equation has the form

$$\Lambda = \Lambda_0 - A\sqrt{N} + BN + DN \log N$$

and gives a value of Λ_0 of 122.70 cm.^{2} ohm^{-1} equiv.$^{-1}$ with B = 14,120 and D = 5,130. This gives a value of $\lambda^0_{Zn^{++}}$ of 55.34 in comparison with a much lower value of 52.8 obtained by Owen and Gurry[5] from their data on zinc sulfate using the assumptions of ion-pair formation. Using instead the assumption of hydrolysis, a value of $\lambda^0_{Zn^{++}}$ of 53.19 is obtained. It is seen that measurements with zinc perchlorate do not give the unequivocal value of the limiting conductance of zinc ion which was sought but instead raise fundamental questions concerning the conductance behavior of 2–1 electrolytes. It is interesting to note that Owen and Gurry[5] comment on an effect of a similar nature which they encountered in dilute solutions of zinc sulfate in water. "It may be significant, however, that our points of $C \simeq 0.000087$ [molarity] would cause the plots in Fig. 1 to curve *abruptly* upward and increase the intercept by about one conductance unit."

Zinc Sulfate.—It is possible to treat the zinc sulfate data theoretically using an adjustable Λ_0. This has been done and the data are included primarily to emphasize the hazards involved in fitting too few experimental curves with too many adjustable parameters. The data were treated in two ways: (1) The standard Fuoss–Onsager calculation[2,3] with the inclusion of ion-pair formation was performed. The fit of conductance data is too good for deviations to show on a graph and is given in Table V. The calculated transference number curve is shown in Fig. 1. (2) The Fuoss–Onsager calculation of the relaxation effect was combined with the calculation of higher electrophoretic terms[4] and involved only the parameter $\mathring{a}$. The results are also given in Table V and in Fig. 1.

It is seen that both treatments satisfactorily reproduce the conductance behavior of $ZnSO_4$ and that the former also gives a suitable limiting form for transference numbers. As soon as the zinc perchlorate data are examined, however, one can see that $\lambda^0_{Zn^{++}}$ is much too high for either method alone to fit conductance or transference number data for $ZnSO_4$. This emphasizes the importance of having independent checks for any theoretical expression.

TABLE V

ZINC SULFATE CONDUCTANCE CALCULATIONS

	Equivalent conductance			
$\sqrt{N}$	F–O with assocn.	F–O with higher terms	Both treat. with Λ_0 = 135.36	Obsd.
0.03	116.52	116.52	116.51	116.55
.04	110.66	110.70	109.69	110.65
.05	105.14	105.26	103.04	105.15
.06	100.37	100.06	97.53	100.20
	Adjustable parameters used			
	Λ_0 = 132.24 A = 55.0 $\mathring{a}$ = 3.6	Λ_0 = 131.5 $\mathring{a}$ = 4.3	$\mathring{a}$ = 6.0 A = 95.0	

Using the value 55.34 as the limiting equivalent conductance for Zn^{++} as demanded by the $Zn(ClO_4)_2$ data, it is possible to fit the conductance and transference data only at the lowest concentrations by a combination of the two treatments mentioned. As Table V and Fig. 1 show, the fit is not good and the deviations from theory are probably due to other causes. We conclude that zinc salts do not form "typical" dilute solutions, but that, perhaps due to the covalent-bonding tendencies of zinc, other factors are influencing the ion transport processes. This research brings up many questions concerning the behavior of 2–1, 1–2 and 2–2 salts in water. We are currently studying some other salts of these charge types which should be devoid of hydrolysis and covalent character in order to shed light on some of these problems.

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EAST LANSING, MICH.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY, MEDICAL SCHOOL, AND DIVISION OF PHYSICAL CHEMISTRY, SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Weak Complexes of the Sodium Ion in Aqueous Solution Studied by Nuclear Spin Resonance

BY OLEG JARDETZKY[1] AND JOHN E. WERTZ

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The nuclear spin resonance absorption of the Na^{23} ion in aqueous solution has been studied as a function of concentration, viscosity and nature of the anionic species. Broadening of the absorption line width and decrease in the amplitude have been observed at higher concentrations (2–3 N) with several of the anions tested, notably phosphates, hydroxy- and keto-acids and alcohols. These effects are attributed to an interaction of the Na^{23} nuclear quadrupole with an electric field gradient and are interpreted in terms of the formation of weak complexes of sodium with the anions in question.

