mean distance of closest approach for $RE_2(SO_4)_3$ and about 3.6 Å. for the mean distance of closest approach for $(RE\ SO_4)_2SO_4$. The ratio of the activity coefficients used is not very sensitive to the choice of the mean distance of closest approach. The values used here were just assumed as reasonable values. Calculations of the ratio from the simple limiting law gave nearly the same values at the concentrations used. Since C is known, K may be calculated if X can be determined.

X may be calculated from the conductance data by applying the Onsager equation for equivalent conductance in the form

$$\lambda_j = \lambda_j^0 - [0.5502(1 - H^{1/2})_{j\sigma}r_\sigma Z_j\lambda_j^0 + 21.17|Z_j|]\Gamma^{1/2}$$

in which the function $(1 - H^{1/2})_{j\sigma}r_\sigma$ is a result of the solution of the time of relaxation effect and is fully described by Onsager and Fuoss.[10] Γ is the ional concentration which is equal to $\sum_i C_iZ^2_i = (30C - 12X)$.

From the definition of the ionic specific conductance

$$l_i = \frac{\lambda_iC_i}{1000}$$

and

$$\sum_i l_i = L = \sum_i \frac{\lambda_iC_i}{1000}$$

one may write the equation for the specific conductance in the form

$$1000L = (\lambda^0_1 - b_1\Gamma^{1/2})(2C - X)^3 + (\lambda^0_2 - b_2\Gamma^{1/2})X + (\lambda^0_3 - b_3\Gamma^{1/2})(3C - X)^2$$

in which λ^0_1 is the rare earth ion equivalent conductance at infinite dilution, λ^0_2 is that for the complex and λ^0_3 is that for the sulfate ion. The b_i's are the interaction terms, in brackets, calculated from the Onsager equation as given above. The value of X can be obtained from the above relation by successive approximations using the experimental L and C and the calculated constants λ^0_i and b_i. The value of λ^0_2 is not known and was, therefore, assumed to be about 40 conductance units, in agreement with the value assumed by Davies.[11] Calculations show that the ionization constant is only affected very slightly by large changes in the value of λ^0_2 assumed.

The ionization constants listed in Table III are a result of extrapolating the calculated constants to infinite dilution as a function of $\Gamma^{1/2}$. Because of the assumptions used in their calculation, these values are probably in error as much as $\pm 0.25 \times 10^{-4}$. Recently, Jenkins and Monk[12] reported a value of 2.4×10^{-4}. Recently, Jenkins and Monk[12] reported a value of 2.4×10^{-4} for the ionization constant of $LaSO_4^+$ while Davies[11] reported 2.8×10^{-4}. Although these constants were calculated by different methods, they are in good agreement with those reported here.

TABLE III

IONIZATION CONSTANTS OF SOME RARE EARTH SULFATE COMPLEXES

Complex	$K \times 10^4$	Complex	$K \times 10^4$
$LaSO_4^+$	2.4	$GdSO_4^+$	2.2
$CeSO_4^+$	2.6	$HoSO_4^+$	2.6
$PrSO_4^+$	2.4	$ErSO_4^+$	2.6
$NdSO_4^+$	2.3	$YbSO_4^+$	2.6
$SmSO_4^+$	2.2	YSO_4^+	3.4

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[10] L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

[11] C. W. Davies, *Endeavour*, **4**, 114 (1945).

[12] I. L. Jenkins and C. B. Monk, THIS JOURNAL, **72**, 2696 (1950).

[CONTRIBUTION NO. 277 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

Conductances, Transference Numbers and Activity Coefficients of Some Rare Earth Perchlorates and Nitrates at 25°

BY F. H. SPEDDING AND S. JAFFE

RECEIVED JULY 27, 1953

The equivalent conductances and cation transference numbers at 25° of aqueous solutions of $La(ClO_4)_3$, $Pr(ClO_4)_3$, $Nd(ClO_4)_3$, $Sm(ClO_4)_3$, $Gd(ClO_4)_3$, $Ho(ClO_4)_3$, $Er(ClO_4)_3$, $Yb(ClO_4)_3$, $La(NO_3)_3$, $Nd(NO_3)_3$, and $Gd(NO_3)_3$ have been determined up to 0.1 N. Also a method has been developed for approximating the mean distance of closest approach of the various ions in these solutions from conductance measurements. This method allows the calculation of activity coefficients from the Debye–Hückel law.

