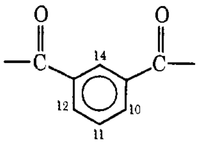
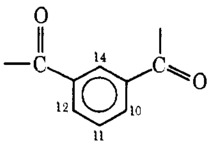
and 4, etc., which would be nonequivalent had the phenyl groups been locked in a particular planar conformation persisting sufficiently long on the esr time scale.

The Q calculated from the ρ value of proton 14 is much too high. We cannot comment on this result, but we could not improve it by introducing different α's for carbon atoms adjacent to the CO groups.

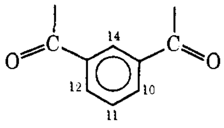
Finally, the stereochemistry of the central ring need be considered. We assumed the carbonyl groups to be coplanar with the inner ring. In this case, three possible conformers could be formed, *viz.*, I–III. We rule out the conformer II because the esr spectrum clearly demonstrates the equivalence of protons 10 and 12. Consideration of steric hindrance makes conformer I more plausible than I, while the dipole–dipole repulsion between the CO groups might favor conformer III.



I



II



III

Acknowledgment. This study was supported by the National Science Foundation and by the Petroleum Research Fund, administered by the American Chemical Society. We wish, also, to thank Professor Freed for his permission to use his endor spectrometer.

Spectroscopic Studies of Ionic Solvation. X. A Study of the Solvation of Sodium Ions in Nonaqueous Solvents by ^{23}Na Nuclear Magnetic Resonance[1]

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Abstract: Chemical shifts of the ^{23}Na nucleus were measured for sodium tetraphenylborate, perchlorate, iodide, and thiocyanate with reference to aqueous sodium chloride solution at different concentrations in a number of nonaqueous solvents. In the case of the first two salts, the chemical shifts were found to be independent of concentration, while for the iodide and, to a lesser extent, for the thiocyanate, they do depend on the concentration of the salt. It is assumed that in the latter case the chemical shifts are influenced by the formation of contact ion pairs. The magnitude of the chemical shift for the ^{23}Na nucleus in different solvents appears to be directly related to the electron donor abilities of these solvents provided that the shifts are not complicated by the formation of contact ion pairs.

Studies of ionic solvation by proton magnetic resonance have been carried out by numerous investigators during the past few years. While such studies have proven to be quite useful in the elucidation of the structures of electrolyte solutions, the information obtained is limited, since the measurements are usually carried out on the magnetic resonance of either the solvent protons or on protons of solvating species dissolved in an "inert" solvent. In most cases the observed protons are several atoms removed from the interaction site[2] and consequently the chemical shifts are only weakly affected by the solvation. It is obvious that much better information can be obtained if one directly observes the resonance of the solvated ions.

The sodium-23 nucleus seems to be particularly well suited for such studies. The relative sensitivity of 0.1 with respect to the proton indicates that the measurements can be carried out in fairly dilute solutions. Narrow line width of ^{23}Na resonance allows the use of high-resolution nmr equipment. Finally, the large quadrupole moment of $0.1\ e/10^{24}\ \text{cm}^2$ renders the sodium nucleus a sensitive probe of the neighboring electronic environment.

Most of the studies carried out thus far on ^{23}Na resonance were done in aqueous solutions.[3-9] Jardetzky and Wertz[3] measured the position, width, and area of the resonance signal of a number of sodium compounds in water with reference to a 3 M NaCl solution as the external standard. While the authors did not observe any chemical shifts with changing concentrations or with different sodium salts, they did observe a considerable amount of line broadening in cases where anion–cation interactions were suspected. The authors consequently attributed the line broadening

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(1) Abstracted in part from the Ph.D. Thesis of R. H. E., Michigan State University, 1971.

(2) For example, in dimethyl sulfoxide: B. W. Maxey and A. I. Popov, *J. Amer. Chem. Soc.*, 90, 4470 (1968).

(3) O. Jardetzky and J. E. Wertz, *ibid.*, 82, 318 (1960).

(4) C. Deverell and R. E. Richards, *Mol. Phys.*, 10, 551 (1966).

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(6) P. A. Speight and R. L. Armstrong, *Can. J. Phys.*, 45, 2493 (1967).

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(8) V. S. Griffiths and Y. Socrates, *J. Mol. Spectrosc.*, 27, 358 (1968).