Introduction

Complexes too weak to be detected readily by conventional methods may prove to be of some importance in the solution of a variety of problems involving the chemistry of the sodium ion. For example, to be a satisfactory candidate for a sodium carrier in the active transport of sodium across living membranes, a complexing agent would have to possess greater affinity for sodium than for potassium to exclude competition from

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the latter, which is present in up to 10 times higher concentration inside cells. However, the absolute lower limit for the stability constant of the corresponding complexes need not be high. Order of magnitude calculations[2] have indicated that complexes with stability constants as low as $K_s = 10^{-2}$ could account for sodium fluxes of the order of 0.7–20 pmoles/cm.^{2}-sec. observed experimentally,[3] if the carrier is present in excess.

Comparatively weak interactions of the sodium ion can be studied readily by the nuclear spin resonance method due to the fact that the Na^{23} nucleus, in addition to a sizable magnetic moment (2.2161 nuclear magnetons), possesses an appreciable electrical quadrupole moment ($0.1e \times 10^{-24}$cm.^{2}). The nuclear quadrupole will interact with the gradient of an asymmetrical electric field surrounding the sodium nucleus, causing the nuclear spin resonance absorption line of the sodium ion to be broadened. The charge distribution and hence the electrical field of an isolated sodium ion are spherically symmetrical. Consequently, an inference concerning the lack of symmetry around the sodium nucleus is in fact equivalent to the inference of an interaction on the part of the sodium ion.[4–7] An asymmetrical electric field surrounding the sodium nucleus can be produced in two ways: (1) polarization of its outer shell electrons by the proximity of a charge which essentially amounts to an ionic bond and (2) addition of one or two electrons to its outer orbitals, as would occur in the formation of a covalent bond. While it is not possible to differentiate between the two types of bonding with certainty, both produce an orientation of the sodium nucleus with respect to the nucleus of a neighboring atom. To be observed, the orientation must be stronger (or, which is equivalent, of longer duration) than the orientation with respect to the adjacent water molecules.

Experimental

The sodium line was detected in a magnetic field of 7030 gauss produced by an electromagnet made of Armco iron, with a pole diameter of 13 inches and a pole gap of 2.25 inches. The power supply of the magnet consisted of 25 .2-v. submarine cells coupled in series to give a current of 30 amp. through the magnet coils. A linear current control compensated for slow changes on the magnet current and permitted manual adjustment of the field strength over a range of approximately 5 gauss. The sweep range was about 1 gauss, the sweep being produced by a saw-tooth generator described already.[8] Details on the construction and characteristics of the magnet have been discussed by Batdorf.[9]

An 8 Mc. oscillating detector modified after an original design of Dr. M. Sanders was used to produce the r.f. current. To ensure stability it was found necessary to couple this unit to a General Radio Type 1105A frequency meter. The field was modulated at 27 c.p.s. from an hp. Model 200CD audio generator. The signal was amplified by a Furst Model 220 amplifier and recorded on a Speedomax Type G recorder, after passing through a Schuster-type phase sensitive detector.[10] A complete description of the apparatus used is given elsewhere.[11]

Solutions were examined in a 3-ml. glass tube with an outside diameter of 10 mm. Field inhomogeneity over the area of the sample was estimated to be of the order of 20–30 milligauss by measurements of proton resonance line width. As the width of the sodium line was found to exceed this somewhat, it was not essential to spin the samples.

Reagent grade chemicals dissolved in distilled water were used for all determinations.

Line width was measured from a record calibrated with the aid of proton resonance equipment. The position of the center of the sodium line on the record was determined at several slightly different field strengths with respect to a marker produced by condenser discharge at the beginning of each sweep. At each field strength the position of the proton signal was observed on an oscilloscope calibrated by 1000 c.p.s. side bands. The differences in the positions of the sodium line in c.p.s. or milligauss could then readily be obtained from the known differences in the corresponding position of the proton line. As the phase-detector output yielded a derivative of the absorption curve, the horizontal distance between the maximum and minimum was taken as a measure of line width. Repeated determinations have resulted in a mean value of 32.6 ± 1.3 milligauss or 36.7 ± 1.45 c.p.s. for the width of the line of 3 *N* NaCl, which was subsequently used as a standard.