Introduction

This paper is the seventh in a series concerning the electrolytic behavior of aqueous solutions of rare earth compounds. The earlier papers[2-4] have presented data on the conductances, transference numbers and activity coefficients of several rare earth chlorides and bromides. This paper extends this investigation to the rare earth perchlorates and nitrates. As discussed in the first articles of this series,[2] such information should be of considerable value in the study of the various factors which enter into the modern theories of electrolytic behavior.

An extension of the electrophoretic correction in the Onsager equation for equivalent conductance has made the estimation of activity coefficients possible from the conductance data presented here.

Experimental

Except as specifically discussed below, the experimental procedures and apparatus were the same as those previously reported.[2-4] All measurements were made at 25 ± 0.02°. The rare earth oxides used in this research are from the

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2055 (1952); **74**, 2778 (1952).

[3] F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2781 (1952).

[4] F. H. Spedding and I. S. Yaffe, *ibid.*, **74**, 2781 (1952).

TABLE I

EQUIVALENT CONDUCTANCES OF SOME RARE EARTH PERCHLORATES AND NITRATES IN AQUEOUS SOLUTION AT 25°[a]

Normality	Equivalent conductances, mhos. cm.$^{-1}$										
	$La(ClO_4)_3$	$Pr(ClO_4)_3$	$Nd(ClO_4)_3$	$Sm(ClO_4)_3$	$Gd(ClO_4)_3$	$Ho(ClO_4)_3$	$Er(ClO_4)_3$	$Yb(ClO_4)_3$	$La(NO_3)_3$	$Nd(NO_3)_3$	$Gd(NO_3)_3$
0.0000	137.0	136.8	137.2	135.8	134.5	133.8	133.5	133.4	140.6	141.3	138.7
.0002	133.4	133.3	133.4	131.9	130.6	130.1	130.0	130.0	136.5	137.4	134.9
.0004	131.9	131.8	131.8	130.4	129.0	128.6	128.5	128.5	134.9	135.7	133.3
.0007	130.3	130.2	130.1	128.8	127.5	127.0	126.9	126.9	133.1	133.9	131.6
.0010	129.1	129.0	128.9	127.7	126.4	125.8	125.7	125.6	131.7	132.6	130.3
.0020	126.3	126.1	125.8	124.8	123.6	122.9	122.8	122.7	128.3	129.0	126.9
.0040	122.3	122.1	121.7	120.9	119.7	119.1	119.0	118.9	123.9	124.2	122.5
.0070	118.3	118.5	118.0	117.1	116.1	115.5	115.3	115.3	119.5	119.5	117.9
.0100	115.8	115.8	115.5	114.5	113.4	113.0	112.9	112.8	116.3	116.0	114.5
.0200	110.2	110.2	110.0	109.2	108.1	107.6	107.5	107.4	109.4	108.8	107.5
.0400	104.3	104.4	104.1	103.5	102.2	101.8	101.7	101.6	102.1	100.7	99.9
.0700	99.7	99.7	99.5	98.7	97.6	97.3	97.2	97.1	96.0	94.2	93.5
.1000	96.8	96.7	96.5	95.8	94.9	94.4	94.3	94.2	92.0	90.0	89.4

[a] The data presented here are smoothed values. Anyone desiring the exact data may obtain them from the authors on request.

same source and have the same analysis as those used in the previous papers.[2-4]

The rare earth salt solutions were prepared by dissolving the rare earth oxides in the proper acid. Doubly vacuum distilled perchloric acid and chemically pure nitric acid were used for this purpose. An excess of rare earth oxide was filtered off after the acid had completely reacted. However, the solutions still contained small amounts of rare earth hydrous oxides which were present in colloidal form. For this reason, the solutions were titrated to the equivalence points which were previously determined by *p*H titrations on aliquots of the solutions. Although these solutions hydrolyze slightly, the effect of the excess hydrogen ions was within the experimental error in the measurements presented here.

Stock solutions of each rare earth salt were analyzed by precipitating rare earth oxalate, igniting this for 12 hours at 900° and weighing as rare earth oxide. The rest of the solutions were prepared from the stock solutions by volume dilutions using calibrated glassware and conductance water with a specific conductance of less than 1×10^{-6} mho-cm.$^{-1}$.