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Table I. Chemical Shifts of ^{23}Na in Different Media

	NaBPh$_4$ concentration, M			NaSCN concentration, M			
	0.5	0.25	0.125	0.25	0.125	0.0625	0.0313
HMPA	−2.87	−3.08	−3.08	0.72	0.90	1.07	
Pyridine	−0.72	−0.72	−0.90	−2.52	−2.52	−2.52	−2.52
DMSO	0.72	0.72	0.90	0.18	0.72	0.72	1.59
DMF	5.23	5.23	5.76	4.68	4.86	5.21	5.76
THF	8.12	8.12	8.31	1.07	3.06	3.60	3.78
Acetone	8.56	8.56	9.13	5.93	6.49	6.86	7.17
Acetonitrile	8.00	8.19	7.75	5.58	6.11	6.49	6.68
Nitrobenzene			7.62[a]		Insoluble		
Nitromethane	16.1	15.6	15.4		Insoluble		
Methanol	4.53	4.53	4.35	4.50	4.31	4.50	4.50
Ethyl acetate	9.38	10.2	9.38		5.03	4.86	4.86

	NaClO$_4$ concentration, M					NaI concentration, M				
	0.5	0.25	0.125	0.0625	0.0313	0.5	0.25	0.125	0.01	0.005
HMPA	−1.98	−1.98	−1.98	−1.80	−2.15	−2.56	−2.44	−2.52		
Pyridine	−0.18	−0.18	−0.18	−0.18	−0.18	−3.78	−2.36	−2.39		
DMSO	1.44	1.44	1.44	1.62	1.62		−0.18	0.90		
DMF	5.94	5.76	5.76	5.76	5.94		5.75	5.92		
THF	9.19	9.19	9.01	9.01	8.82	−6.25	−6.36	−5.98		
Acetone	10.3	10.1	9.70	9.89	10.1	3.44	4.50	5.15	6.86	7.75
Acetonitrile	8.25	8.44	8.44	8.12	8.44	4.77	6.07	6.80	7.76	
Nitrobenzene			Insoluble					Insoluble		
Nitromethane					14.0[a]			Insoluble		
Methanol	5.22	5.22	4.86	4.86	4.86	4.22	4.46	4.68		
Ethyl acetate	10.8	10.6	10.6	10.6	10.6			−2.54[a]		

[a] Saturated solution.

to the formation of ion pairs. Deverell and Richards[4] studied the concentration dependence of the chemical shifts of the ^{23}Na, ^{39}K, ^{87}Rb, and ^{133}Cs nuclei in aqueous solutions. The behavior of the sodium solutions was quite different from that of the other nuclei, which was attributed to the much higher degree of solvation of the sodium ion. The dependence of chemical shifts on the salt concentration was interpreted to be due to increasing cation–anion interactions in more concentrated solutions.

There seems to be in the literature only one comprehensive study of the ^{23}Na magnetic resonance in nonaqueous solvents.[10] The authors measured the ^{23}Na resonance of sodium iodide in several solvents and at several different salt concentrations. The chemical shifts were calculated with reference to a saturated aqueous sodium chloride solution. Large chemical shifts were noted in different solvents. In each solvent the shifts were also concentration dependent.

The present study was undertaken in order to extend such measurements to new solvents and also to determine the influence of different anions on the ^{23}Na chemical shifts. The preliminary report on our results has been previously published.[11]

Experimental Part

Chemicals. Sodium salts used in this investigation were of reagent grade and were not purified before use except for drying. The solvents were obtained in the purest commercial form available. Nitromethane was purified by a method previously described.[12] Pyridine was dried over KOH pellets and distilled. All other solvents were dried over molecular sieves (Linde Type 4A) prior to use. All solutions were prepared by weighing out the desired amount of the salt in a 5-ml volumetric flask and diluting to the mark with the respective solvent.

Measurements. The nuclear magnetic resonance spectrometer used was the Varian DA-60 in wide-line configuration which was modified to allow the recorder sweep potentiometer to sweep the magnet power supply. A Model V4310C rf unit, modified for phase detection and operating at 15.88 MHz, was employed. Since the natural line width for the sodium-23 resonance is on the order of few hertz, we used standard, nonspinning, 15-mm test tubes for our sample tubes. The reference was a saturated aqueous solution of sodium chloride. For measurements in which the salt concentration was greater than 0.1 M, the reference solution was placed in a standard 8-mm nmr tube inserted coaxially into the sample tube. For more dilute samples, the reference was placed in a sealed melting point capillary. The spectra were calibrated by means of the side bands produced by the wide-line modulation unit operating at 400 Hz, and the chemical shift of the samples was determined by linear interpolation from the side bands. A sweep rate of 250 sec per sweep was employed, and each spectrum was retraced at least three times to negate the effects of field drift.

