

der we would predict since it represents the order of decreasing diamagnetism. In other words, apparently the diamagnetism of the ligands is significantly retained in the complex and is not quenched.

However, as Proctor and Yu suggest, the mere diamagnetic effect is not large enough to explain these large shifts in resonance frequency. Instead, these authors are led to assume "the existence of electronic energy levels very close to that of the ground state" an assumption which is justified by a temperature dependence¹⁶ of the resonant frequency. These low lying electronic energy levels correspond, as Ramsey points out,¹⁷ to those encountered in Van Vleck's second order paramagnetism.

In the case of the pentammine complexes meas-

(17) N. F. Ramsey, *Phys. Rev.*, **86**, 245 (1952).

ured in this work, we can therefore account for the high "residual paramagnetism" by assuming low lying excited states. In going from the nitro complex to the formate complex, it will not be surprising to find an appreciable change in magnetic moment since the magnetic susceptibility depends not only on the nature of the excited state but also on its symmetry. The symmetry may be particularly important since the orbital quenching of the moment in the excited state is very sensitive to the electrical symmetry in the complex.

Measurements on the nuclear magnetic resonance of cobalt in these complexes would be of great interest as also would be a study of the temperature dependence of both the magnetic susceptibility and the nuclear resonance shift.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Thermodynamic Properties of Sodium Borohydride and Aqueous Borohydride Ion

BY WALTER H. STOCKMAYER, DALE W. RICE AND CLARK C. STEPHENSON

RECEIVED NOVEMBER 8, 1954

From isotonic measurements the dissociation pressure of sodium borohydride dihydrate at 25° is 6.23 mm. and the activity of water in its saturated (14.9 molal) aqueous solution is 0.294. From these results the standard free-energy change at 298°K. of the reaction $\text{NaBH}_4(\text{s}) = \text{Na}^+ + \text{BH}_4^-$ is -5660 ± 70 cal., leading to a value of $+28.6 \pm 0.1$ kcal. for the standard free energy of formation of BH_4^- (aq.). The standard entropy of the ion is estimated at 25.5 ± 1 e.u. The properties of sodium borohydride are compared to those of the sodium halides and discussed in terms of ionic radius and polarizability. The polarizability of borohydride in its alkali salts is 3.94 \AA^3 .

The increasing use of the alkali borohydrides¹ as reducing agents makes accurate knowledge of their thermodynamic properties desirable. The free energies of solid anhydrous LiBH_4 and NaBH_4 are known from the thermochemical measurements of Davis, Mason and Stegeman² and the heat capacity studies of Johnston and Hallett,³ but reliable figures for the aqueous borohydride ion have not yet been published. We have measured by a simple isotonic method the dissociation pressure of sodium borohydride dihydrate¹ and the activity of water in its saturated solution at 25°. From these results we have computed the solubility product of the anhydrous salt and thus obtained the standard free energy of the aqueous borohydride ion.

In its physical behavior, borohydride ion resembles the halide ions much as ammonium ion resembles the alkali ions. Its ionic radius⁴ of 2.03 \AA . lies between those of bromide and iodide ions, but its polarizability (see below) is slightly less than that of bromide. From these facts we are able to estimate the entropy of the aqueous borohydride ion by several independent methods, as well as to discuss the thermodynamic properties of its alkali salts in comparison to those of the halides.

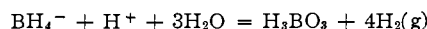
We have also attempted to determine the solubility product of the dihydrate by studying equilibria between an aqueous phase and solid solutions

of $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ with $\text{NaBr} \cdot 2\text{H}_2\text{O}$ and $\text{NaI} \cdot 2\text{H}_2\text{O}$, which form in all proportions. However, the solid solutions displayed sufficient departure from ideal behavior to preclude accurate evaluation of the equilibrium constant, and we merely remark that the results were in rough agreement with that obtained by the direct method.

