Included in column 7 of Table III are the Walden products, $\Lambda_0\eta$, for the two systems. From these results it would appear that the viscosity of the solvent media largely determines the mobilities of the species present at infinite dilution. While a direct comparison between the two solvent systems using one metal is not possible, it would be expected that the product would be somewhat smaller for lithium than for sodium in any case, since the former would probably be heavily solvated.

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Transference Numbers and Conductances of Multivalent Salts in Aqueous Solution: Zinc Sulfate and Zinc Perchlorate[1]

BY JAMES L. DYE, M. PATRICIA FABER AND DAVID J. KARL

RECEIVED JULY 23, 1959

The transference number of $ZnSO_4$ in water as a function of concentration was measured by the moving boundary method at 25°. The equivalent conductance of aqueous $Zn(ClO_4)_2$ also was measured and found to deviate markedly from the Onsager equation even in dilute solutions. Attempts to explain this behavior on the basis of ion-pairing, hydrolysis and purely electrostatic interactions were unsatisfactory. The conductance data for $ZnSO_4$ taken alone can be adequately fit by either the Fuoss–Onsager theory including ion-association or including instead higher terms of the electrophoretic equation. The former treatment also fits the transference data. However, when λ_0 for Zn^{++} from measurements on $Zn(ClO_4)_2$ is used, neither theory alone describes the behavior adequately. It is postulated that the covalent-bonding tendencies of Zn^{++} give deviations from any theory which is based upon the assumption of non-polarizable ions.

Introduction

With the recent publication of excellent theoretical papers by Fuoss and Onsager[2] dealing with the time-of-relaxation effect in conductance, and the application to ion-pairing systems by Fuoss,[3] the theoretical treatment of dilute solutions of 1–1 electrolytes in solvents of dielectric constant greater than about 20 is on firm ground. Unfortunately this cannot be said of unsymmetrical electrolytes even for dilute solutions in water. It has been shown[4] that extended terms in the electrophoretic effect are significant for 2–1 and 3–1 electrolytes and it is reasonable to assume that these non-linear terms in the distribution function also are important in the time-of-relaxation expression. We are currently studying the conductances, transference numbers and activity coefficients of a variety of multivalent electrolytes as tests of the various theoretical expressions. Since the Fuoss–Onsager Theory is capable of handling symmetrical electrolytes, it appeared to be of interest to apply the extended theories to the conductance of zinc sulfate, a 2–2 electrolyte for which accurate conductances are available.[5]

An attempt to fit conductance data alone would require three parameters, (1) the limiting equivalent conductance of zinc sulfate, (2) the ion-size parameter $\mathring{a}$ and (3) the ion-association constant A. It would be an unusual equation which could *not* fit a single smooth curve with the aid of three adjustable parameters. In order to reduce the arbitrariness of fit, it was decided to determine the limiting equivalent conductance of zinc ion by measuring the equivalent conductance of zinc perchlorate as a function of concentration. To test further the theoretical expressions, the transference number of zinc sulfate was determined as a function of concentration. The only reasonable data available for transference numbers are those of Purser and Stokes[6] based upon the e.m.f. method and Gold[7] based upon the Hittorf method. These methods are subject to rather large errors and we employed the more accurate moving boundary method. The present paper gives the experimental results obtained and the comparison of theory and experiment.

Experimental

Transference numbers were determined by the moving boundary method. All measurements were made with descending boundaries. The cell employed was the hollow barrel stopcock type with an added stopcock at the bottom of the graduated portion for use with rising boundaries. The transference tube was calibrated with mercury as recommended by Longsworth.[8] Constant currents were obtained with an electronic controller and balancing motor. Current was determined from the potential drop across a standard resistor in series with the cell. Compensation for minor fluctuations not eliminated by the electronic apparatus was made by feeding the unbalance from the Leeds and Northrup type K-1 potentiometer to a Brown "Electronik" 356358-1 amplifier which was used to drive a Brown 76750-3 balancing motor. A cadmium plug anode and silver–silver chloride cathode were utilized. An aquarium type water bath was maintained at 25.00 ± 0.05°. Stopwatches were calibrated using the standard WWV signal. The entire apparatus was checked at intervals by measuring the transference number of potassium chloride followed by lithium chloride. These results agreed with published values to within 0.05%.