For a number of samples the chemical shift was so small that the sample resonance was masked by the reference resonance. In these cases, a saturated solution of sodium tetraphenylborate in nitromethane was used as a secondary standard.

A positive value of Δ, the shift from the reference, corresponds to an upfield chemical shift.

Results and Discussion

The chemical shifts with respect to a saturated aqueous solution of sodium chloride were determined, whenever possible, at several concentrations in a number of solvents. The data thus obtained are presented in Table I. It is immediately obvious that the nature of the anion plays an important role in the resulting chemical shift. Confirming the results of Bloor and Kidd,[10] the chemical shifts for the sodium iodide solutions are concentration dependent, with the degree of this dependence being roughly an inverse function of the dielectric constant of the medium. Chemical shifts for the sodium thiocyanate are also concentration dependent, although to a lesser extent than for the iodides. Again there is a suggestion of an inverse relationship between the dielectric constant and magnitude of the concentration dependence.

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

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

(12) D. M. Bowers, R. H. Erlich, S. Policec, and A. I. Popov, *J. Inorg. Nucl. Chem.*, **33**, 81 (1971).

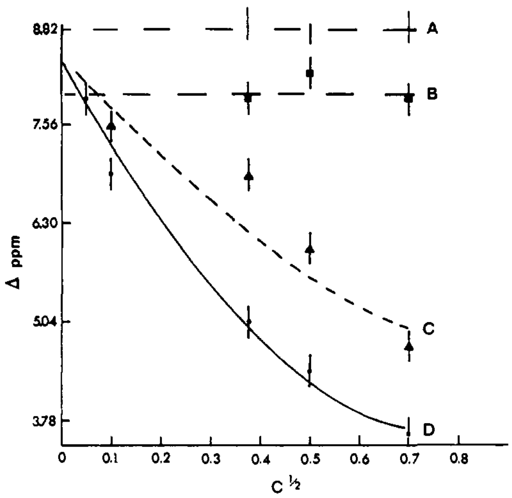

Figure 1. Variation in the ^{23}Na chemical shifts with concentration: (A) $NaBPh_4$ in acetone, (B) $NaBPh_4$ in acetonitrile, (C) NaI in acetonitrile, (D) NaI in acetone.

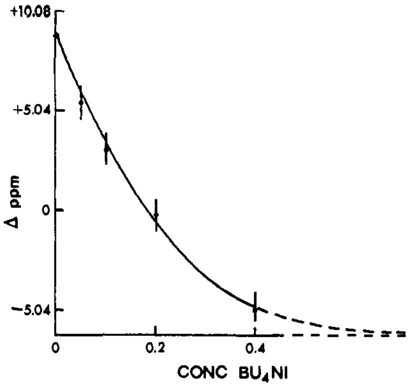

Figure 2. Variation in the ^{23}Na chemical shift of $NaClO_4$ in THF solution as a function of concentration of added Bu_4NI.

A very different type of behavior was found for the tetraphenylborates and the perchlorates. Except in the case of nitromethane, where there was a very slight shift with concentration, the ^{23}Na resonances of the tetraphenylborate solutions do not show a concentration dependence in the 0.5–0.1 *M* range within the limits of detectability of our instrument (±0.3 ppm). Similar constancy of the ^{23}Na resonance was observed for the $NaClO_4$ solutions. Corresponding solutions of sodium iodide were much more concentration dependent with downfield shifts of ≥ 2 ppm for the same concentration range, while in the thiocyanate solutions concentration dependent shifts of almost 3 ppm were observed. Moreover, the solvent dependence of the chemical shift (with reference to aqueous solutions) is quite different in the case of the perchlorates and tetraphenylborates than with the iodides and thiocyanates. For example, the chemical shift of ^{23}Na in THF (0.5 *M* solutions) is 8.12 ppm for $NaBPh_4$, 9.19 for $NaClO_4$, and −6.25 for NaI.

It was shown by Bloor and Kidd[10] that the magnitude and the direction of the chemical shift for the sodium nucleus is determined by a number of factors, the two most significant being the diamagnetic shielding term σ_d and the paramagnetic term σ_p, whose respective values in this case are +9.7 ppm and −270 ppm. Obviously, the complete donation of an electron would not occur in the case of anion–cation or cation–solvent interactions of the type being observed in our studies. Nevertheless, a downfield shift is to be expected when a moiety in the vicinity of the sodium ion is replaced by one with a greater electron donor ability.