Results

A. Conductances.—The equivalent conductances of the rare earth salts are given in Table I. The conductances of the rare earth perchlorates generally show the same changes with atomic number as is observed with the halides. The decrease in conductance with an increase in atomic number is attributed to the effective increase in ionic radii due to hydration, in spite of the decreasing ionic radii as determined from crystallographic measurements.

The equivalent conductances at infinite dilution were obtained by extrapolation of the Onsager equation. The equivalent conductance at infinite dilution of the perchlorate ion was taken to be 67.32 as determined by Jones[5] and that of the nitrate ion has the value of 71.44 from the work by MacInnes, Shedlovsky and Longsworth.[6] The equivalent conductances at infinite dilution of the rare earth ions calculated from the above were in reasonable agreement with those calculated from other salts in earlier work.

The values of Λ_0' were calculated from the experimental points by the method of Shedlovsky.[7] The extrapolation to infinite dilution of the Λ_0' values as a function of the square root of the normality may be used as an indication of the applicability of the Onsager limiting law since the theory is being followed when the slope of the curve is zero. The rare earth perchlorates are apparently beginning to obey the simple limiting law only at around 0.0003 *N* while the nitrates seem to obey the theory out at 0.001 *N*. It will be shown that the agreement with the theory can be extended to almost 0.01 *N* solutions by the application of a graphical integration of the electrophoretic term of the Onsager equation.

B. Transference Numbers.—The transference numbers of the rare earth perchlorates and nitrates were found to be linear functions of the square root of the normality. The least squares equations and the average deviations of the experimental points from these equations appear in Table II. These data are represented in Figs. 1 and 2.

TABLE II

TRANSFERENCE NUMBER EQUATIONS FOR SOME RARE EARTH PERCHLORATES AND NITRATES AT 25°

Salt	Least-squares eq., $T^+ =$	Average deviation
$La(ClO_4)_3$	$0.5038-0.101\ N^{1/2}$	0.0002
$Pr(ClO_4)_3$	$.5067-\ .102\ N^{1/2}$	.0004
$Nd(ClO_4)_3$	$.5067-\ .0931\ N^{1/2}$	.0002
$Sm\ (ClO_4)_3$	$.5072-\ .102\ N^{1/2}$	.0002
$Gd(ClO_4)_3$	$.501\ -\ .100\ N^{1/2}$	.0002
$Ho(ClO_4)_3$	$.4909-\ .0924\ N^{1/2}$	.0003
$Er(ClO_4)_3$	$.4947-\ .112\ N^{1/2}$	.0005
$Yb(ClO_4)_3$	$.4930-\ .111\ N^{1/2}$	.0005
$La(NO_3)_3$	$.4895-\ .0597\ N^{1/2}$	.0002
$Nb(NO_3)_3$	$.4922-\ .0698\ N^{1/2}$	.0003
$Gd(NO_3)_3$	$.4857-\ .0746\ N^{1/2}$	.0005

The solvent corrections on the transference numbers were made in the usual way using the conductance data presented in Table I. However, since lithium chloride was used as indicator solution, the volume correction was modified slightly to include the partial molal volume changes between the lithium chloride and lithium perchlorate and nitrate solutions. These corrections were made as

$$\bar{V}_{RE(ClO_4)_3} = -\frac{\bar{V}_{Cd}}{2} + \frac{\bar{V}_{CdCl_2}}{2} + \bar{V}_{ClO_4^-} - \bar{V}_{Cl^-} - \frac{T_+}{3}\bar{V}_{RE(ClO_4)_3}$$

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(5) J. H. Jones, THIS JOURNAL, **67**, 855 (1945).

(6) D. A. MacInnes, T. Shedlovsky and L. G. Longsworth, *ibid.*, **54**, 2758 (1932).

(7) T. Shedlovsky, *ibid.*, **54**, 1405 (1932).