Conductivity measurements were carried out in two Leeds and Northrup "Type A" cells, which were modified by sealing them to 500-ml. erlenmeyer flasks. This permitted measurement of the water conductance and the addition of solute without exposure to atmospheric CO_2. Similar cells were used by Kraus and co-workers.[9] The cells, whose electrodes were very lightly platinized (40 seconds)

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[1] Presented in part at the 133rd meeting of the American Chemical Society, April, 1958, San Francisco, Calif.

[2] R. M. Fuoss and L. Onsager, *Proc. Natl. Acad. Sci.*, **41**, 274, 1010 (1955); *J. Phys. Chem.*, **61**, 668 (1957).

[3] R. M. Fuoss, THIS JOURNAL, **79**, 3301 (1957); R. M. Fuoss and C. A. Kraus, *ibid.*, **79**, 3304 (1957); see also references in R. M. Fuoss, *ibid.*, **81**, 2659 (1959).

[4] J. L. Dye and F. H. Spedding, *ibid.*, **76**, 888 (1954).

[5] B. B. Owen and R. W. Gurry, *ibid.*, **60**, 3074 (1938).

[6] E. P. Purser and R. H. Stokes, *ibid.*, **73**, 5650 (1951).

[7] R. Gold, Ph.D. Thesis, New York University, 1954; *Dissertation Abstr.*, **15**, 988 (1955).

[8] L. G. Longsworth, THIS JOURNAL, **52**, 1897 (1930).

[9] H. M. Daggett, E. J. Bair and C. A. Kraus, *ibid.*, **73**, 799 (1951).

according to the recommendations of Jones and Bollinger,[10] showed very little Parker effect upon calibration over the same range of resistances as were used with the samples. The bridge employed was designed by Thompson and Rogers.[11] The temperature of the oil-bath was 25.00 ± 0.015° as measured with a platinum resistance thermometer. Conductivity water, which was prepared by distillation from alkaline permanganate and redistillation under nitrogen, had a specific conductance which was never higher than 7.3×10^{-7} ohm^{-1} cm.$^{-1}$. Water was forced into the cell by nitrogen pressure and all additions were made with a stream of wet nitrogen passing through the cell. Zinc sulfate stock solutions were prepared from Mallinckrodt analytical reagent grade salt after several recrystallizations from conductivity water. Concentrations were determined by evaporation and ignition to the anhydrous sulfate at 400° as suggested by Cowperthwaite and LaMer,[12] and also by ignition to the oxide at 900°. Weight dilutions of the stock solution were made and normalities calculated with the aid of measured densities. At the conclusion of the experiments, check determinations of the concentration were made by ignition to the oxide at 900° and by precipitation as barium sulfate.

Zinc perchlorate (G. F. Smith Chemical Co.) was recrystallized three times from conductivity water. The stock solutions were analyzed by adding sulfuric acid to weighed aliquots and evaporating to fumes of SO_3. The residues were dried to zinc sulfate at 400° and then ignited to the oxide at 900°. Weight dilutions were made with CO_2-free conductivity water.

Stock solutions of tetra-*n*-butylammonium sulfate were prepared by converting the iodide to the hydroxide with silver oxide and titrating the filtered solution to a *p*H value of 7.0 with standard sulfuric acid as recommended by Fowler, *et al.*[13] Volume dilutions were made when necessary.

Lithium chloride solutions were made from volume dilutions of a stock prepared by the method of Scatchard and Prentiss.[14]

Potassium chloride solutions were made by weight dilutions of stock prepared by dissolving the purified salt in CO_2-free conductance water. Purification of the Baker C.P. salt consisted of two recrystallizations from boiling conductivity water followed by fusion under nitrogen.