Experimental

Sodium borohydride (Metal Hydrides, Inc., Beverly, Mass., "Research" grade, ca. 90% NaBH_4) was recrystallized from Eastman isopropylamine by two methods. Large crystals (5 mm.) of high purity (99.5% NaBH_4) were obtained by dissolving the crude salt in the solvent at reflux, cooling and filtering and allowing to stand in a filter flask connected to a Dry Ice-acetone trap. After most of the solvent had passed into the cold trap, crystals were removed with forceps, washed with dry ether and dried under vacuum. Smaller crystals (ca. 0.5 mm.) of slightly lower purity (99.0% NaBH_4) were obtained in much shorter time by charging the crude salt to the thimble of a Soxhlet extractor, adding about twice the volume of solvent necessary to fill the thimble and start the siphon, and extracting for about 8 hours. The crystals that formed in the flask were removed by filtration and washed and dried as before. The small crystals were used for most of our experiments.

Analyses for borohydride by hydrogen evolution¹ according to the reaction



were performed in an all-glass apparatus by slowly dropping 6 N HCl into a magnetically stirred solution of the sample in 0.5 N NaOH. The water level in the 100-ml. gas buret was periodically adjusted by a levelling bulb, the final adjustment to atmospheric pressure being made a few minutes after hydrogen evolution had ceased. Successive determinations on a given sample usually checked to within 0.5%. Several check analyses were also performed by the acidimetric method,² which however tends to give high results.

(1) H. I. Schlesinger, H. C. Brown and collaborators, *THIS JOURNAL*, **75**, 186 (1953).

(2) W. D. Davis, L. S. Mason and G. Stegeman, *ibid.*, **71**, 2775 (1949).

(3) H. L. Johnston and N. C. Hallett, *ibid.*, **75**, 1467, 1496 (1953).

(4) S. C. Abrahams and J. Kalnajs, *J. Chem. Phys.*, **22**, 434 (1954).

Isotonic measurements were made with a simple apparatus similar to that of Sinclair.⁵ It consisted of a small (170 mm.) vacuum desiccator and a cylindrical brass block (2" × 2") with two holes into which 15-ml. glass weighing bottles fitted snugly. The dissociation pressure of sodium borohydride dihydrate (easily prepared by exposing the anhydrous salt to humid air) was measured by placing a mixture of anhydrous salt and dihydrate in one of the weighing bottles and charging the other with about 0.4 g. of a solution of C.P. sulfuric acid whose vapor pressure was near that estimated for isotonic equilibrium. The bottles were placed in the brass block in the desiccator, which was then evacuated to a pressure of about 6 mm. A few drops of water were put into the bottom of the desiccator before evacuation to ensure nearly complete removal of air. During the experiment the temperature of the room was kept to within one degree of 25°, which is believed sufficient to determine the water activity at 25° to within 2%. After several days, dry air was admitted to the desiccator and the final concentration of the sulfuric acid measured by titration and checked by the change in weight of the solution. Experiments were run in which equilibrium was approached from both directions. The activity of water in the sulfuric acid solutions was found by interpolating in the table of Shankman and Gordon.⁶ The same method was used to measure the vapor pressure of a saturated solution (see below) of NaBH₄·2H₂O, and also, as a check on the method, the dissociation pressure of NaBr·2H₂O. The results of the isotonic experiments are displayed in Table I.

TABLE I
ISOTONIC EXPERIMENTS

System	H ₂ SO ₄ concn., <i>m</i>		Equilib. activity H ₂ O	Equilib. vapor pressure, mm.
	Initial	Final		
NaBH ₄ -NaBH ₄ ·2H ₂ O	16.1	12.18	0.262	6.23
NaBH ₄ -NaBH ₄ ·2H ₂ O	9.50	12.18	.262	6.23
NaBH ₄ ·2H ₂ O-soln.	9.50	11.48	.289	6.9
NaBH ₄ ·2H ₂ O-soln.	9.50	11.27	.298	7.1
NaBr-NaBr·2H ₂ O	6.40	9.43	.392	9.3

Solubility of sodium borohydride dihydrate was determined by tumbling a bottle containing 0.01 *m* NaOH and excess of the salt in a 25° temperature bath regulated to 0.01° for 24 hours. This concentration of sodium hydroxide was sufficient to ensure negligible decomposition of borohydride during this time,^{4,7} but dilute enough to cause negligible change in solubility. After the equilibration period the liquid phase was decanted, cooled by Dry Ice-acetone and dried under vacuum, the water content being found from the loss in weight. The residue from the drying process was then analyzed for sodium borohydride by the hydrogen method. Check determinations gave the solubility of the dihydrate at 25° as 14.9 weight-molal.

