[Contribution No. 276 from the Institute for Atomic Research and Department of Chemistry, Iowa State College[1]]

Conductances, Solubilities and Ionization Constants of Some Rare Earth Sulfates in Aqueous Solutions at 25°

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The equivalent conductances and solubilities of the sulfates of La, Ce, Pr, Nd, Sm, Gd, Ho, Er, Yb and Y were measured in aqueous solutions at 25°. The conductances are very much lower than is expected for strong electrolytes. The deficiency in conductance is attributed to the formation of complexes of the type MSO_4^+ in dilute solutions. The ionization constants for the dissociation of the complexes are calculated from the conductance data and the Onsager equation for equivalent conductance.

Introduction

This paper is the sixth in a series concerning the electrolytic behavior of aqueous solutions of rare earth compounds. The earlier papers[2-5] have presented data on the conductances, transference numbers and activity coefficients of several rare earth chlorides, bromides, perchlorates and nitrates. This paper extends this investigation to rare earth sulfates. As discussed in the first article of this series,[2b] such information should be of considerable value in the study of the various factors which enter into the modern theories of electrolytic behavior.

Experimental

The experimental procedures and apparatus were the same as those reported in the previous papers,[2a,4] except for the preparation of the salts. The rare earth oxides had the same analysis as previously reported. The Y_2O_3 had about 0.2% Dy_2O_3 and 0.02% Tb_4O_7 as detected by spectrographic analysis. All measurements were made at 25 ± 0.02°, and the conductance water had less than 1×10^{-6} mho cm.$^{-1}$ specific conductance.

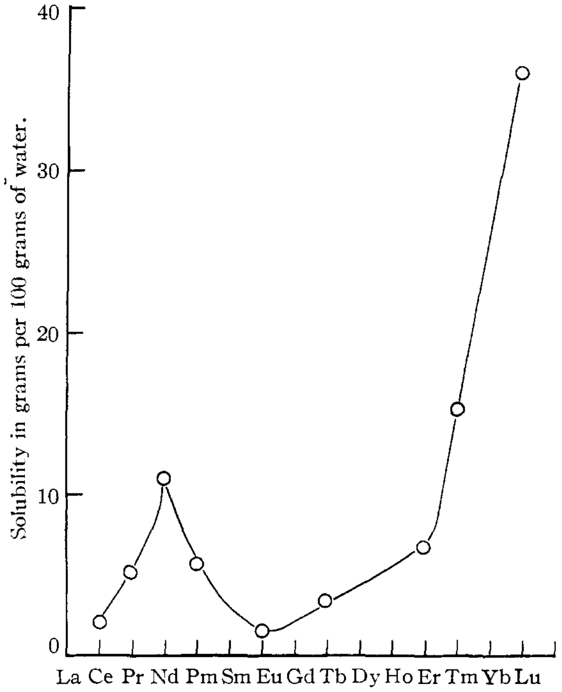

Fig. 1.—Solubilities of some rare earth sulfates at 25°.

The rare earth sulfate solutions were prepared by dissolving the pure rare earth oxides in a very slight excess of C.P. sulfuric acid. The excess acid was removed by precipitating the rare earth sulfate salts from pure absolute ethanol.[6] Further recrystallization from conductance water did not produce any measurable change in the *p*H of the solutions. The rare earth sulfates were then dried slowly and finally ignited at about 500° to remove any excess alcohol.

Saturated solutions of the rare earth sulfates were prepared by dissolving an excess of the salt in water at about 18 to 20°. Since the rare earth sulfates have a negative temperature coefficient, hydrated rare earth sulfate crystallized out of the clear solutions when they were warmed up to 25° in the thermostat. These solutions were allowed to reach equilibrium at 25° for at least 48 hours. The concentrations of the filtered solutions were determined by precipitating the rare earths with oxalic acid, igniting the oxalates at 900° and weighing them as rare earth oxides. The densities of the saturated solutions were measured with a 50-ml. pycnometer at 25° so that the solubilities of the rare earth sulfates could be reported in grams of rare earth sulfate per 100 g. of water.