Results

The transference number of zinc sulfate as a function of concentration, corrected for volume and solvent effects, is given in Table I and shown graphically in Fig. 1. It proved to be a linear function of $N^{1/2}$ with N in equivalents per liter. The least-squares equation is

TABLE I

TRANSFERENCE NUMBER DATA FOR ZINC SULFATE IN WATER AT 25°

Normality	(Normality)$^{1/2}$	T_+ (obsd.)	T_+ (calcd.)[a]	$\Delta T_+ \times 10^4$
0.009692	0.09845	0.3826	0.3830	−4
.009692	.09845	.3830	.3830	0
.02270	.1507	.3799	.3797	+2
.03549	.1884	.3772	.3773	−1
.3549	.1884	.3779	.3773	+6
.05095	.2257	.3747	.3749	−2
.07510	.2740	.3719	.3719	0
.07510	.2740	.3720	.3719	+1
.07510	.2740	.3721	.3719	+2
.09027	.3004	.3698	.3702	−4

[a] T_+(calcd.) = $0.3892 - 0.0633\ N^{1/2}$.

$$T_+ = 0.3892 - 0.0633N^{1/2}$$

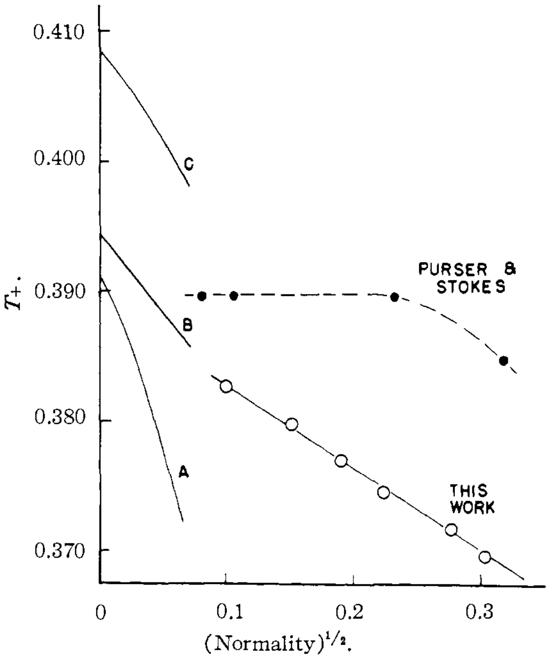

Fig. 1.—Transference number of $ZnSO_4$: A, calcd. with extended electrophoretic equation; Λ_0 adjusted to fit $ZnSO_4$ conductance data; B, calcd. with Fuoss-Onsager equation and association constant; Λ_0 adjusted to fit $ZnSO_4$ conductance data; C, calcd. with both of the above; Λ_0 from $Zn(ClO_4)_2$ conductance data.

standard deviation, 0.08% for ten determinations. All measurements were made with descending boundaries using tetra-*n*-butylammonium sulfate as the indicator electrolyte. This salt was chosen because of the low mobility of the cation. The transference number proved to be independent of current and indicator concentration within reasonable limits. For those concentrations in Table I involving duplicate runs, the current and/or indicator concentration are different by 10 to 20%. The results of Purser and Stokes[6] are also shown in Fig. 1.

The conductance cells were calibrated with KCl using the same operations as with the samples. All additions of the stock solutions were made by weight and the cell constant was calculated using the empirical expression of Owen[15] for the equivalent conductance of potassium chloride. A check determination was made with one of the cells utilizing $BaCl_2$. The equivalent conductance obtained agrees well with the results of Shedlovsky and Brown.[16] All of the calibration data are summarized in Table II.

The equivalent conductance of zinc perchlorate as a function of concentration is given in Table III and is shown graphically in Fig. 2. The very slight platinization used to prevent adsorption resulted in some frequency dependence of the resistance and resistance readings at 400, 600, 1000, 2000 and 4000 cycles per second were taken and plotted *versus* $f^{-1/2}$ for extrapolation to infinite frequency. Reasonable straight lines were obtained, and whenever the value of R_∞ differed

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[10] B. Jones and G. M. Bollinger, THIS JOURNAL, **57**, 280 (1935).

[11] H. B. Thompson and M. T. Rogers, *Rev. Sci. Instr.*, **27**, 1079 (1956).

[12] I. A. Cowperthwaite and V. K. LaMer, THIS JOURNAL, **53**, 4333 (1931).

[13] D. E. Fowler, W. V. Loebenstein, D. B. Paul and C. A. Kraus, *ibid.*, **62**, 1140 (1940).

