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Conductances, Transference Numbers and Activity Coefficients of Aqueous Solutions of Some Rare Earth Chlorides at 25°

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The equivalent conductances, cation transference numbers and activity coefficients at 25° of aqueous solutions of $DyCl_3$, $HoCl_3$ and $TmCl_3$ have been determined for concentrations up to 0.1 *N*. Since the rare earth elements undergo a slight amount of hydrolysis, which becomes more evident for the heavier members of this series, the measurements were made on solutions at the equivalence *p*H. The equivalence *p*H was determined by acid titration of the solutions. To determine whether the hydrolysis has a measurable effect upon the properties, the measurements were repeated for solutions of $NdCl_3$, $ErCl_3$ and $YbCl_3$ at the equivalence *p*H. The slight deviation from equivalence shown by solutions which were prepared by dissolving the anhydrous chloride, as prepared, in water in a closed system, was found to have a negligible effect upon the properties of solutions of the light rare earth chlorides, but exceeded the experimental error by a small amount for the heavier rare earth chlorides.

Introduction

This paper is the fifth 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 some rare earth chlorides and bromides.

This paper extends this investigation to include three more chlorides and to determine the effect of hydrolysis on these properties. As discussed in the first article of this series, such information should be of considerable value in the study of the various factors which enter into the modern theories of electrolytic behavior.

Experimental

Except as discussed below, the experimental procedures and apparatus were the same as those previously reported.[2-4]

The samples of Nd_2O_3, Ho_2O_3 and Yb_2O_3 used for this work had the same analyses as those previously reported. The purities of the other rare earth oxides used were: Dy_2O_3: $\sim$ 0.02% Y_2O_3, 0.1% Ho_2O_3, 0.05% Er_2O_3, trace of CaO; Er_2O_3: $\sim$0.1% Ho_2O_3, 0.05% Y_2O_3, 0.02% Tm_2O_3, $<$ 0.01% Yb_2O_3, trace of CaO; Tm_2O_3: $\sim$ 0.025% Yb_2O_3, $<$ 0.025% Y_2O_3, $<$ 0.025% Er_2O_3, trace of CaO. All analyses were made by spectrographic methods and all oxides were further purified by a minimum of two oxalate precipitations from acid solution.

The rare earth chloride solutions were prepared in either of two ways. (1) The oxide was dissolved with heating in an insufficient quantity of HCl, the excess oxide being filtered off. This gave solutions with *p*H values around 6.0 which contained a small amount of colloidal oxide or basic salt, as shown by the Tyndall cone the solution exhibited when examined with a beam of light, and also by the subsequent titration. (2) The rare earth oxide was completely dissolved in a slight excess of HCl and evaporated to wet crystals several times. This resulted in a solution whose *p*H value was only slightly on the basic side of the equivalence *p*H and which contained very little colloidal material.

After preparation by either method, the solution was diluted; a sample was withdrawn and titrated with dilute hydrochloric acid to determine the equivalence *p*H value. The bulk of the solution was then brought to this *p*H value with hydrochloric acid. This stock solution was analyzed for both chloride and rare earth using gravimetric methods. The chloride was weighed as silver chloride and the rare earth as the oxide following precipitation as the oxalate. The chloride and rare earth analyses agreed in all cases to at least 0.1%. Using calibrated glassware, dilutions were made from these stock solutions to obtain solutions of the desired concentrations. The dilutions were made with conductance water having a specific conductance of less than 1.0×10^{-6} mho. All measurements reported were made at 25 ± 0.02°.