Results and Discussion

Absorption curves have been studied in a number of solutions of inorganic sodium compounds at varying concentrations. No chemical shifts were found for a series of inorganic sodium salts, such as the halides, NaN_3, Na_2SO_3, $NaClO_4$, Na_3PO_4, Na_2SO_4 and NaOH. There exists thus far only one report of a shift for sodium in a liquid system. The position of the line in $Na_2B_2O_4$ differs by about 4 line widths from that of the NaBr line.[12] With the possible exception of this compound there is little to indicate variation in the electron density about the sodium ion, and hence little variation in its ionic character.

On the other hand, one would expect a shift and appreciable broadening in cases where sodium is strongly bound, as strong binding could hardly take place without affecting the electronic shell of the sodium atom. In fact, repeated attempts have failed to detect a resonance signal for sodium bound on an ion-exchange resin. It was also impossible to find a signal for concentrated solutions of sodium alcoholates and a number of other organic compounds discussed below. This was taken to indicate that very strong interactions broaden the line beyond detection and hence that resonance can be observed only for sodium ions whose shell is distorted relatively little.

The binding of sodium by the resin can be followed quantitatively, illustrating the possible use of nuclear spin resonance as a method for ready determination of ionic sodium in chemically heterogeneous systems. As seen from Fig. 1 the case here is especially simple, the line width of sodium remaining in solution not being at all affected by the resin suspension. The amplitude is hence proportional to the amount of sodium not adsorbed on the resin. When increasing amounts of Dowex AG-50 X-8 cation-exchange resin (200–400 mesh) are allowed to equilibrate

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(2) O. Jardetzky and C. D. Jardetzky, to be published.

(3) M. Maizels, M. Remington and R. Truscoe, *J. Physiol.*, **140**, 48 (1958).

(4) J. E. Wertz, *J. Phys. Chem.*, **61**, 51 (1957).

(5) J. E. Wertz and O. Jardetzky, *J. Chem. Phys.*, **25**, 357 (1956).

(6) O. Jardetzky and J. E. Wertz, *Arch. Biochem. Biophys.*, **65**, 569 (1956).

(7) O. Jardetzky and J. E. Wertz, *Am. J. Physiol.*, **187**, 608 (1956).

(8) "Waveforms," Vol. XIX, Sec. 5-16, MIT Radiation Laboratory Series, McGraw-Hill Book Co., New York, N. Y., 1948.

(9) R. L. Batdorf, Ph.D. Thesis, University of Minnesota, 1955.

(10) N. A. Schuster, *Rev. Sci. Instr.*, **22**, 254 (1951).

(11) O. Jardetzky, Ph.D. Thesis, University of Minnesota, 1956; University Microfilms, Mic 56-3985.

(12) R. E. Sheriff and D. Williams, *Phys. Rev.*, **82**, 651 (1951).

TABLE I

NUCLEAR SPIN RESONANCE ABSORPTION LINES OF IONIC SODIUM IN AQUEOUS SOLUTIONS OF SODIUM SALTS

Line widths relative to that of a 3 *N* NaCl solution. The reproducibility of the individual measurements corresponds to a relative s.d. ±0.05