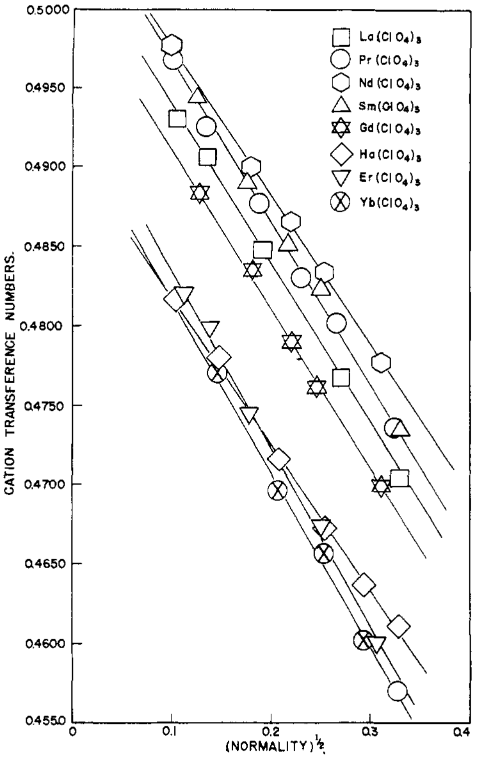

Fig. 1.—Transference numbers of some rare earth perchlorates at 25°.

and

$$\bar{V}_{\mathrm{RE(NO_3)_3}} = -\frac{\bar{V}_{\mathrm{Cd}}}{2} + \frac{\bar{V}_{\mathrm{CdCl_2}}}{2} + \bar{V}_{\mathrm{NO_3^-}} - \bar{V}_{\mathrm{Cl^-}} - \frac{T_+}{3}\,\bar{V}_{\mathrm{RE(NO_3)_3}}$$

in which

$$\bar{V}_{\mathrm{ClO_4^-}} - \bar{V}_{\mathrm{Cl^-}} \cong \bar{V}_{\mathrm{LiClO_4}} - \bar{V}_{\mathrm{LiCl}} = 26.48$$

and

$$\bar{V}_{\mathrm{NO_3^-}} - \bar{V}_{\mathrm{Cl^-}} \cong \bar{V}_{\mathrm{LiNO_3}} - \bar{V}_{\mathrm{LiCl}} = 10.86$$

The densities used in employing these corrections are listed in Table III.

TABLE III

DENSITIES OF AQUEOUS SOLUTIONS OF RARE EARTH PERCHLORATES AND NITRATES AT 25°[a]

Salt	Density	Salt	Density
La(ClO$_4$)$_3$	0.9970 + 0.334C_m	Yb(ClO$_4$)$_3$	0.9970 +0.383C_m
Pr(ClO$_4$)$_3$	.9969 + .358C_m	La(NO$_3$)$_3$	.9970 + .274C_m
Nd(ClO$_4$)$_3$	.9971 + .347C_m	Nd(NO$_3$)$_3$	.9971 + .279C_m
Sm(ClO$_4$)$_3$	.9968 + .364C_m	Gd(NO$_3$)$_3$	.9970 + .289C_m
Gd(ClO$_4$)$_3$	.9970 + .372C_m	LiClO$_4$	.9971 + .0623C_m
Ho(ClO$_4$)$_3$	.9970 + .369C_m	LiNO$_3$	.9971 + .0398C_m
Er(ClO$_4$)$_3$	.9970 + .382C_m	LiCl	.9971 + .0241C_m

[a] The data for LiClO$_4$ was obtained from work by Jones[7] and the data for LiCl and LiNO$_3$ were calculated from data given in Harned and Owen's text.[8] Other relations were obtained from measurements of densities over the range from 0.001 to 0.1 N with a 50-ml. pycnometer. C_m is the molar concentration and m is the molal concentration.

The cation transference numbers of the rare earth perchlorates are in relatively the same order as those of the halides.[2,4] The transference

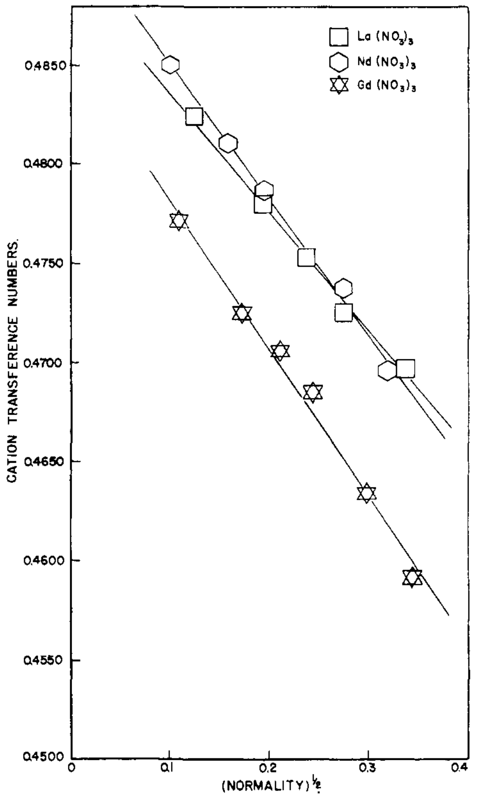

Fig. 2.—Transference numbers of some rare earth nitrates at 25°.