The triple point at which the three phases NaBH₄(s), NaBH₄·2H₂O(s) and solution are in equilibrium under 1 atmosphere was observed by slowly heating the dihydrate in a melting point apparatus, the mean of several runs being 35 ± 1°.

Refractive indices of anhydrous sodium, potassium, rubidium and cesium borohydrides were roughly determined by the immersion method, in order to find the polarizability of borohydride ion. White light was used and the room temperature, though not controlled, was near 25°. The

TABLE II
REFRACTIVE INDICES OF ALKALI BOROHYDRIDES

Salt	Purity, %	Refractive index	Polarizability of BH ₄ ⁻ , Å. ³
NaBH ₄	99.5	1.542	4.06
KBH ₄	99.3	1.494	3.96
RbBH ₄	97.3	1.483	3.94
CsBH ₄	97.1	1.496	3.78
Av.			3.94 ± 0.07

(5) D. A. Sinclair, *J. Phys. Chem.*, **37**, 495 (1933).

(6) S. Shankman and A. R. Gordon, *THIS JOURNAL*, **61**, 2370 (1939).

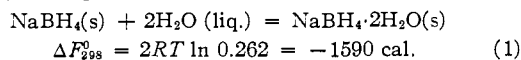
(7) R. L. Pecsok, *ibid.*, **75**, 2862 (1953).

samples were the same ones used in an X-ray study.⁴ The results are in Table II. To obtain the polarizability, the X-ray densities were used in the Lorentz equation and the polarizabilities of the alkali cations were taken from the recent compilation of Tessman, Kahn and Shockley.⁸

In view of their inconclusive nature, the experiments with solid solutions are not described further.

Free Energy of Borohydride Ion.—The results of the isotonic experiments are in Table I. The last experiment gives a dissociation pressure for NaBr·2H₂O in good agreement with the value of 9.1 mm. calculated⁹ from the best available data, and indicates the reliability of the method.

The first two experiments of Table I agree perfectly and give at once



The mean experimental value for the activity of water in the saturated (14.9 *m*) solution of the dihydrate is 0.294, corresponding to an osmotic coefficient

$$\phi = - (55.51/2 \times 14.9) \ln 0.294 = 2.28$$

We have not determined the water activity in less concentrated solutions, and must therefore estimate the mean activity coefficient of the ions from this single result. We thus assume the ion activity coefficients to obey the familiar expression

$$\ln \gamma = - (Ax/a)/(1+x) + Bm$$

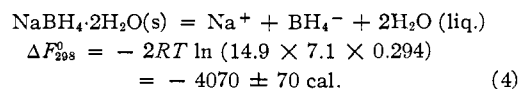
$$x \equiv \alpha\sqrt{m} \quad (2)$$

where $A = 1.1708$ and $\alpha = 0.324a$ at 25° in water, a being the distance of closest approach in ångströms. This expression fits the results for the alkali halides quite well up to high concentrations and should also be satisfactory for sodium borohydride. The osmotic coefficient corresponding to eq. 2 is

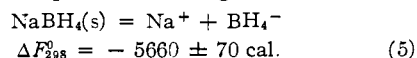
$$\phi = 1 - AZ + Bm/2$$

$$Z \equiv [1 + x - (1 + x)^{-1} - 2 \ln(1 + x)]/x^2 \quad (3)$$

By assuming a reasonable value for α , we can obtain B from our observed osmotic coefficient by eq. 3 and then use eq. 2 to evaluate γ_{\pm} for the saturated solution. We find for $\alpha = 1.00$ that $B = 0.188$ and $\gamma_{\pm} = 6.52$; for $\alpha = 1.20$ that $B = 0.184$ and $\gamma_{\pm} = 7.10$; and for $\alpha = 1.50$ that $B = 0.180$ and $\gamma_{\pm} = 7.50$. The value $\alpha = 1.20$ is close to those recorded¹⁰ for the other sodium halides, and the others represent reasonable upper and lower limits. It is reassuring that the B -value thus obtained for sodium borohydride falls exactly at the observed ionic radius⁴ on a plot of B against ionic radius for the sodium halides. Taking the intermediate value of α as preferred, we thus obtain



Combination of eq. 1 and 4 then gives



This figure corresponds, with eq. 2, to a solubility of 15.5 *m* for the anhydrous salt at 25° as compared to

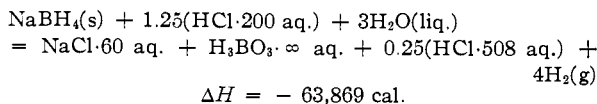
(8) J. R. Tessman, A. H. Kahn and W. Shockley, *Phys. Rev.*, **92**, 890 (1953).