Results

A. Hydrolysis.—Some of the earlier studies in this Laboratory were made with rare earth chloride solutions which were prepared by dissolving the anhydrous chlorides in water in a closed system.[2b-4] The resulting solutions were clear, and showed no visible evidence of hydrolysis, with *p*H values slightly greater than six for 0.1 *N* solutions. Because of the possibility of unsuspected hydrolysis, the solutions which had been made by dissolving the anhydrous chloride in water, were examined carefully, and were found to exhibit a slight Tyndall cone upon examination with a beam of light. This indicated that a small amount of colloid was present in the solutions previously used. The effect of this slight lack of equivalence was studied by repeating the experimental measurements on neodymium chloride, erbium chloride and ytterbium chloride. The new solutions were carefully brought to the equivalence *p*H, to eliminate the possibility of colloid formation.

The conductances and transference numbers obtained with neodymium chloride, erbium chloride and ytterbium chloride show that the data obtained from the previous measurements on rare earth chlorides were generally in agreement with those obtained at equivalence. However, the differences for the heavier rare earths exceeded the usual experimental error by a small amount. The values obtained for the conductances were slightly higher for solutions at the equivalence *p*H while the transference numbers were slightly lower than those for solutions containing a trace of colloidal material. The average differences in conductance were 0.10% for $NdCl_3$, 0.32% for $ErCl_3$ and 0.56% for $YbCl_3$. These percentages should be a fair measure of the amount of colloidal material which was formed in the solutions when they were made up by dissolving the anhydrous chloride in water, since the colloid is presumably non-conducting. The nature of the colloidal material, and the exact values of the hydrolysis constants await the procurement of more accurate hydrolysis data.

B. Conductances.—The following equation was used to calculate the specific conductance of the solution

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[1] Work was performed in the Ames Laboratory of the A.E.C.

[2] (a) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2055 (1952); (b) **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**, 4751 (1952).

$$L = k/R - L_{H_2O} - L_{H^+}$$

in which L is the specific conductance of the solution due only to the solute, k is the cell constant, R is the measured resistance, L_{H_2O} is the specific conductance of the water used in the preparation of the solutions, and L_{H^+} is the specific conductance of the hydrogen ion in the solution minus the specific conductance of the hydrogen ion in the water used to prepare the solutions. The specific conductance of the hydrogen ion in the solution and solvent is calculated from its approximate concentration as measured with a pH meter and its equivalent conductance as calculated by the Onsager equation.

The equivalent conductance of the six rare earth chlorides investigated are listed in Table I. For the extrapolation of conductance data to infinite dilution using the Onsager equation, λ^0_- for the chloride ion was taken as 76.34 mhos cm.$^{-1}$. Because the solutions were at pH values below 6, it was necessary to make a small correction for the conduction of current by the hydrogen ion.

The values of Λ_0' were calculated from the experimental points and the Onsager equation by the method of Shedlovsky.[5] The extrapolation curves for Λ_0' are illustrated in Fig. 1. The ordinates are staggered to separate the various curves. The values of λ^0_+ obtained agree well with previous measurements on other salts. The horizontal portion of each curve indicates the concentration range in which the Onsager law is obeyed; this is true up to approximately 0.0008 N for the salts measured. An extension of the mathematics of Onsager's treatment of conductance is described in another paper.[6] The experimental values agree with this extended treatment up to concentrations of 0.008 N for the rare earth chlorides.