[14] G. Scatchard and S. S. Prentiss, *ibid.*, **65**, 4355 (1943).

[15] B. B. Owen, *ibid.*, **61**, 1393 (1939).

[16] T. Shedlovsky and A. S. Brown, *ibid.*, **56**, 1066 (1934).

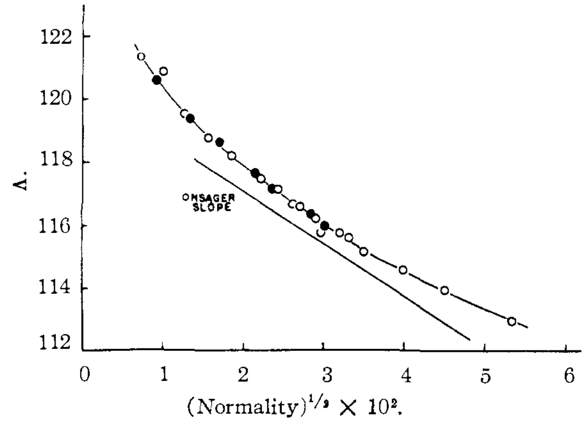

Fig. 2.—Conductance of $Zn(ClO_4)_2$: ○, cell 2; ●, cell 3.

from R_{400} by more than 0.3%, the cells were cleaned and re-platinized. The uncertainty of extrapolation is estimated as less than ±0.02%. Because of the curvature of the conductance function it is difficult to make an estimate of experimental error. An estimate of the precision of the data in dilute solutions is obtained from the standard deviation of the experimental points below 9×10^{-4} normal from the Owen function.[15] The standard deviation of fourteen experimental points involving three runs and two different cells is 0.02 Λ unit. The accuracy probably is limited by the analysis of the stock solution, four determinations giving a standard deviation from the mean of 0.10%. Unfortunately, lack of knowledge of the proper extrapolation function makes the uncertainty in Λ_0 much greater than this.

Table II

Conductance Cell Calibration Data

Run no.	KCl calibn. $N \times 10^4$	k
	Cell No. 2	
I	3.0325	0.25028
	5.2551	.25028
	7.6917	.25013
	9.8326	.24998
II	2.4124	.25031
	3.9681	.25017
	5.7619	.25026
	7.8759	.25023
	10.0597	.25007
111	1.8854	.25009
	3.9054	.24995
	6.4277	.24995
	Cell No. 3	
I	4.1094	1.0339
	6.8161	1.0365
	10.216	1.0357
	12.409	1.0356
	15.841	1.0341

BaCl₂ calibn. $N \times 10^4$	Λ (Shedlovsky)	Λ (This Lab.)
Cell No. 3		
3.3428	136.76	136.44
4.8282	136.06	136.06
6.2329	135.55	135.57
8.7246	134.72	134.63
10.8954	134.10	134.06

Table III

Conductance Data for $Zn(ClO_4)_2$

Run no.	10^4N	$10^2\sqrt{N}$	$\Lambda_{cor.}$	Λ_0'
1	20.566	4.535	113.98	121.79
$L_{H_2O} = 0.530 \times 10^{-6}$	29.123	5.397	112.92	122.21
2	1.0190	1.009	120.92	122.70
$L_{H_2O} = 0.641 \times 10^{-6}$	2.5296	1.590	118.82	121.60
	5.6920	2.386	117.17	121.29
	7.4784	2.735	116.61	121.35
	8.9795	2.997	115.77	120.96
	15.9383	3.992	114.59	121.48
3	0.5556	0.7454	121.40	122.72
$L_{H_2O} = 0.349 \times 10^{-6}$	1.6844	1.298	119.60	121.87
	3.5303	1.879	118.22	121.50
	5.0971	2.258	117.46	121.39
	6.9506	2.636	116.69	121.27
	8.6128	2.935	116.22	121.30
	10.505	3.241	115.78	121.39
	12.582	3.547	115.15	121.28
	16.309	4.038	114.59	121.56
5	0.86897	0.9322	120.55	122.20
$L_{H_2O} = 0.729 \times 10^{-6}$	1.8144	1.347	119.37	121.74
	2.9193	1.709	118.62	121.61
	4.6545	2.157	117.62	121.38
	5.8167	2.412	117.12	121.31
	8.0631	2.840	116.33	121.25
	9.3703	3.061	115.92	121.22
	10.9866	3.315	115.59	121.32