(9) C. C. Stephenson, unpublished calculations.

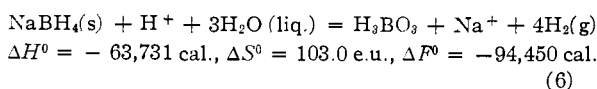
(10) R. A. Robinson and H. S. Harned, *Chem. Revs.*, **28**, 452 (1941).

14.9 *m* for the hydrate. This difference appears reasonable, since the triple point, hydrate-anhydrous salt-solution is found at 35°.

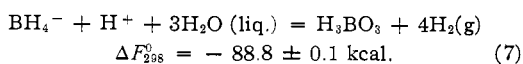
The result of eq. 5 can now be combined with published data to obtain the standard free energy of the borohydride ion. Davis, Mason and Stegeman² found



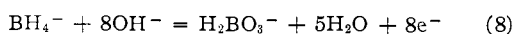
Combining this figure with the heats of dilution,¹¹ and taking the entropy of NaBH₄(s) from Johnston and Hallett³ and the entropies of the other substances from Latimer,¹² we obtain at 298°K.



Addition of eq. 5 and 6 then leads to



which with the free energies¹² of water and boric acid gives the standard free energy of formation of borohydride ion in aqueous solution at 298°K. as +28.6 ± 0.1 kcal. Thus for the half-reaction



we find $\Delta F^0 = -228.9$ kcal. and $E^0 = +1.24$ volts at 298°K. Pecsok⁷ obtained 1.23 volts for this couple, although he used too high a value for the entropy of BH₄⁻ and neglected entirely the heat of solution of sodium borohydride.

Entropy of Borohydride Ion.—We may estimate the standard entropy of the aqueous borohydride ion by three different methods, which give remarkably similar results. First, we use the equation of Powell and Latimer¹³ for monatomic anions, taking the crystallographic radius of the ion⁴ as 2.03 Å., and add to it the rotational entropy of a free BH₄⁻ ion with a B-H bond length¹⁴ of 1.26 Å., the vibrational entropy being negligible. In this way, we obtain the value $S^0 = 26$ e.u. Since the internal entropy of the aqueous solute should be somewhat less than that of the gaseous ion, we might expect this method to give slightly high results, as indeed it does for ammonium ion.

In the second method, we apply without modification the recent formula of Cobble¹⁵ for tetrahedral oxy-anions, again taking the B-H distance as 1.26 Å., and once more obtain $S^0 = 26$ e.u.

Third, the change in entropy^{9,12} of the reaction $\text{NaX}(\text{s}) = \text{Na}^+ + \text{X}^-$ for the sodium halides is plotted against the crystal radius of the anion (or, perhaps better,¹³ against its squared reciprocal). Interpolation to the radius of the borohydride ion gives $\Delta S_{298}^0 = 15.0 \pm 0.5$ e.u. for reaction (5), which corresponds to $S^0 = 25$ e.u. for borohydride ion.

(11) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties."

(12) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Inc., New York, N. Y., (1952).

(13) R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

(14) W. C. Price, *ibid.*, **17**, 1044 (1949).

(15) J. M. Cobble, *ibid.*, **21**, 1443 (1953).

This method implies that the internal entropy of the ion in solution is no greater than in the crystal, and thus might be expected to give too low a result.

In view of the excellent agreement among the three methods, we take $S^0 = 25.5 \pm 1$ e.u. for BH₄⁻(aq.) at 298°K. Then $\Delta H_{298}^0 = -1.0 \pm 0.4$ kcal. for reaction (5), which leads to a value of +12.4 kcal. for the standard heat of formation of aqueous borohydride ion.