numbers are consistent with the conductance data except for samarium which has transference numbers about equal to those of praseodymium while the conductances are lower than praseodymium. This behavior also was observed in the case of the chlorides.[2] Since only three nitrates have been measured so far, a discussion of their behavior will be reserved until the series is more nearly complete.

The transference numbers of the rare earth perchlorates and nitrates do not approach the Onsager limiting slopes in the range of concentrations measured. However, the agreement between experiment and theory is greatly improved when the electrophoretic term in the Onsager equation is evaluated according to Dye and Spedding.[9]

Calculation of Activity Coefficients

A. Introduction.—The Debye–Hückel limiting law for activity coefficients may be used to calculate the mean activity coefficients of strong electrolytes in moderately dilute solutions. It has been shown[3,4] that the activity coefficients of rare earth halides thus calculated agree remarkably well with those obtained experimentally from e.m.f. measurements. It may be assumed, therefore, that the rare earth perchlorates and nitrates obey the same theory at the same concentrations.

However, in order to evaluate the activity coefficients from the equation

$$\log \gamma_{\pm} = -\frac{A\sqrt{C_m}}{1 + B\mathring{a}\sqrt{C_m}} - \log\,(1 + 0.001m\nu M_1)$$

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[8] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., Inc., New York, N. Y., 1950, p. 556.

[9] J. L. Dye and F. H. Spedding, THIS JOURNAL, **76**, 888 (1954).

the mean distance of closest approach for the solutes must be known. The distances of closest approach have not been evaluated previously for the rare earth perchlorates and nitrates.

The mean distance of closest approach may be evaluated from the conductance data by a consideration of the dependence on $\mathring{a}$ of the electrophoretic term in the Onsager equation for conductance. Dye and Spedding[9] have shown that the electrophoretic correction for 3–1 electrolytes may be expressed by the relations

$$\Delta\lambda_+ = M\int_{\kappa a}^{\infty} \rho\left[e^{-9P}\frac{e^{-\rho}}{\rho} - e^{3P}\frac{e^{-\rho}}{\rho}\right] \mathrm{d}\rho$$

and

$$\Delta\lambda_- = M\int_{\kappa a}^{\infty} \rho\left[e^{-P}\frac{e^{-\rho}}{\rho} - e^{3P}\frac{e^{-\rho}}{\rho}\right] \mathrm{d}\rho$$

in which

$$M = \frac{FDkT}{1800\pi\eta\epsilon(|z_+| + |z_-|)} = 3.209$$

$$P = \frac{\kappa e^{\kappa a}\epsilon^2}{DkT(1 + \kappa a)} = 7.135 \times 10^{-8}\frac{\kappa e^{\kappa a}}{1 + \kappa a}$$

and $\rho = \kappa r$.

The values of the integrands may be plotted as functions of κr and the integrals may then be evaluated from the areas under the curves. The change in the conductance due to the electrophoretic effect is quite sensitive to the a value used, since this is the lower limit of the integration and the curve rises rapidly for small values of a.

The procedure is to assume a series of a values for the perchlorates and nitrates and calculate the electrophoretic correction for each a at various concentrations. These values are included in the Onsager equation for equivalent conductance and an extrapolation to infinite dilution of the calculated Λ_0' values as a function of $C^{1/2}$ is made. When the proper a value is used, the curve remains flat from infinite dilution to about 0.008 N. If the a value is too small, the curve rises from the flat portion at very low concentrations, and if the a value is too large, the curve dips below the true Λ_0 value. Figure 3 is an example of the evaluation of a for $Nd(NO_3)_3$ by the method described above. It can be seen that a reasonable a value can be obtained when the best extrapolation curve is found.

