Conductance Study of Anhydrous Rare Earth Bromides Dissolved in Methanol

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Conductance data are reported for methanol solutions of anhydrous bromides of La, Pr, Sm, Gd, Ho, Er, and Yb at 20° and 45° C. For the series, the molar conductances show a maximum at gadolinium.

WHEN the properties of the rare earths are observed as a series, a discontinuous change in slope at gadolinium often occurs. Such changes in slope, which are maxima or minima for some properties and systems, have been observed for the crystal ionic radii of the rare earth oxides (*12*), the distribution coefficients for extraction with the system, tributyl phosphate-HNO_3 (*8*), stability constants of complexes with EDTA (*13*) and nitrilotriacetic acid (*9*), the distribution coefficients for the system, Amberlite IRA-400–aqueous solution of disodium ethylenediaminetetraacetate (*7*), and the molar conductances of the hydrated chlorides and nitrates dissolved separately in methanol (*5*, *6*). The interpretations of these effects have generally been related to the half-filled 4*f* subshell of gadolinium.

Notable among the properties which show a gradual systematic decrease as the series is traversed from La to Lu are the conductances of the rare earth bromides, chlorides, and nitrates dissolved in water (*10*). The decrease is predicted if ions of greater charge density produce larger, slower transport particles by orienting more solvent molecules about the ion core.

The conductance data reported here at 20° and 45° C. show a maximum at Gd for the anhydrous bromides of La, Pr, Sm, Gd, Ho, Er, and Yb dissolved separately in methanol.

EXPERIMENTAL

The analyses, source, colors, and concentration ranges studied for each salt are shown in Table I.

The anhydrous rare earth bromides were prepared by the method of Taylor and Carter (*11*). After evaporating a solution of HBr, R_2O_3, and 6 moles of NH_4Br per mole of rare earth to apparent dryness in the open atmosphere, the excess water and ammonium bromide were eliminated by applying a vacuum of less than 40 mm. of Hg while raising the temperature of the sample to about 450° C. over an 8-hour span. The analyses and the excellent clarity of the solutions indicate that the method is successful in eliminating oxybromides and water. The salts are very hygroscopic. All solutions were made and transferred to the conductance cells in a dry bag containing dry nitrogen (Airco, oil pumped, dew point −31° C., used as received). The methanol was purged with dry nitrogen for 30 minutes just prior to use.

Four conductance cells with cell constants from 0.1105 to 0.1255 were used in all runs. A run consisted of 12 solutions covering a 100-fold concentration range. Resistances were measured with a General Radio Co. Impedance Bridge (Type 1650A) standardized with N.B.S. calibrated resistors. The measuring temperatures of 20° and 45° C. were controlled to ±0.02°.

Duplicate samples in each run and reruns on different samples of the same salt show that the molar conductances can be reproduced easily within a maximum error of 1.0% and an average error of 0.63%. Concentrations were corrected for temperature effects by using measured densities. Within experimental error, the resistances of the solutions were constant for at least 24 hours at 20° C. and for a minimum of 1½ hours at 45° C. The conductance of the solvent (Table I) was subtracted from the specific conductances of the solutions.

RESULTS

Plots of the molar conductance *vs.* the square root of the concentration for these systems show the typical deviations from linearity for weak electrolytes.

The molar conductances at 20° and 45° C. for overlapping concentration ranges are shown in Table II. At 20° C. and a salt concentration of 0.0009*M*, there is a 4.2% increase in molar conductance from La to Gd, and a 6.7% decrease from Gd to Yb; at 20° C. and 0.0025*M*, a 6.1% increase

Table I. Analyses and Concentration Ranges of Compounds Used

Salt	Color	% Deviation of Cation from Stoichiometric[a]	% Deviation of Anion from Stoichiometric[b]	Concentration Range, *M/L*
$LaBr_3$	White	...[c]	+0.4	0.0009-0.09
$PrBr_3$	Green	−0.3	+0.4	0.0002-0.02
$SmBr_3$	Grey	−0.4	+0.25	0.0002-0.02
$GdBr_3$	White	+0.2	+0.65	0.0004-0.04
$HoBr_3$	Tan	+0.08	−0.2	0.0002-0.02
$ErBr_3$	Pink	+0.2	+0.5	0.0002-0.01
$YbBr_3$	White	+0.3	+1.0	0.0001-0.01

[a] Cations analyzed by EDTA Method (*2*). [b] Bromides analyzed by Fajans Method (*3*). [c] Insufficient sample for analysis.