Discussion

The nearly constant value obtained for the polarizability of borohydride ion (Table II) shows that the alkali borohydrides are essentially ionic crystals, as already concluded from infrared spectra.¹⁴ We may therefore assert with some confidence that the physical properties of these salts and of aqueous borohydride ion should in general resemble those of the alkali halides and the aqueous halide ions, as ammonium ion resembles the alkali ions and methane the noble gases. To be sure, certain properties (*e.g.*, crystal lattice type,⁴ order-disorder phenomena in crystals^{3,16}) depend more or less directly on the tetrahedral structure of the ion, but for many others the distinction between tetrahedral and spherical shape is unimportant. Further, some properties may to a good approximation be treated as functions of but a single parameter, the ionic radius. Examples are the entropy of hydration and of solution (as in the preceding section), the limiting conductance of the ion, the coefficient *B* in eq. 2 and 3, and a similar coefficient in the equation for viscosity of salt solutions.¹⁷

Other properties, however, depend also on the magnitude of the van der Waals forces, and hence also on the ionic polarizability. Among these are heats and free energies of solution. In particular, the value of ΔF^0 for reaction (5), when plotted against the lattice constant of NaBH₄, lies about 600 cal. below a smooth curve through the corresponding values for the sodium halides; that is, NaBH₄ is more soluble than would be expected from simple interpolation between NaBr and NaI. From the preceding section, we must conclude that this increased solubility is principally due not to a larger entropy of solution but to an algebraically lower ΔH^0 . We now show by a crude calculation that the effect can reasonably be explained in terms of van der Waals forces.

If the polarizabilities of the halide ions⁸ are plotted against their crystal radii, it is found by interpolation that a hypothetical halide ion X⁻ of radius 2.03 Å. would have a polarizability of about 4.9 Å.³, while the observed value for BH₄⁻ is only 3.94 Å.³ Thus the hypothetical crystal NaX is more stable than NaBH₄. For a quantitative estimate, we plot Mayer's¹⁸ values of the dispersion energy coefficients *C* and *D* for the sodium halides against the anion polarizabilities and interpolate to the values for BH₄⁻ and X⁻, obtaining $C = 250 \times 10^{-60}$ erg cm.⁶ and $D = 280 \times 10^{-76}$ erg cm.⁸ for NaBH₄ and $C = 340 \times 10^{-60}$ erg cm.⁶ and $D =$

(16) W. H. Stockmayer and C. C. Stephenson, *ibid.*, **21**, 1311 (1953).

(17) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953, Chaps. 9, 10.

(18) J. E. Mayer, *J. Chem. Phys.*, **1**, 270 (1933).

410×10^{-76} erg cm.⁸ for NaX. The difference in lattice energy is therefore

$$\Delta U = \Delta C/r^8 + \Delta D/r^8 \approx 1750 \text{ cal./mole} \quad (9)$$

where $r = 3.08 \text{ \AA}$. This figure is not yet the difference in ΔH^0 , for there is also a difference in dispersion energy in the aqueous solution. To estimate this second term, we take the well known Slater-Kirkwood-Buckingham formula¹⁹ for the dispersion energy between two unlike molecules

$$u = -cr^{-6}; c = (3\hbar e n^{1/2}/4\pi m^{1/2})\alpha_1\alpha_2/(\alpha_1^{1/2} + \alpha_2^{1/2}) \quad (10)$$

where α_1, α_2 are the polarizabilities, e and m are electronic charge and mass, \hbar is Planck's constant and n is the number of outer-shell electrons, taken as 8. We obtain $c \approx 150 \times 10^{-60}$ erg cm.⁶ for $\text{H}_2\text{O}-\text{X}^-$ and $c \approx 130 \times 10^{-60}$ erg cm.⁶ for $\text{H}_2\text{O}-\text{BH}_4^-$. Assuming six water molecules in the first hydration sphere at a distance of 3.5 \AA . from the ion center, and estimating the contribution of more distant water molecules as about that of two more nearest neighbors, we find

$$\Delta U \approx 8 \times 20 \times 10^{-60}/(3.5 \times 10^{-8})^6 \text{ erg./ion} \\ \approx 1250 \text{ cal./mole} \quad (11)$$

The difference between eq. 9 and 11, which should be the difference in ΔH^0 and ΔF^0 of solution between NaX and NaBH_4 , is thus estimated at about 500 cal., in somewhat fortuitously good agreement with observation. Clearly our calculation contains some rather arbitrary assumptions, particularly in the evaluation of the solution term of eq. 11,