	Concn. (moles/l.)											
Compound	0.2	0.5	1	2	3	4	5	6	7	8	9	10
NaCl	1.04	1.02	0.99	1.00	1.00	1.04	1.01	1.02	..	..	..	..
$NaClO_3$	1.01	1.02	1.00	1.00	..	1.01	..	1.03	..	..	..	..
$NaClO_4$	1.00	..	1.02	..	1.01	1.06	..	1.19	1.22	1.26	..	1.40
NaI	1.00	..	1.00	1.01	1.00	1.02	1.05	1.07	1.09	1.11	..	..
$NaNO_3$	1.02	..	1.01	1.02	1.02	1.02	..	1.04	..	1.08	1.10	..
Na_2S	1.02	..	0.98	1.00	1.00	..	..	..	..	..	..	..
NaSCN	1.02	1.01	1.02	1.00	1.02	..	..	1.04	1.02	1.10	..	1.26
Na_2SO_3	1.01	..	0.99	..	1.02	..	..	..	..	..	..	..
Na_2SO_4	1.02	1.02	1.00	..	1.03	1.05	..	..	..	..	..	..
Na_2CO_3	1.00	..	1.03	1.01	0.99	1.01	1.06	1.04	..	..	..	..
Na-formate	0.99	..	0.99	0.98	0.99	1.01	1.02	1.02	..	..	..	..
Na-acetate	1.00	..	1.02	1.06	1.05	1.03	..	..	..	..	..	..
Na-propionate	0.96	..	0.98	0.98	1.00	1.07	..	1.11	..	..	..	..
Na-pyruvate	1.08	1.18	1.37	1.49	1.60	2.24	3.82	..	..	..	..	..
Na-lactate	1.06	1.11	1.12	1.16	1.30	1.48	2.15	3.88	4.42	..	..	..
Na-malate	1.10	1.11	1.11	1.20	1.45	1.82	..	..	..	..	..	..
Na-malonate	1.00	1.00	1.00	1.02	1.04	..	1.05	..	1.20	..	2.12	..
Na-citrate	1.32	1.30	1.33	1.61	1.77	2.01	2.40	3.44	..	..	..	..
Na-glycinate	1.06	..	1.02	1.04	1.09	1.12	1.13	..	..	..	..	..
Na-alanine	1.00	..	1.00	1.03	1.10	1.12	1.20	1.31	..	..	..	..
Na-leucine	0.99	..	1.00	1.02	1.11	1.22	1.38	..	..	..	..	..
Na-arginine	1.02	1.01	1.03	1.07	..	..	..	..	..	..	..	..
Na-glutamate	0.98	1.01	1.04	1.17	..	..	..	..	..	..	..	..
Na-proline	1.00	1.01	1.06	1.00	..	..	..	..	..	..	..	..
Na-hydroxyproline	1.03	..	1.00	1.06	..	..	..	..	..	..	..	..
Na-histidine	1.01	..	1.06	1.20	1.68	..	..	..	..	..	..	..
Na-methionine	0.98	..	0.95	1.02	1.03	1.08	1.20	..	..	..	..	..
Na_4-EDTA	1.24	..	1.29	1.50	1.70[a]	..	..	..	..	..	..	..
Na-mercaptoacetate	0.96	..	0.98	..	0.99[a]	1.03	1.04	..	..	..	..	..
Na-glycocholate	0.98	..	1.00	..	1.02[a]	..	..	..	..	..	..	..
Na-benzoate	1.02	1.00	0.98	1.00	1.01	..	..	..	..	..	..	..
Na-benzenesulfonate	1.03	..	0.97	0.99	0.99	..	..	..	..	..	..	..
Na-sulfanilate	0.96	..	0.97	1.00[b]								
Na-*o*-hydroxybenzoate (salicylate)	1.01	..	1.05	1.11	1.18	1.36	1.58	..	..	..	..	..
Na-*m*-hydroxybenzoate	1.00	..	1.07	1.11	1.20	1.90[c]						
Na-*p*-hydroxybenzoate	0.98	..	0.97	0.97	1.02	..	..	..	..	..	..	..
Na-ethyl-isoamyl barbiturate	1.00	..	1.06	1.40	2.78	..	..	..	..	..	..	..
Na-ethyl-1-methyl barbiturate	1.01	..	1.00	1.12	..	..	..	..	..	..	..	..

[a] 2.5 *N* solution. [b] 1.5 *N* solution. [c] 4.5 *N* solution.

with 4 ml. of 2.5 *N* NaOH, the amplitude decreases in a straight line. A very similar plot is obtained by addition to 3 *N* NaCl, until one reaches high resin concentrations, at which complete removal of sodium fails to occur. Since up to several days had been allowed for equilibration, this is likely to reflect a change in the equilibrium between the resin and the sodium ion, due to the high acidity of the medium resulting from exchange.

A study of the concentration dependence of line widths and amplitudes reveals that the behavior of the sodium ion in different solutions falls into two distinct patterns. The first case is illustrated in Fig. 2, in which line width and amplitude, taken relative to 3 *N* NaCl, are plotted for different concentrations of NaF, NaBr, NaCl and NaN_3. Data for other compounds falling into this category may be found in Tables I and II. For all of these the width remains constant from concentrations of about 0.1 *N* to the limit of solubility and the amplitude increases linearly with concentration.

The second category is represented by sodium hydroxide and several sodium phosphates in Fig. 3. Here the width shows an increase with concentration, while the amplitude reaches a plateau or goes through a maximum. It is worth noting that for NaOH there is essentially no difference in relative width apparent for concentrations up to 5–6 *N*, while the relative amplitude shows a linear increase. In the case of phosphates on the other hand the broadening sets in at lower concentrations. Regardless of the anion, some decline in amplitude and increase in line width can invariably be observed in solutions of concentration higher than 7–8 *N*. It is probable that this reflects various stages of ion-pair formation as in solutions of this concentration there are 4–6 or fewer water molecules per sodium ion, so that not even a single hydration layer can be present at all times.