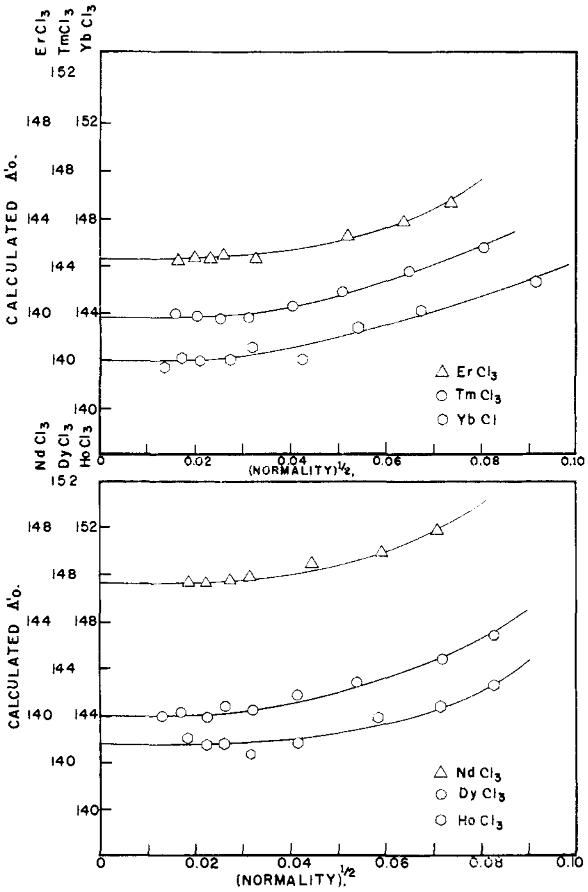

Fig. 1.—Extrapolation of conductance data to infinite dilution using the Onsager equation.

Table I

Equivalent Conductance of Aqueous Solutions of Some Rare Earth Chlorides at 25°[a]

Normality	Equivalent conductances, mhos cm.$^{-1}$					
	$NdCl_3$	$DyCl_3$	$HoCl_3$	$ErCl_3$	$TmCl_3$	$YbCl_3$
0.0000	145.7	142.0	142.6	142.3	141.8	142.0
.0002	141.7	138.1	138.7	138.3	137.9	138.1
.0004	140.1	136.5	137.1	136.8	136.4	136.6
.0007	138.3	134.7	135.4	135.1	134.7	135.0
.0010	137.0	133.4	134.0	133.8	133.3	133.7
.0020	133.8	130.3	130.7	130.5	130.0	130.5
.0040	129.3	136.1	126.4	126.3	126.0	122.1
.0100	122.1	119.2	119.3	119.1	119.0	119.1
.0200	115.5	113.0	113.1	113.0	112.8	113.0
.0400	108.5	106.3	106.4	106.3	105.9	106.1
.0700	102.9	100.7	100.8	100.6	100.4	100.5
.1000	99.3	97.1	96.8	96.6	96.1	96.4

[a] The data of this table are smoothed values. Anyone desiring the exact data for the experimental points may obtain them from the authors upon request.

C. Transference Numbers.—The cation transference numbers for $NdCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$ and $YbCl_3$ were determined by the moving boundary method and the data for each salt were found to be well represented by a linear function of the square root of the concentration. These data were subjected to a least squares analysis, and the equations so obtained are given in Table II. The slopes of the lines so obtained differ from those predicted by the Onsager theory by a factor of about one-fifth, but agree reasonably well with the predictions of the new treatment of Onsager's equation mentioned in the preceding section.[6] The

Table II

Summary of Data on Transference Numbers of Some Rare Earth Chlorides

Salt	Least-squares equation[a]	Average deviation
$NdCl_3$	$0.4776-0.120N^{1/2}$	0.0004
$DyCl_3$	$.4655- .120N^{1/2}$	.0003
$HoCl_3$	$.4613- .126N^{1/2}$	.0005
$ErCl_3$	$.4601- .125N^{1/2}$	.0003
$TmCl_3$	$.4604- .118N^{1/2}$	.0003
$YbCl_3$	$.4604- .125N^{1/2}$	.0004

[a] N = Normality.

Table III

Densities of Some Rare Earth Chlorides at 25°

Salt	Least-squares equation[a]
$NdCl_3$	$0.99707 + 0.236C$
$DyCl_3$	$.99699 + .252C$
$HoCl_3$	$.99695 + .259C$
$ErCl_3$	$.99711 + .264C$
$TmCl_3$	$.99703 + .260C$
$TbCl_3$	$.99709 + .265C$

[a] C = Molarity.

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[5] T. Shedlovsky, This Journal, **54**, 1405 (1932).