TABLE IV

ELECTROPHORETIC CORRECTIONS ON CONDUCTANCE AT VARIOUS $\mathring{a}$ VALUES FOR 3–1 ELECTROLYTES IN AQUEOUS SOLUTION AT 25°

$\mathring{a}$ in Å.	At 0.0100 N	At 0.0035 N	At 0.0010 N
3.0	28.34	15.60	7.15
4.0	16.90	10.66	5.57
5.0	14.20	9.04	5.07
5.49	13.62	8.64	4.87
5.92	13.01	8.35	4.77
6.5	12.30	8.00	4.65
7.0	11.95	7.75	4.61
7.5	11.50	7.25	4.50

TABLE V

MEAN DISTANCE OF CLOSEST APPROACH FROM EXTRAPOLATION OF CONDUCTANCE DATA

Salt	$\mathring{a}$ in Å.	Salt	$\mathring{a}$ in Å.
$La(ClO_4)_3$	7.0	$Er(ClO_4)_3$	6.8
$Pr(ClO_4)_3$	7.2	$Yb(ClO_4)_3$	7.2
$Nd(ClO_4)_3$	6.0	$La(NO_3)_3$	4.4
$Sm(ClO_4)_3$	6.8	$Nd(NO_3)_3$	4.5
$Gd(ClO_4)_3$	6.4	$Gd(NO_3)_3$	4.4
$Ho(ClO_4)_3$	6.3		

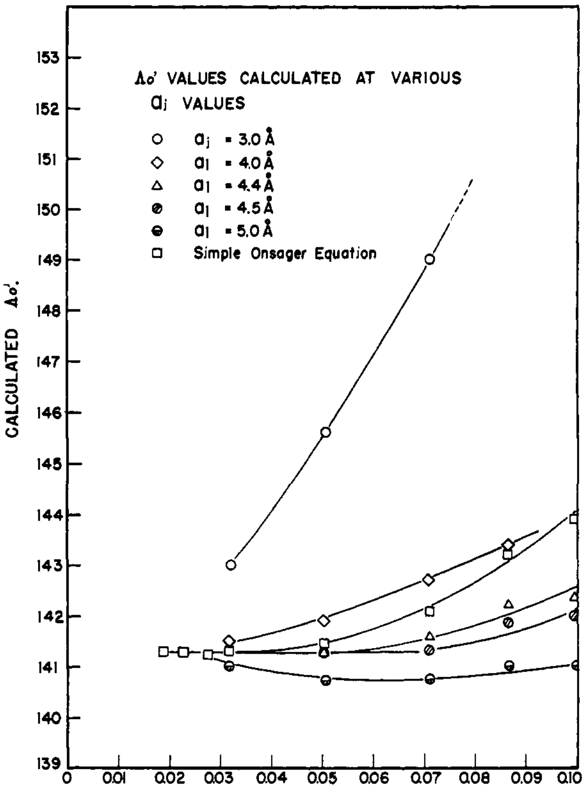

Fig. 3.—Evaluation of the mean distance of closest approach from conductance data on neodymium nitrate.

B. Results.—The changes in the equivalent conductances due to the electrophoretic effect were calculated for several $\mathring{a}$ values at several concentrations by the graphical method described above. Table IV lists a convenient selection of these values. A series of curves were plotted from these data to obtain interpolated values of the corrections at intermediate $\mathring{a}$'s and concentrations. The $\mathring{a}$ values that were obtained for the rare earth perchlorates and nitrates are listed in Table V.

The average $\mathring{a}$ value for the rare earth chlorides is about 5.7 Å.[5] This value supports the physical picture that a monomolecular layer of water surrounds the rare earth cation. This picture seems to hold for the perchlorates as well, since the perchlorate ion radius is about 1 Å. larger than that of the chloride and the expected $\mathring{a}$ value is about 6.7 Å. This is in remarkable agreement with the values found by the conductance method. The value of $\mathring{a}$ for the nitrates may also be made to fit this picture if one considers that the effective radius of the nitrate ion in this case is about 1 Å. Since the rare earth ion is about 1 Å. in radius and the water molecule is about 2.8 Å. in diameter, the value of 4.5 Å. for the rare earth nitrates seems reasonable.

From these data, it is, of course, impossible to say how far the Debye–Hückel limiting law involving perchlorates and nitrates will hold for activity coefficients. However, in light of the fact that a constant value of $\mathring{a}$ results in agreement of experiment and theory for the chlorides and bromides up to 0.1 N, it is reasonable to assume that the limiting law would hold equally well for the perchlorates and nitrates.