TABLE II

NUCLEAR SPIN RESONANCE ABSORPTION LINES OF IONIC SODIUM IN AQUEOUS SOLUTIONS OF SODIUM SALTS

Line amplitudes relative to that of a 3 *N* NaCl solution. The reproducibility of the individual measurements corresponds to a relative s.d. ±0.06

Compound	Concn. (moles/l.)										
	0.2	0.5	1	2	3	4	5	6	7	8	9	10
NaCl	0.06	0.17	0.32	0.69	1.00	1.32	1.68	1.98	..	..	..	..
$NaClO_3$	.06	.21	.31	.68	..	1.28	..	1.75	..	..	..	..
$NaClO_4$	.06	.16	.24	.60	0.90	1.06	..	1.32	1.38	1.36	..	1.08
NaI	.08	..	.30	.66	1.02	1.32	1.52	1.73	1.81	1.80	..	..
$NaNO_3$	.04	..	.30	.65	1.03	1.32	..	1.96	..	1.94	1.95	..
Na_2S	.08	..	.30	.63	1.00	..	..	..	..	..	..	..
NaSCN	.06	.19	.36	.66	1.01	..	..	1.84	1.59	1.60	..	1.26
Na_2SO_3	.06	..	.35	..	1.00	..	..	..	..	..	..	..
Na_2SO_4	.06	.15	.32	..	0.97	1.31	..	..	..	..	..	..
Na_2CO_3	.06	..	.32	.72	1.04	1.30	1.12	..	..	..	..	..
Na-formate	.06	..	.36	.67	1.02	1.32	1.60	1.71	..	..	..	..
Na-acetate	.08	..	.35	.68	0.98	1.26	..	..	..	..	..	..
Na-propionate	.06	..	.36	.63	.93	1.18	..	1.24	..	..	..	..
Na-pyruvate	.04	.08	.23	.37	.38	0.22	0.06	..	..	..	..	..
Na-lactate	.06	.12	.30	.60	.70	.61	0.36	0.10	0.02	..	..	..
Na-malate	.06	.18	.37	.60	.46	.13	..	..	..	..	..	..
Na-malonate	.06	.16	.39	.70	1.04	..	1.43	..	0.75	..	0.20	..
Na-citrate	.04	.11	.22	.30	0.31	.24	0.13	.05	..	..	..	..
Na-glycinate	.06	..	.36	.68	.94	1.24	1.00	..	..	..	..	..
Na-alanine	.06	..	.34	.62	.90	1.12	1.07	.60	..	..	..	..
Na-leucine	.06	..	.31	.45	.55	0.54	0.40	..	..	..	..	..
Na-arginine	.04	.19	.33	.59	..	..	..	..	..	..	..	..
Na-glutamate	.06	.18	.37	.49	..	..	..	..	..	..	..	..
Na-proline	.06	.16	.34	.60	..	..	..	..	..	..	..	..
Na-hydroxyproline	.06	..	.34	.51	..	..	..	..	..	..	..	..
Na-histidine	.05	..	.32	.52	.35	..	..	..	..	..	..	..
Na-methionine	.06	..	.32	.50	.51	.42	.22	..	..	..	..	..
Na_4-EDTA	.06	..	.12	.16	.15[a]	..	..	..	..	..	..	..
Na-mercaptoacetate	.06	..	.36	..	.48[a]	.55	.62	..	..	..	..	..
Na-glycocholate	.07	..	.35	..	.79[a]	..	..	..	..	..	..	..
Na-benzoate	.06	.15	.35	.68	1.00	..	..	..	..	..	..	..
Na-benzenesulfonate	.05	..	.33	.65	1.02	..	..	..	..	..	..	..
Na-sulfanilate	.06	..	.31	.49[b]	..	..	..	..	..	..	..	..
Na-*o*-hydroxybenzoate	.07	..	.34	.66	0.91	.82	.70	..	..	..	..	..
Na-*m*-hydroxybenzoate	.06	..	.31	.48	.43	.15[c]	..	..	..	..	..	..
Na-*p*-hydroxybenzoate	.07	..	.30	.47	.54	..	..	..	..	..	..	..
Na-ethyl-isoamyl barbiturate	.06	..	.25	.20	.07	..	..	..	..	..	..	..
Na-ethyl-1-methyl barbiturate	.05	..	.27	.34	..	..	..	..	..	..	..	..