The extent of hydrolysis of zinc perchlorate was checked in two ways: (1) The pH of the stock solution and several dilutions were determined using a Beckman Model B pH meter. (2) These solutions acidified to pH 3 with perchloric acid, were titrated with sodium hydroxide and the equivalence pH was determined graphically. The two methods agreed to 0.05 pH unit indicating little or no free acid in the zinc perchlorate sample. The average value of the hydrolysis constant corrected for activity coefficients for the equilibrium

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+$$

was found to be $0.9 \pm 0.3 \times 10^{-9}$, but this is only approximate because of the irreversibility of the glass electrode and the uncertainty arising because of the chloride–perchlorate junction potential. Kolthoff and Kameda,[17] using a hydrogen electrode, obtained a value of 2.65×10^{-10} from measurements on zinc sulfate.

Discussion

Zinc Perchlorate.—As was previously mentioned, the conductance measurements on the zinc perchlorate system were undertaken to determine λ_0 for zinc ion so that this parameter could be used to calculate the theoretical conductance curve for zinc sulfate. The conductance of zinc perchlorate falls below the Onsager tangent at very low concentrations. This effect is shown in Fig. 3 by the pronounced minimum in the Λ_0' *vs.* $\sqrt{N}$ curve. If the system obeyed the Onsager equation Λ_0' would be constant. This marked deviation of the conductance of zinc perchlorate from the Onsager

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(17) I. M. Kolthoff and T. Kameda, This Journal, **53**, 832 (1931).

limiting tangent was unexpected in view of the normal behavior of alkaline earth and rare earth salts. While such deviations occur for many higher-charge electrolytes such as $K_4Fe(CN)_6$[15] and $Co(en)_3Cl_3$,[18] they had not been found previously for 2–1 electrolytes. A slight effect of this type was observed with Na_2SO_4 and K_2SO_4 by Jenkins and Monk,[19] who attributed this behavior to ion-pair formation. Recently a pronounced deviation of this type has been found for $K_2Pt(CN)_4$.[20] It appears, then, that this effect is not unique to the zinc perchlorate system. Nevertheless, one must be sure that the effect is a real one and not due to experimental error. Many runs with different cells, the behavior during calibration with KCl and a check run with $BaCl_2$ afford convincing evidence that the apparatus is not giving erroneous results. While analyses and *p*H studies indicate the absence of impurities in the stock, even if such impurities were present, they would only raise or lower the general value of Λ and could not produce the observed minimum in the Λ_0' curve.

The most obvious explanation for this type of behavior involves the assumption of ion-pair formation of the type $ZnClO_4^+$. It is not possible to make an exact calculation of the association constant for this system because of the lack of information on the "normal" behavior of unassociated 2–1 electrolytes and because the ion-pair has a net charge of +1 and so a residual mobility. In spite of these difficulties, by following the method of Davies[21] it should be possible to obtain a reasonable value for A, the association constant. Inspection of the Λ_0' curve (Fig. 3) shows that a value of Λ_0 of at least 123 conductance units is required for $Zn(ClO_4)_2$ which gives a value of 56 or greater for λ_0 of Zn^{++}. Using three points from the conductance curve at concentrations lower than that giving a minimum in the Λ_0' curve, and trial values of 56 and 59 conductance units for $\lambda^0_{Zn^{++}}$, with λ_0 for $ZnClO_4^+$ arbitrarily set at 45 Λ units, values of A were determined. The simple Onsager equation was assumed valid for the ionic species in solutions and corrections for activity coefficients were made. The results are completely unsatisfactory. Table IV gives the values of A obtained. This fivefold variation of A over a rather narrow concentration range shows that simple ion-pair formation is not responsible for the deviations observed. In addition to the wide variation in A, its magnitude is much too large for electrostatic ion-pair formation in 2–1 electrolyte systems. Changing the value of λ_0 for $ZnClO_4^+$ does not improve the situation.