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

standard volume and solvent corrections were applied to the observed transference numbers to obtain the corrected values. The partial molar volumes of the rare earth chlorides required for the volume corrections were calculated from density measurements made with a 50-ml. pycnometer. The densities measured were linear functions of the concentration within experimental error. The equations for the densities are listed in Table III.

D. Activity Coefficients.—Concentration cells with transference of the type

$$\text{Ag, AgCl, DyCl}_3(m_1)\ \text{DyCl}_3(m_2)\text{, AgCl, Ag}$$

were used to determine the activity coefficients. The Ag, AgCl electrodes were prepared as described previously.[3] For the determination of the activity coefficients from the e.m.f. measurements, the transference numbers calculated from the equations listed in Table II were employed. To illustrate the consistency of the e.m.f. data, a typical plot of the straight line obtained with the extended Debye–Hückel equation, and the e.m.f. data, is shown for $DyCl_3$ in Fig. 2. The method of calculation has been described previously.[4] Table IV lists the experimentally determined $\mathring{a}$ values, and the average absolute difference between the experimentally determined coefficients and those calculated from the Debye–Hückel law using these $\mathring{a}$ values. Within experimental error, the experimentally determined activity coefficients obey the Debye–Hückel law.

TABLE IV

MEAN DISTANCES OF CLOSEST APPROACH FOR SOME RARE EARTH CHLORIDE SOLUTIONS AND THE AVERAGE DIFFERENCES BETWEEN CALCULATED AND OBSERVED ACTIVITY COEFFICIENTS

Salt	$\mathring{a}$	$\Delta\gamma_\pm$
$NdCl_3$	5.49	0.0011
$DyCl_3$	5.32	.0013
$HoCl_3$	6.04	.0023
$ErCl_3$	5.92	.0012
$TmCl_3$	5.81	.0010
$YbCl_3$	5.90	.0021

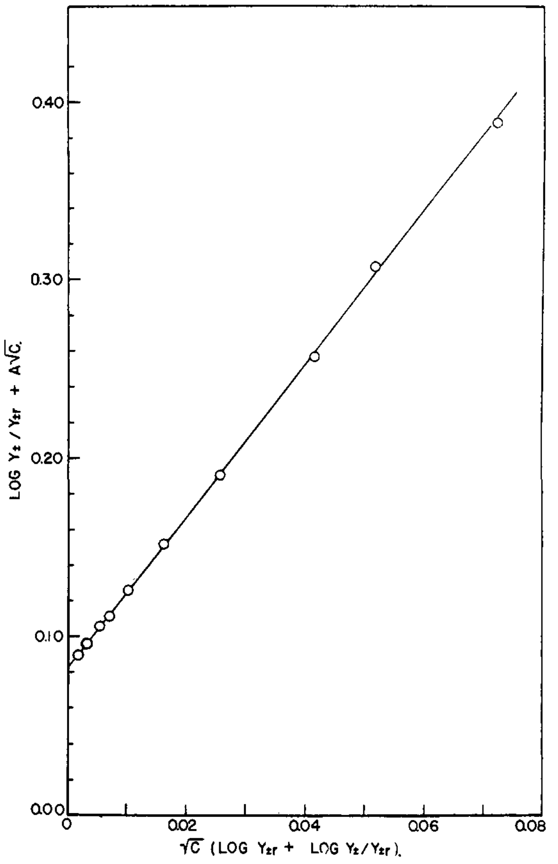

Fig. 2.—Extrapolation of e.m.f. data to infinite dilution using the extended Debye–Hückel equation.

Although the $\mathring{a}$ values for the high atomic number rare earth chlorides are generally larger than those for the low atomic weight members, there is no regular variation among these values. Unfortunately, the value of $\mathring{a}$ obtained is very sensitive to experimental errors and it is difficult to determine whether these variations are real. Before more definite conclusions can be made, these investigations should be extended and correlated with other physical measurements on the rare elements and their compounds.

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