[a] 2.5 *N* solution. [b] 1.5 *N* solution. [c] 4.5 *N* solution.

Effects of Organic Anions.—Although following the same general patterns, the effects of organic anions were found in some instances to be much more pronounced. While in the case of formate, acetate, propionate and butyrate there is no effect on line width (Table I) and only a small effect on amplitude (Table II), this is not the case for lactate, pyruvate,[6] α- and β-hydroxybutyrate (Fig. 4) and citrate. Here the line width, already slightly larger than that of the standard in dilute solutions, shows a rapid increase with concentration, with correspondingly low amplitudes. At higher concentration of sodium pyruvate and α-hydroxybutyrate the absorption line is broadened beyond detection.

Since the only structural difference between the two sets of compounds consists of an additional hydroxy or keto group in an α- or β-position to the carboxyl, it naturally suggests that the latter is involved in the interaction with sodium through the formation of a chelate. The relatively stronger interaction displayed by the α-hydroxy- as compared to β-hydroxybutyrate, adds weight to this consideration.

Sodium benzoate and its hydroxy derivatives are of interest by analogy with the aliphatic hydroxy acids. Inasmuch as comparisons can be made despite differences in solubility, it appears from the tabulated data that no interactions occur with sodium benzoate, benzene sulfonate or sulfanilate, while they do appear, when a hydroxyl group is added to the ring. The differences between the compounds having the OH in *o*, *m* and *p*-position, respectively, again suggest a probable role of this group in the interaction.

Of the amino acids, tetrasodium Versenate shows the most pronounced effect, consistent with the weak complex formation detectable by titration techniques.[13] A similar effect is observed in sodium histidine, while all the other amino acids give rise to much weaker interactions, if any.

Sodium salts of ethyl-isoamylbarbituric acid

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[13] G. Schwarzenbach and H. Ackerman, *Helv. Chim. Acta*, **30**, 1798 (1947).

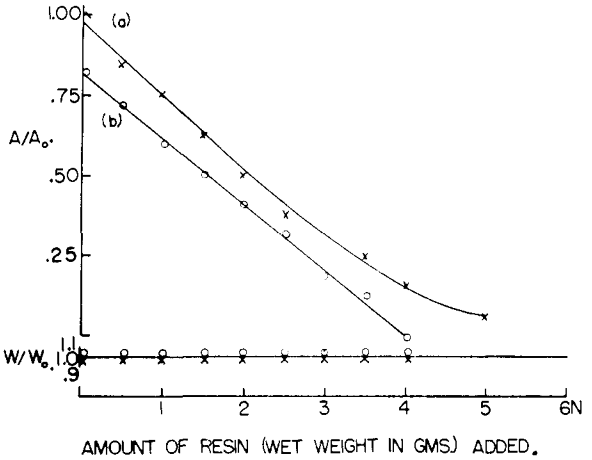

Fig. 1.—Effects of adding increasing amounts of resin to 4 ml. of 3 *N* NaCl (a) and 4 ml. of 2.5 *N* NaOH (b): A/A_0 = amplitude relative to that of 3 *N* NaCl; W/W_0 = width relative to that of 3 *N* NaCl.

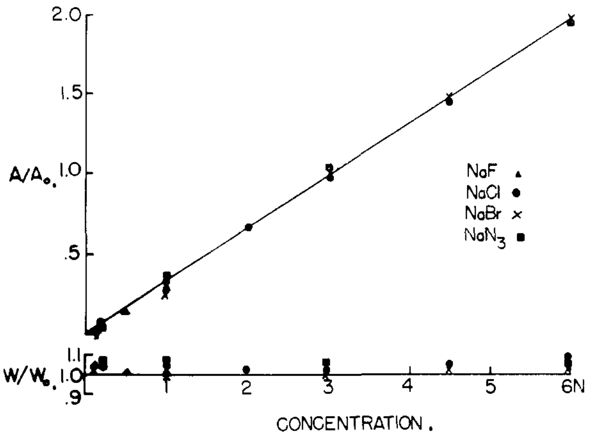

Fig. 2.—Relative amplitude and width as functions of concentration for NaF, NaCl, NaBr and NaN_3: A/A_0 = amplitude relative to that of 3 *N* NaCl; W/W_0 = width relative to that of 3 *N* NaCl.

(amytal) and ethyl-1-methylbarbituric acid (nembutal) were tested because of their depressant action on nervous activity in view of the presumed connection between active sodium transport and the latter. Both compounds show some effect, which is especially prominent in the case of amytal.