It seems reasonable to assume that the concentration dependence of the iodide and of the thiocyanate may be due to the relative ease with which these anions form contact ion pairs by replacing a solvent molecule (or molecules) in the inner solvation shell of a metal ion. Such tendency is largely absent in the large symmetrical anions such as the perchlorate or the tetraphenylborate. Recent studies of the vibrational spectra of lithium perchlorate solutions in acetone–nitromethane mixtures have shown that the 935-cm^{-1} Raman band of the perchlorate ion remains unchanged when the mole ratio of acetone:Li^+ is $\geq$ 4:1, but begins to broaden and shift to higher frequency when the ratio falls below 4:1.[13] Likewise, additions of tetraalkylammonium halides to lithium perchlorate solutions in pure acetone resulted in spectral changes in the cation–solvent vibrational band.

If we assume that the ^{23}Na resonance frequency observed in the perchlorate or the tetraphenylborate solutions reflects the electronic environment of the cation in a solvation cage, while that observed for the NaI solutions in the same solvent is indicative of sodium ion in a contact ion pair, it is obvious that upon dilution the latter frequency should progressively approach the value characteristic of the solvated Na^+ ion. At infinite dilution the two values should be identical. Although the present instrumentation does not allow us to make measurements at concentrations below 0.01 *M*, which renders such extrapolation uncertain, it is seen from Figure 1 that the trend is indeed in the right direction, at least in the case of two solvents investigated, acetonitrile and acetone. Similarly, the addition of tetrabutylammonium iodide to a sodium perchlorate solution produced a gradual shift of the resonance from that of the original salt to that characteristic of sodium iodide at the same concentration (Figure 2).

Addition of iodine to a solution of sodium iodide should result in the formation of the triiodide ion I_3^- which should have much less tendency to form ion pairs with the cation than I^-. Electrical conductance studies on the tetraalkylammonium halides and polyhalide solutions in acetonitrile have shown an appreciable extent of ion pairing for the simple halides, while the trihalides behave as completely dissociated electrolytes.[14] In the present case, the variation in the chemical shift of ^{23}Na in a solution of sodium iodide in tetrahydrofuran was studied as a function of added iodine. The results, shown in Figure 3, indicate that chemical shift varies linearly with increasing concentration of iodine until a 1:1 mole ratio is reached. After this point the shift is independent of further increase in the I_2 concentration. In general, since the formation constant of the I_3^- ion in nonaqueous solvents is of the order of 10^7, it would be expected that

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(13) M. K. Wong, W. J. McKinney, and A. I. Popov, *J. Phys. Chem.*, 75, 56 (1971).

(14) A. I. Popov and N. E. Skelly, *J. Amer. Chem. Soc.*, 76, 5309 (1954).

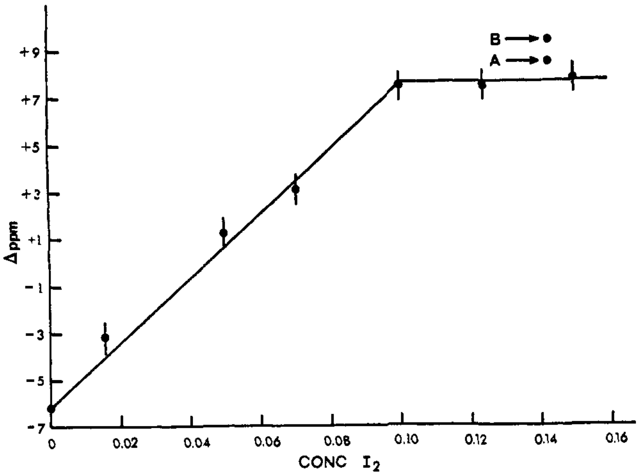

Figure 3. Variation in the ^{23}Na chemical shift in a 0.1 *M* solution of NaI in THF as a function of concentration of added I_2: point A, $NaBPh_4$; point B, $NaClO_4$.