(19) See, for example, H. Margenau, *Phys. Rev.*, **56**, 1000 (1939).

so that the above result should be regarded merely as indicating order of magnitude. Additional instability of solid NaBH_4 compared to NaX could arise from extra repulsion due to the non-spherical nature of BH_4^- , but from the low temperature (190°K .) of the order-disorder transition^{8,16} we believe this cannot be a major effect. A pragmatic test of the above considerations could be made by comparing the solubility products of the other alkali borohydrides in the same way to those of the respective alkali halides, but at present data are not available.

It appears that the difference in dispersion energy discussed above also persists largely in the dihydrate, for the value of ΔF^0 for reaction (1) is very close to that obtained by interpolation on a curve for the sodium halide dihydrates. Hence $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ is also more soluble than the hypothetical $\text{NaX} \cdot 2\text{H}_2\text{O}$. We may thus understand the low temperature (35°) of the triple point, dihydrate-anhydrous salt-solutions, for NaBH_4 as compared to 0.15° for NaCl, 50.7° for NaBr and 64.3° for NaI,²⁰ and also why the solid solutions of $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ with $\text{NaBr} \cdot 2\text{H}_2\text{O}$ and $\text{NaI} \cdot 2\text{H}_2\text{O}$ show considerable departure from ideality.

We thank Dr. M. D. Banus of Metal Hydrides, Inc., for the samples of the higher alkali borohydrides.

(20) Gmelin's "Handbuch der Anorganischen Chemie," Vol. 8, Teil 21.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CLARK UNIVERSITY]

Thermodynamics of Ion Pair Formation in Some Non-aqueous Solvents¹

BY KURT H. STERN² AND ARTHUR E. MARTELL

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Ion conductances have been measured for several quaternary ammonium salts in three alkyl chloride solvents over a range of temperature. The results have been used to calculate thermodynamic functions associated with ion-pair formation and to interpret these in terms of solute-solvent interactions.

It has long been recognized that to account for the mobility of ions and differences in the dissociation constants of ion pairs in different solvents not only the macroscopic physical constants such as viscosity and dielectric constant are of importance, but that the specific constitutional and structural factors of solvents and solutes must also be considered. For instance, in the case of ethylene chloride and ethylidene chloride we have an example of two isomeric solvents with practically the same dielectric constant and similar chemical constitution but with quite different boiling points, viscosities and densities. These solvents offer, therefore, an unusual opportunity to measure the effects of constitutional factors on the properties of solutions. Healey and Martell³ have measured

(1) In part from the Ph.D. dissertation of K. H. Stern. Presented before the Division of Physical and Inorganic Chemistry, 124th meeting, American Chemical Society, September, 1953.

(2) Department of Chemistry, University of Arkansas, Fayetteville, Ark.

(3) F. H. Healey and A. E. Martell, *THIS JOURNAL*, **73**, 3296 (1951).

ion conductances of several salts in ethylidene chloride and Kraus and co-workers⁴⁻⁸ have obtained corresponding data in ethylene chloride. Some of the structural factors involved in solute-solvent interactions in these two solvents have been discussed previously by Stern, Healey and Martell.⁹

In the present work it was considered of interest to determine whether the thermodynamic functions which can be calculated from the temperature dependence of the ion-pair dissociation constants offer any significant correlation with the forces operative in electrolytic solutions. Almost no work of this kind has been done for neutral electrolytes in non-aqueous solvents. The only exception is a series of measurements by Bien, Fuoss and

(4) D. L. Fowler and C. A. Kraus, *ibid.*, **62**, 2237 (1941).

(5) L. F. Gleysteen and C. A. Kraus, *ibid.*, **69**, 451 (1947).

(6) L. M. Tucker and C. A. Kraus, *ibid.*, **69**, 454 (1947).

(7) E. R. Kline and C. A. Kraus, *ibid.*, **69**, 814 (1947).

(8) W. E. Thompson and C. A. Kraus, *ibid.*, **69**, 1016 (1947).

(9) K. H. Stern, F. H. Healey and A. E. Martell, *J. Chem. Phys.*, **19**, 1114 (1951).