Several attempts have been made to detect the resonance line of sodium in organic solvents. The only success was achieved with a solution of $NaClO_4$ in acetone, for which a line very similar to that in aqueous media was observed, with a relative width of 1.1 and relative amplitude of 0.62 for a 2 *N* solution. The lack of success in detecting sodium in compounds soluble in benzene, toluene, dimethylsulfoxide and dioxane, such as sodium salicylaldehyde hydrate, sodium alizarin sulfonate and sodium triphenylmethyl, may have been due partially to the instrumental difficulty of detecting sodium at very low concentrations. However, failure to find any signal in alcoholic solutions could not have been explained in this manner. The signal was absent in solutions up to 6 *N* in sodium in absolute or 95% alcohols. Addition of increasing amounts of methyl or ethyl alcohol, ethylene glycol or glycerol to a 1 *N* NaOH solution revealed progressive broadening accompanied by a decrease in amplitude. Similar findings are obtained for sodium methylate in up to 10 *N* concentrations (Fig. 5). The interaction of sodium with an alcohol thus appears to be more pronounced than its interaction with water.

It should be noted that none of the effects discussed above can be accounted for on the basis of viscosity. Apart from rough theoretical considerations,[5] the most viscous solution examined (that of 2.5 *N* sodium glycocholate with a relative viscosity of 30) gave rise to a line indistinguishable from that of 2.5 *N* NaCl.

Conclusions.—It is probable that the natural width of the resonance line due to sodium ion in aqueous solution is to a large extent determined by quadrupolar interactions, although it is not possible to predict this effect quantitatively. Proximity of the unshared electron pairs on the oxygen atoms of water can be expected to polarize the electron shell of sodium somewhat, thus introducing asymmetry into the electric field at the sodium nucleus. The fact that the sodium line is still comparatively narrow suggests that the distribution of water molecules around a sodium ion is highly symmetrical and/or that the distortion of the electron shell of sodium produced by individual water molecules is rapidly averaged out. It is not likely that molecules other than those in immediate contact with the ion could appreciably distort the symmetry of the electric field at the nucleus since the effects of a charge decrease with the square of the distance. Ions or molecules whose interaction with the sodium ion is of the same order of magnitude as for water (in terms of extent of polarization and duration of contact) would not alter the natural width of the sodium line. Those whose interactions are weaker will not be found in the immediate vicinity of the ion with appreciable frequency except when present in excess over water. On the other hand, those tending to interact more strongly are always likely to produce a larger distortion of the electric field and impair its averaging, giving rise to a broader line.

Depending on the conditions of observation the broadening observed in different compounds may be due to either of two effects. When occurring only in highly concentrated solutions, it can be attributed to ion pair formation enhanced by a relative unavailability of solvent molecules. In contrast, its presence in more dilute solutions probably signifies an actual preference on the part of the sodium ion for the given complexing agent, over a solvent molecule. Because of mass action the second effect will likewise be accentuated with increasing concentration. Sodium hydroxide, sodium iodide and sodium thiocyanate would fall into the first category, with sodium pyrophosphate, sodium Versenate and sodium citrate representing the second.

Much remains to be learned from the study of *p*H effects, of ion competition and of multicom-