AMES, IOWA

[CONTRIBUTION NO. 279 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

The Application of Onsager's Theory of Conductance to the Conductances and Transference Numbers of Unsymmetrical Electrolytes

BY J. L. DYE AND F. H. SPEDDING

RECEIVED JULY 27, 1953

Consideration of the transference number behavior of unsymmetrical electrolytes in aqueous solution led to an examination of the mathematical development of Onsager's theory of conductance. A mathematical treatment of Onsager's theory of conductance is described, which employs graphical methods to evaluate integrals which were only approximately evaluated by Onsager. The approximate methods, while satisfactory for 1–1 electrolytes, are unable to explain the transference number behavior of unsymmetrical electrolytes. The new treatment of the theory was applied to the conductances and transference numbers of $CaCl_2$, $NdCl_3$ and $ErCl_3$. The agreement between theory and experiment was greatly improved for both transference numbers and conductances of these unsymmetrical electrolytes.

Introduction

In a theoretical study of the processes of diffusion and electrical conduction in electrolytic solutions, Onsager[2] developed equations which quantitatively describe the changes in conductance with concentration in sufficiently dilute solutions. Because the theory was developed for the individual ionic species in the solution, the results were also applicable to the transference numbers of the constituent ions. The theory predicted the transference number to be a linear function of the square root of the concentration in dilute solutions. This has actually been found to be the case for most electrolytes, and the slope of the resultant straight line agrees quite well with the predicted slope for 1–1 electrolytes. It has been pointed out, however,[3–5] that unsymmetrical electrolytes for which the transference numbers have been measured exhibit slopes which differ by as much as a factor of one-fifth from the slope predicted by the Onsager equation.

Because of this dependence upon charge type, it was deemed advisable to re-examine the mathematical development of the conductance equation. The change in the conductance of an electrolytic solution with concentration may be said to be due to two factors, which are called the "time of relaxation effect" and the "electrophoretic effect." The electrophoretic effect normally makes the larger contribution to the conductance. If the fundamental assumptions of Onsager's treatment of conductance are assumed to be correct, it can be shown that for ions of high charge an exponential expansion and subsequent neglect of high order terms in the usual treatment of the electrophoretic effect, is invalid even at quite low concentrations. In attempting to include the complete integral, however, the equation could not be put into an analytical form, and certain integrals were evaluated graphically. The results are compared with experimental values of the transference numbers and conductances.

Development of the Method

From the treatment of the electrophoretic effect upon conductance given by Onsager[2] one may obtain the electrophoretic correction to the conductance to be

$$|\Delta\lambda_j| = \frac{96{,}500}{450\eta}\int_{a_j}^{\infty} r\left[\sum_{i=1}^{s}(n_{ji} - n_i)\right]\mathrm{d}r \qquad (1)$$

in which n_{ji} is the concentration of the ith kind of ion at a distance r from any j ion and is given by the Boltzmann distribution to be approximately

$$n_{ji} = n_i \exp\left[-\frac{e_i\psi_j^0}{kT}\right] \qquad (2)$$

in which ψ_j^0 is the electrostatic potential at a distance r from the jth ion and was found by Debye and Hückel to be

$$\psi_j^0 = \left[\frac{e_j e^{\mathrm{K}a_j}}{D(1 + \mathrm{K}a_j)}\right]\left[\frac{e^{-\mathrm{K}r}}{r}\right] \qquad (3)$$

The quantities in these equations are defined by

η is the viscosity of the solvent
e_i is the charge on the ith ion and includes the sign of the charge on the ion
k is the Boltzmann constant
D is the dielectric constant of the solvent
a_j is the mean distance of closest approach of the ions to the j ion

$$\mathrm{K}^2 = \frac{4\pi\epsilon^2}{DkT}\sum_{j=1}^{s} n_i Z_i^2 \qquad (4)$$

s is the total number of kinds of ions in the solution, and
ϵ is the charge on the electron

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) (a) L. Onsager, *Physik. Z.*, **28**, 277 (1927); (b) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(3) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publ. Corp., New York, N. Y., 1950, p. 165.

(4) L. G. Longsworth and D. A. MacInnes, THIS JOURNAL, **60**, 3070 (1938).

(5) F. H. Spedding, P. E. Porter and J. M. Wright, *ibid.*, **74**, 2778 (1952).