Results

A. Solubilities.—The solubilities of the rare earth sulfates are listed in Table I and shown as a function of atomic numbers in Fig. 1. This anomalous behavior previously has been observed for the solubility of the octahydrates at 20 and 40°.[7] There is not yet enough evidence to ascribe a definite reason for this behavior. It may be due to a combination of factors such as changes in crystal structure[8,9] with increase in atomic number, changes in hydration and perhaps differences in the various rare earth complexes present in saturated solutions. Data on the heats of solution of the rare earth sulfates should prove very valuable in providing some of the answers to their solubility behavior.

Table I

Solubilities of Some Rare Earth Sulfates in Water at 25°

Salt	Solubility in g. per 100 g. of water	Salt	Solubility in g. per 100 g. of water
$La_2(SO_4)_3$	2.142	$Gd_2(SO_4)_3$	3.299
$Ce_2(SO_4)_3$	5.063	$Ho_2(SO_4)_3$	6.705
$Pr_2(SO_4)_3$	10.88	$Er_2(SO_4)_3$	15.19
$Nd_2(SO_4)_3$	5.591	$Yb_2(SO_4)_3$	36.01
$Sm_2(SO_4)_3$	1.488	$Y_2(SO_4)_3$	9.673

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

[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).

[5] F. H. Spedding and S. Jaffe, *ibid.*, **76**, 884 (1954).

[6] T. Moeller, *J. Phys. Chem.*, **50**, 242 (1946).

[7] K. S. Jackson and G. Rienäcker, *J. Chem. Soc.*, 1687 (1930).

[8] S. Singh, *Z. Krist.*, **105**, 384 (1944).

[9] V. I. Iveronova, V. P. Tarasova and M. M. Umanskii, *Izvest. Akad. Nauk S.S.S.R., Ser. Fiz.*, **15**, 164 (1951).

TABLE II

EQUIVALENT CONDUCTANCES IN MHOS CM.$^{-1}$ OF SOME RARE EARTH SULFATES IN AQUEOUS SOLUTION AT 25°

Normality	$La_2(SO_4)_3$	Normality	$Ce_2(SO_4)_3$	Normality	$Pr_2(SO_4)_3$	Normality	$Nd_2(SO_4)_3$	Normality	Sm_2-$(SO_4)_3$
0.1021	25.20	0.5302	16.17	1.1477	12.81	0.4807	16.85	0.2575	19.39
.08164	26.77	.2121	20.51	0.5739	15.84	.3845	17.77	.1288	23.22
.06123	28.91	.1060	24.59	.1148	24.18	.2884	19.16	.07725	26.52
.04082	32.21	.07953	26.65	.08608	26.05	.1923	21.29	.05150	29.59
.02041	38.66	.05302	29.63	.05739	29.12	.09613	25.50	.03863	31.91
.01021	46.25	.02651	35.90	.02869	35.05	.07210	27.53	.02575	35.47
.005103	55.49	.01060	45.84	.01148	44.50	.04807	30.66	.01288	42.42
.002551	66.38	.007953	49.21	.008608	47.87	.03605	33.08	.006438	50.83
.0005103	99.60	.005302	54.60	.005739	53.24	.02403	36.82	.003863	58.08
.0002551	113.7	.002651	65.67	.002869	64.27	01202	44.07	.002575	64.79
.0000	149.5	.001060	85.49	.001148	81.13	.007210	50.16	.001288	77.52
		.0007953	89.05	.0008608	86.67	.004807	55.87	.0006438	91.89
		.0005302	100.1	.0005739	95.14	.002403	67.14	.0003219	106.2
		.0002651	114.1	.0002869	110.7	.001202	79.94	.0000	148.5
		.0001060	126.6	.0000	149.5	.0007210	90.16		
		.0000	149.5			.0004807	99.12		
						.0000	149.5		