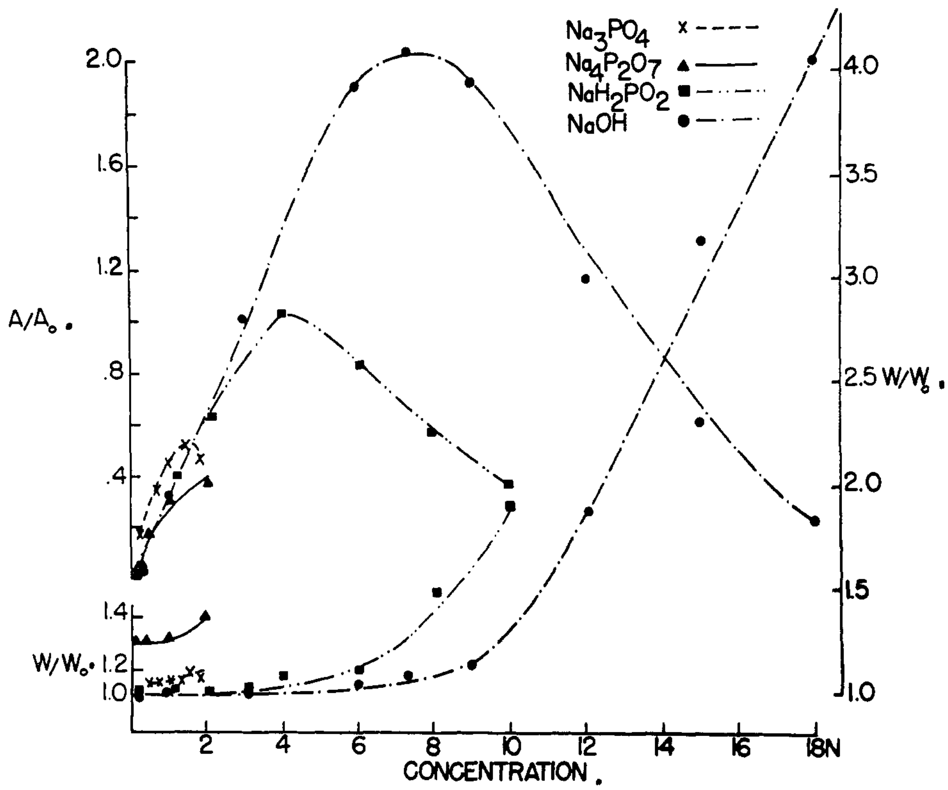

Fig. 3.—Relative amplitude and width as functions of concentration for NaOH, Na_3PO_4, $Na_4P_2O_7$ and NaH_2PO_2.

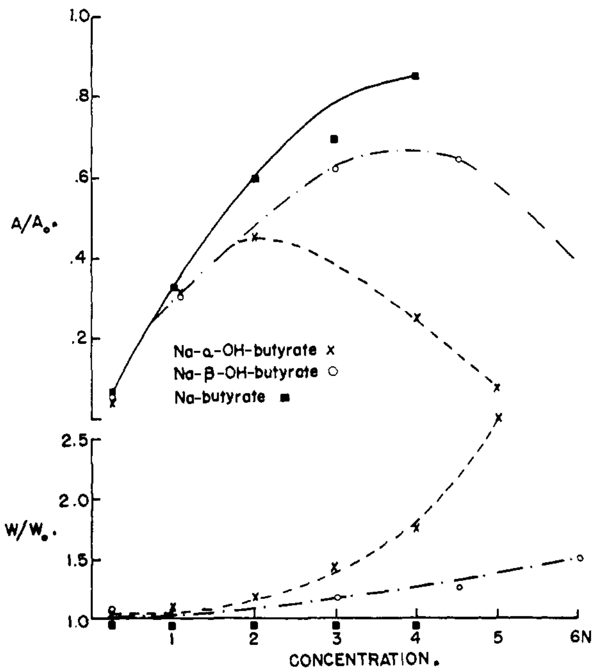

Fig. 4.—Relative amplitude and width as functions of concentration for Na butyrate, Na α-hydroxybutyrate and Na β-hydroxybutyrate: A/A_0 = amplitude relative to that of 3 N NaCl; W/W_0 = width relative to that of 3 N NaCl.

ponent systems. However, the data presented here constitute strong evidence for the existence of sodium complexes not detected by other methods as well as for the practical usefulness of nuclear spin resonance as a method for their investigation.

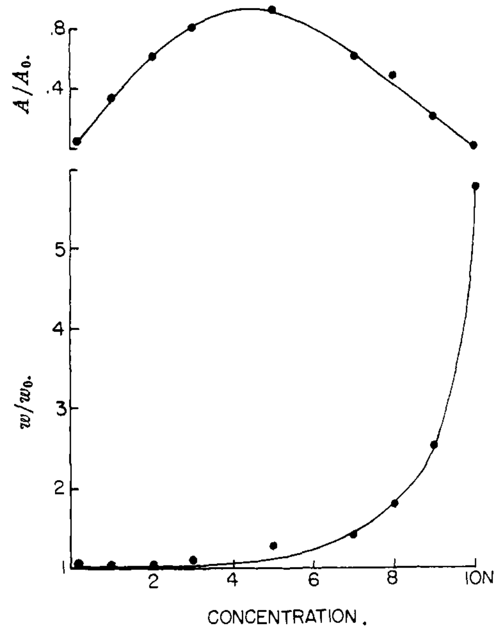

Fig. 5.—Relative amplitude and width as functions of concentration for Na methylate: A/A_0 = amplitude relative to 3 N NaCl; W/W_0 = width relative to 3 N NaCl.

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