TABLE IV

ASSOCIATION CONSTANTS CALCULATED FOR $Zn(ClO_4)_2$

$N \times 10^4$	$A \times 10^{-6}$ Using $\lambda^0_{Zn^{++}} = 56$	 Using $\lambda^0_{Zn^{++}} = 59$
1.00	19.7	18.2
2.56	8.45	6.12
7.36	3.69	3.33

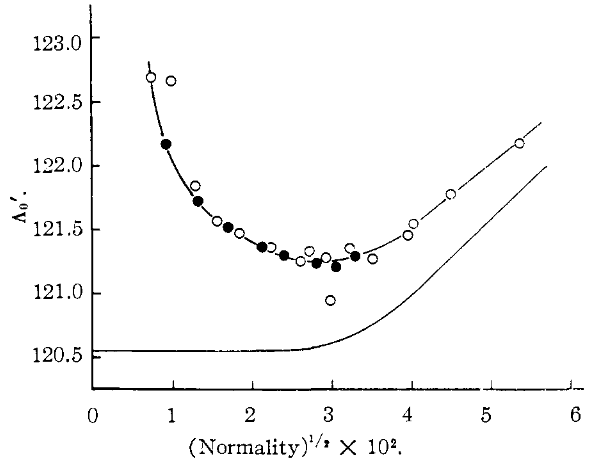

Fig. 3.—$\Lambda_0' = \Lambda + (\alpha\Lambda_0 + \beta)/\sqrt{N}$ plotted *vs.* $N^{1/2}$. Lower curve is obtained by using the adjustable "hydrolysis constant" = 1.1 × 10^{-8}; ○, cell 2; ●, cell 3.

The type of behavior observed here would be expected of a system undergoing *extensive* hydrolysis according to

$$Zn^{++} + H_2O \rightleftharpoons ZnOH^+ + H^+$$

However, all raw data already had been corrected for hydrolysis, using *p*H data on more concentrated solutions to evaluate the hydrolysis constant. It proved possible to calculate a "hydrolysis constant" which would "correct" the conductance data to bring them in accord with the Onsager equation at low concentrations. The "corrected" curve is shown as the bottom one in Fig. 3. This is not satisfactory, however, because the hydrolysis constant required to give this curve has a value of 1.1 ± 0.1 × 10^{-8} while that obtained by *p*H measurements averaged 0.094 × 10^{-8} and the value obtained by Kolthoff and Kameda was 0.0265 × 10^{-8}. This discrepancy in K values is very large and all but rules out hydrolysis as a cause of the deviations from the Onsager equation. Only if some mechanism were operating which greatly suppressed hydrolysis at higher concentrations, could these results be compatible. If the explanation involved a highly hydrolyzable impurity, this too would have to give pronounced *p*H effects in the higher concentration region.

Another possible explanation for these deviations from the simple theory is the inadequacy of present theory to deal with unsymmetrical electrolytes. Perhaps higher terms in the electrophoretic and relaxation equations would account for this behavior. However, in view of the range of ion sizes represented by the alkaline earth ions, which show no anomaly of this sort, it seems unlikely that this is the explanation.

We are forced to conclude that the anomalous conductance behavior of zinc perchlorate must be due either to an effect on the water structure or to the covalent-bonding tendencies of the zinc ion, although the effect of higher terms in the conductance equation cannot be ruled out completely. The result is that we have no theoretical extrapolation function to use to evaluate Λ_0. It is possible to make use of the empirical function of Owen[15] to fit the data below the minimum. This

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(18) I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, 68 (1951).

(19) I. L. Jenkins and C. B. Monk, THIS JOURNAL, **72**, 2695 (1950).

(20) K. O. Groves, J. L. Dye, and C. H. Brubaker, Jr., to be published.

(21) C. W. Davies, *Trans. Faraday Soc.*, **23**, 351 (1927).

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 $\lambda^0_{\mathrm{Zn}^{++}}$ 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 $\lambda^0_{\mathrm{Zn}^{++}}$ 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 $\lambda^0_{\mathrm{Zn}^{++}}$ 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	Λ_0 = 131.5	$\mathring{a}$ = 6.0	
	A = 55.0	$\mathring{a}$ = 4.3	A = 95.0	
	$\mathring{a}$ = 3.6			

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

RECEIVED MAY 19, 1959

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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