The rare earth oxides were from Lindsay Chemical Co., and were 99%+ pure individual rare earth. The methanol was Baker and Adamson Electronic Grade Absolute with measured specific conductivity of 6.0 × 10^{-7} mhos. cm.$^{-1}$ at 20° C. Literature value is 9 × 10^{-7} mhos. cm.$^{-1}$ (*4*).

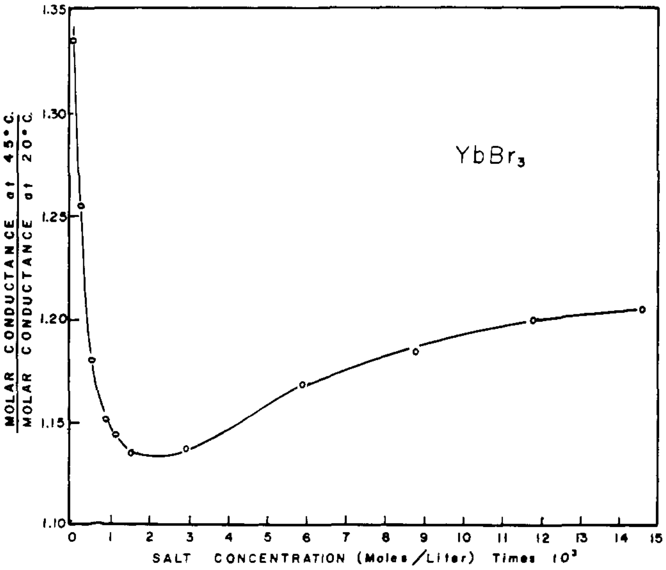

Figure 1. Typical curve for plots of ratios of molar conductance of 45° C. to molar conductance at 20° C. *vs.* salt concentration of rare earth bromides dissolved in methanol

Table II. Molar Conductances of Anhydrous Rare Earth Bromides Dissolved in Methanol at 20° and 45° C.

Concn., *M/L*	La	Pr	Sm	Gd	Ho	Er	Yb
				20° C.			
0.0004	. . .	169.1	175.5	185.5	184.2	183.0	176.0
0.000625	. . .	158.2	163.3	170.5	168.5	168.5	162.2
0.0009	153.2	144.4	153.6	159.6	155.1	154.6	144.6
0.001225	142.0	141.8	145.4	150.8	144.8	144.3	138.0
0.0016	135.5	135.1	138.2	143.2	136.3	135.5	128.3
0.002025	128.8	129.0	132.0	136.6	129.4	128.3	120.6
0.0025	123.4	123.6	126.8	130.9	123.1	122.1	114.1
0.003025	118.8	118.7	122.1	126.0	117.6	116.3	108.8
0.0036	114.7	114.4	117.6	121.7	113.1	111.2	104.3
0.004025	111.0	110.8	113.8	118.2	109.2	106.9	100.4
0.0049	107.7	107.7	110.5	114.8	105.7	103.1	97.2
0.005625	104.4	104.8	107.6	111.6	102.6	99.6	94.1
0.0064	101.6	102.1	105.0	108.7	99.9	96.7	91.5
0.007225	98.8	99.6	102.5	105.7	97.5	94.2	89.3
0.0081	96.2	97.2	100.2	102.8	95.2	92.2	87.3
0.010	91.4	92.7	95.7	97.7	90.8	. . .	83.4
0.0121	87.5	89.2	91.8	93.4	86.8	. . .	80.0
0.0144	84.0	86.0	88.1	89.7	82.8	. . .	77.6
				45° C.			
0.0009	184.3	185.0	187.5	193.7	174.1	174.0	169.0
0.00125	172.7	173.4	177.6	178.5	161.0	161.0	154.0
0.0016	162.3	164.4	168.9	170.9	150.2	149.1	143.2
0.002025	153.6	156.2	160.6	162.4	142.0	140.0	134.9
0.0025	146.3	149.1	153.1	155.5	135.4	132.9	128.2
0.003025	140.3	142.9	146.6	149.5	130.0	127.3	122.9
0.0036	135.1	137.6	141.3	144.3	125.4	122.9	118.8
0.004025	130.9	133.0	136.5	139.6	121.6	119.4	115.4
0.0049	127.1	129.0	132.3	135.1	118.1	116.4	112.2
0.005625	123.5	125.2	128.2	131.1	115.0	113.6	109.4
0.0064	120.0	121.6	124.8	127.4	112.1	111.1	107.0
0.007225	116.7	118.5	121.6	124.0	109.3	108.7	104.7
0.0081	113.5	115.6	118.8	121.7	106.7	106.4	102.8
0.010	108.1	110.4	113.8	115.1	101.8	. . .	99.0
0.0121	103.5	106.0	108.9	110.3	97.9	. . .	95.7
0.0144	99.5	102.5	104.7	106.1	95.0	. . .	92.8