Normality	$Gd_2(SO_4)_3$	Normality	$Ho_2(SO_4)_3$	Normality	$Er_2(SO_4)_3$	Normality	$Yb_2(SO_4)_3$	Normality	Y_2-$(SO_4)_3$
0.3272	18.53	0.6509	15.54	1.4536	13.66	3.3345	9.884	1.2357	14.98
.1636	22.19	.1953	22.57	0.2907	20.96	0.3335	21.51	0.2471	22.08
.09817	25.32	.09769	26.86	.1644	24.02	.1000	28.40	.1606	24.49
.06545	28.24	.05858	30.68	.08721	28.17	.06669	31.35	.09885	27.68
.03272	33.68	.02931	36.51	.05814	31.16	.05002	33.62	.04943	32.94
.01636	40.37	.009769	48.22	.02907	37.18	.03335	37.27	.02471	39.16
.009817	45.92	.005858	55.00	.01454	44.27	.01000	50.53	.01606	43.58
.006545	51.05	.002931	65.63	.008721	50.42	.006669	55.50	.009885	49.23
.003272	61.13	.0009769	86.21	.005814	55.90	.005002	60.05	.004943	58.59
.001636	73.21	.0005858	96.68	.002907	66.20	.003335	66.63	.002471	69.99
.0009817	83.01	.0002931	109.7	.001454	79.60	.00100	89.67	.001606	77.86
.0006545	91.15	.00009769	128.5	.0008721	90.01	.0006252	98.79	.0009885	87.15
.0003272	105.8	.0000	146.3	.0005814	97.96	.0003335	109.9	.0004943	100.9
.0001636	121.0			.0002907	110.3	.0001000	131.9	.0002471	115.0
.0000	147.4			.0000	145.9	.0000	145.2	.0001606	121.6
								.0000	144.7

B. Conductances.—The equivalent conductances of the rare earth sulfates investigated are listed in Table II. The conductance of $La_2(SO_4)_3$, $Ce_2(SO_4)_3$, $Pr_2(SO_4)_3$ and $Nd_2(SO_4)_3$ are rather close to each other. However, there is a slight fall in the conductance of $Sm_2(SO_4)_3$ with a minimum presumably at $Eu_2(SO_4)_3$. The conductances of the heavier rare earth sulfates rise steadily from $Gd_2(SO_4)_3$ to $Yb(SO_4)_3$ with $Y_2(SO_4)_3$ coming between $Ho_2(SO_4)_3$ and $Er_2(SO_4)_3$.

The conductances of the rare earth sulfates as a whole are very much lower than would be expected for strong electrolytes. The low conductance is attributed to the formation of complexes which remove sulfate ions from solution and reduce the charge on the rare earth ions. Migration experiments showed that the most important complex at concentrations below 0.1 N is most probably of the form MSO_4^+, in which M is the rare earth. A discussion of the calculation of ionization constants for these complexes is included in the next section.

The extrapolation to infinite dilution of the calculated Λ_0' values from the Onsager equation gave very poor results. The curves showed a minimum at about 0.0009 N and then rose steeply to the proper equivalent conductance at infinite dilution. When the Onsager equation is being obeyed, the curves approach infinite dilution with zero slope. This discrepancy in the case of the rare earth sulfates is attributed to the fact that, because of the complexes in solution, the incorrect values of valencies and concentrations had been inserted in the Onsager equation. The equivalent conductances at infinite dilution have the same order as those previously reported[2a,4,5] since the rare earth sulfates are completely dissociated at infinite dilution.

C. Calculation of Ionization Constants.—The equilibrium under consideration is the dissociation of the complex

$$RESO_4^+ = RE^{+++} + SO_4^=$$

neglecting any higher complexes and hydrogen ions due to hydrolysis. If the molar concentration of the salt as $RE_2(SO_4)_3$ is C and the molar concentration of the complex is X, the resulting concentrations of Re^{+++} and $SO_4^=$ ions will be $(2C - X)$ and $(3C - X)$, respectively. Then the ionization constant will be

$$K = \frac{(2C - X)(3C - X)}{X} \frac{f_{1\pm}^{5/2}}{f_{2\pm}^{3/2}}$$

in which $f_{1\pm}$ is the mean activity coefficient of the $RE_2(SO_4)_3$ and $f_{2\pm}$ is that for $(RESO_4)_2SO_4$. The activity coefficients may be calculated from the Debye–Hückel limiting law using about 5 Å. for the 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

$$l_j = \frac{\lambda_j C_j}{1000}$$

and

$$\sum_i l_i = L = \sum_i \frac{\lambda_j C_i}{1000}$$

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°

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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).