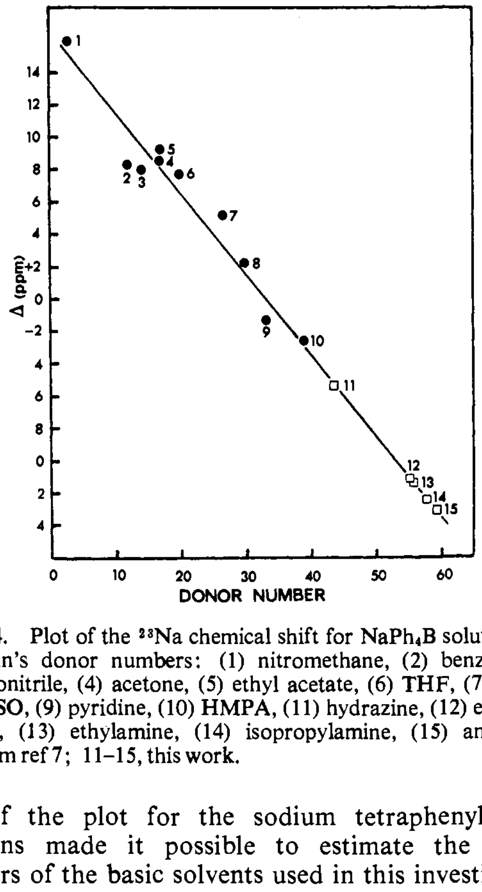

Figure 4. Plot of the ^{23}Na chemical shift for $NaPh_4B$ solutions *vs.* Gutmann's donor numbers: (1) nitromethane, (2) benzonitrile, (3) acetonitrile, (4) acetone, (5) ethyl acetate, (6) THF, (7) DMF, (8) DMSO, (9) pyridine, (10) HMPA, (11) hydrazine, (12) ethylenediamine, (13) ethylamine, (14) isopropylamine, (15) ammonia. 1–10 from ref 7; 11–15, this work.

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(18) V. Gutmann, "Coordination Chemistry in Nonaqueous Solutions," Springer-Verlag, Vienna, 1968.

basic solvents which would further diminish the water–cation interaction. We can conclude, therefore, that traces of water which may be present in the basic solvents studied in this investigation, would have only a negligible effect on the measured chemical shifts.

It is also interesting to note that except for ammonia, there seems to be a good correlation between the donor number of the solvents and their basicity constants in aqueous solutions. Such correlation has been proposed by Bloor and Kidd[19] from their ^{23}Na magnetic resonance measurements on sodium iodide solutions. However, in that case, the possible correlation was somewhat obscured by the influence of the contact ion pairing on the chemical shifts.

Acknowledgment. The authors gratefully acknowledge the support of this work by a grant from the National Science Foundation. One of us (M. H.) is indebted to the Centre National de la Recherche Scientifique (Paris) and to NATO for a fellowship and to Mr. R. H. Erlich for help with the instrumentation.

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[19] E. G. Bloor and R. G. Kidd, *Can. J. Chem.*, 46, 3425 (1968).

Metal Surface Base Function. Adsorption of Boron Trifluoride and Boron Trichloride

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Abstract: In a continuing effort to characterize metal surfaces by their interaction with different classes of molecules, the base function of metal surfaces is examined *via* adsorption of BF_3 and BCl_3. Using infrared spectroscopy, the following information has been obtained about the adsorption of the pure Lewis acids BF_3 and BCl_3. BF_3 chemisorbs without dissociation on vanadium, iron, nickel, copper, and palladium films. No chemisorption on aluminum films is detected. The BF_3–metal surface complexes are quite stable with respect to air. CO replaces adsorbed BF_3 on nickel and palladium. It replaces BF_3 on iron to a much smaller extent. BF_3 chemisorbed on vanadium and copper is not replaced by CO. Chemisorbed BF_3 is electron withdrawing compared to chemisorbed CO. BCl_3 adsorbs on Fe and Ni without dissociation. Basicity of the metal surface is demonstrated to be a useful concept by showing that the displacement of BF_3 by CO correlates with the expected basicity of the surface as measured by valence-state ionization potentials.

One area of surface chemistry which is insufficiently explored with modern techniques is the chemical characterization of metal surfaces by their interaction with different classes of molecules that have evolved from studies of coordination complexes. If one takes the point of view that a metal atom in a surface can be regarded as a metal atom in a coordination complex, one becomes immediately aware of several possibilities. While metal cations are customarily regarded as acids, metal basicity has received some attention.[1] Metal basicity has recently been demonstrated through the discovery of compounds in which the metal serves as a donor toward molecular Lewis acids such as BF_3, BH_3, H^+, O_2, SO_2, and tetracyanoethylene. Since basicity of metal cations has been found to be promoted by low oxidation states, zerovalent metal atoms in a surface should be prime candidates for base functioning. Certainly a clear understanding of electron-donor properties of metal surfaces is necessary to understanding the electron-transfer processes accompanying catalytic reactions on metal surfaces.

Discussion of the nature of the chemisorption bond to metals and most discussions of coordination complexes have concentrated on adsorbates or ligands that are electron donors, *i.e.*, Lewis bases, or are σ donors and π acceptors. While a metal surface should be able to function as a pure Lewis base, there appear to have been no studies of the interaction of molecules that can serve only as Lewis acids with metal surfaces. The questions arise as to whether this type of molecule will even chemisorb and if so whether it will do so only with dissociation, and as to its relative strength of adsorption compared to such widely studied adsorbates as CO.

To be useful as surface ligands in infrared studies, molecules should adsorb without dissociation. If dissociation occurs, the surface becomes covered with fragments of varying structures, and interpretation becomes extremely difficult. There do not appear to be many chemical compounds which meet this condition. Carbon monoxide is one of the few molecules which adsorb and desorb without appreciable dissociation and, consequently, its interactions with metal surfaces have been widely studied.[2,3]

Molecular Lewis acids have vacant orbitals which can accept electrons but have no electrons available for donation. One of the most important of these is boron trifluoride, which forms adducts by accepting a share in an electron pair from a donor molecule. Corrosion experiments have shown that there is no appreciable attack by boron trifluoride on any of the metals or alloys examined at temperatures up to

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[1] D. F. Shriver, *Accounts Chem. Res.*, 3, 231 (1970).

[2] L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966.

[3] M. L. Hair, "Infrared Spectroscopy in Surface Chemistry," Marcel Dekker, New York, N. Y., 1967.