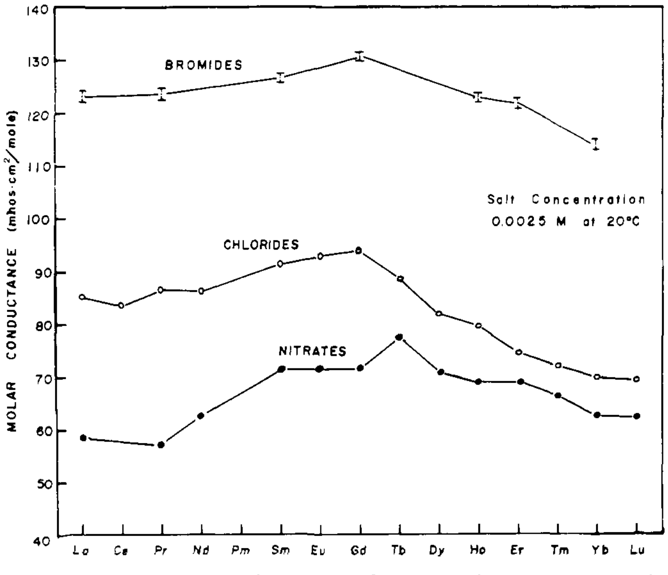

Figure 2. Molar conductances for anhydrous rare earth bromides compared with hydrated rare earth chlorides and nitrates (5) at a representative salt concentration and 20° C. Solvent is methanol. Maximum experimental error limits are shown for the bromides

and a 14.6% decrease, respectively, occur; at 45° C. and 0.0025*M*, a 6.3% increase and a 21.2% decrease are shown. Experimental error is 1%.

Ratios of the molar conductance at 45° C. to the molar conductance at 20° C. *vs.* the salt concentration show a minimum (Figure 1). Similar minima are shown for the hydrated rare earth chlorides and nitrates dissolved in methanol (*6*).

DISCUSSION

It may not be coincidental that the maximum in the molar conductances of the series coincides with the maximum number of unpaired 4*f* electrons if the 4*f* electrons can influence the formation of the bonds between the ligand and the central metal ion by action at a distance. If methanol is a stronger complexing agent than bromide, the maximum may result, then, from methanol preferentially complexing Gd and thus freeing more bromide ions from Gd than from members to either side; this complexing in some way is strengthened by the number of unpaired electrons. A comparison with the chlorides and nitrates (Figure 2) indicates the following order of strengths of complexing agents: methanol > nitrate > chloride = bromide. This is consistent with the ion conductances of nitrate (60.8), chloride (52.4), and bromide (56.5) in methanol at 25° C. (*1*). The fact that $YbBr_3$ has a lower conductance than $LaBr_3$ may result from ion size and charge density effects described by Spedding and Atkinson (*10*) gaining importance when complexing with methanol is weakened.

Plots of the molar conductance *vs.* the square root of salt concentration as well as the ratios of the molar conductances of 45° to 20° C. *vs.* concentration indicate different equilibria are prominent in certain ranges of concentration. By using the value of molar conductance at infinite dilution for the bromide ion as 56 (*1*), an equilibrium of the type,

$$RBr(CH_3OH)_x^{+2} = R(CH_3OH)_{x+1}^{+3} + Br^-$$

could be prominent near 0.0004*M* salt concentration when the molar conductance is 180 mhos, while the type,

$$RBr_2(CH_3OH)_y^{+} = RBr(CH_3OH)_{y+1}^{+2} + Br^-$$

may be prominent near 0.0025*M* where the molar conductance is 130 mhos.

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