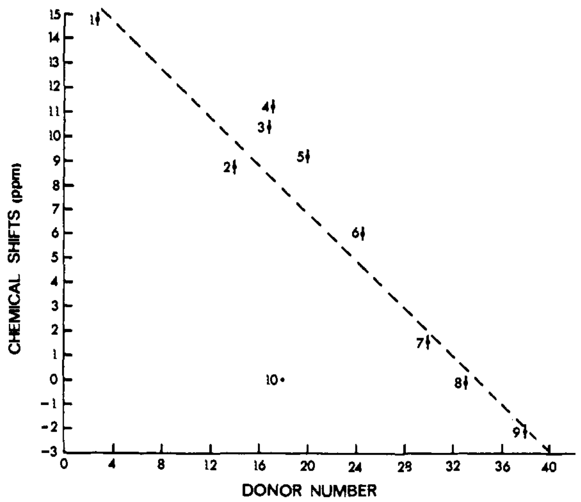

Figure 4. Plot of the ^{23}Na chemical shift for $NaClO_4$ *vs.* Gutmann's donor numbers: (1) nitromethane, (2) acetonitrile, (3) acetone, (4) ethyl acetate, (5) THF, (6) DMF, (7) DMSO, (8) pyridine, (9) hexamethylphosphoramide, (10) water.

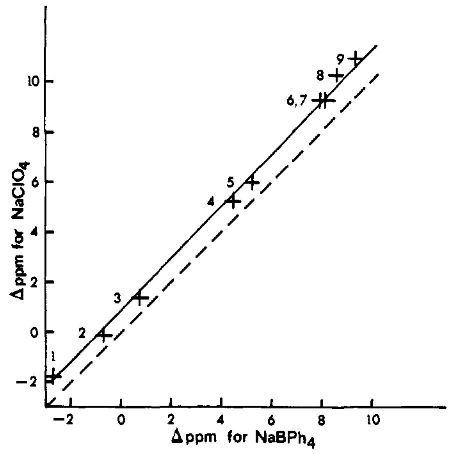

Figure 5. Plot of the ^{23}Na chemical shift for $NaClO_4$ *vs.* that for $NaBPh_4$ in various solvents: (1) hexamethylphosphoramide, (2) pyridine, (3) DMSO, (4) methanol, (5) DMF, (6) acetonitrile, (7) THF, (8) acetone, (9) ethyl acetate.

the formation of I_3^- ion upon addition of I_2 to I^- would be quantitative.[15] It seems, therefore, that the linear plot of Figure 3 offers additional evidence for the formation of contact ion pairs in the NaI solutions. The limiting value of the shift for 1:1 mole ratio of $I_2:I^-$ is close to, but not identical with, the value for the sodium perchlorate and tetraphenylborate solutions. The difference is rather small (~1 ppm) and may be due to inherent inaccuracies in the experimental data, as shown by some scatter of the experimental points from the best straight line.

It should be emphasized that at this time it appears that the magnitude and the direction of the chemical shifts of ^{23}Na do not allow the differentiation between free solvated ions and solvent-separated ion pairs, since the chemical shifts primarily reflect the immediate electronic environment of the sodium ion.

In our preliminary communication[11] we mentioned that the plot of the chemical shifts for the sodium tetraphenylborate solutions *vs.* Gutmann's donor numbers[16] is linear. Similarly, a linear plot has been obtained for sodium perchlorate solutions, as shown in Figure 4. It is seen, therefore, that the magnitude of the chemical shift of ^{23}Na in different solvents is a direct measure of the donor ability of these solvents, provided that the shifts are not complicated by the formation of contact ion pairs in the solution.

It is evident, however, that if we assume that in the case of the perchlorate and the tetraphenylborate we were observing chemical shift due *solely* to the solvated cation, the magnitude of the shift should be completely independent of the anion. The data in Table I show that the chemical shifts for the two salts *are not identical.* Nevertheless, in contrast to the iodide and the thiocyanate, they are linearly related, as shown in Figure 5. In all cases the chemical shifts for sodium tetraphenylborate are slightly more negative (~0.5–1.0 ppm) than those for sodium perchlorate. This difference may be due to a weak interaction of the tetraphenylborate ion with the solvated sodium ion. Additional work, however, is needed in order to elucidate this point.

Acknowledgment. The authors gratefully acknowledge the support of this research by the National Science Foundation and the predoctoral fellowship from the U. S. Public Health Service to R. H. E.

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[15] A. I. Popov in "Halogen Chemistry," Vol. I, V. Gutmann, Ed., Academic Press, New York, N. Y., 1967, p 253.

[16] V. Gutmann, "Coordination Chemistry in Nonaqueous Solutions," Springer-Verlag, Vienna, 1968.