Conductances, Transference Numbers, and Activity Coefficients of Some Aqueous Terbium Halides at 25°C

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The electrical conductances, transference numbers, activity coefficients, and densities of dilute aqueous solutions of $TbCl_3$ and $TbBr_3$ were measured at 25°C. In addition, the dilute solution electrical conductances of aqueous $DyCl_3$ were redetermined. Dilute solution electrical conductance data in the literature were reviewed, and a set of aqueous rare earth cation limiting conductances at 25°C is recommended.

For a number of years this laboratory has been concerned with the measurement of accurate thermodynamic and transport data of aqueous solutions of strong electrolytes of the rare earths. A review of some of this dilute solution data has been published (*10*). These data include the dilute solution electrical conductances, transference numbers, and activity coefficients. None of these data is available for Tb electrolytes; therefore, these three properties were measured for aqueous $TbCl_3$ and $TbBr_3$ at 25°C. Since the data for very dilute solutions of the Dy halides did not seem to be in complete agreement with the data for the adjacent rare earths, the electrical conductances of $DyCl_3$ were remeasured.

Experimental

Solutions of the stoichiometric salts were prepared by the method of Spedding et al. (*12*). The concentration of each stock solution was determined by the standard gravimetric silver halide method or by a gravimetric oxide analysis for the rare earth. The stock solution concentrations are reliable to ±0.1% or better. Dilutions were made by volume into calibrated glassware. The temperature baths were controlled to 25.00° ± 0.02°C.

The electrical resistances were measured with a Leeds and Northrup conductivity bridge of the type described by Dike (*1*). A cathode-ray oscilloscope was used as a null-point indicator. Mineral oil was used as the temperature bath liquid. Leeds and Northrup conductivity cells were used after platinization of the electrodes. Measurements were performed at 500, 1000, and 2000 cps; no significant variation of resistance with frequency was observed. The cell constants were determined by calibration with Shedlovsky's KCl data (*8*), and all resistances were corrected for the Parker effect.

A moving boundary cell, similar to that of MacInnes and Longsworth (*5*), was used to determine the transference numbers. This type of cell has been used previously for rare earth halides (*13*). This cell contains a hollow bore stopcock to shear the boundary. Silver-silver halide and cadmium-cadmium halide electrodes were used. The cell tube consisted of a 2-ml graduated pipet, and the volumes between graduations were calibrated by use of mercury. The lithium halides corresponding to the rare earth halides were used as indicator solutions. The boundary was observed with a telescope cathetometer utilizing the differences in refractive indices of the indicator and leading solutions. The average deviation in each experimental cation transference number is usually 0.0004 or less.

The activity coefficients were measured by use of concentration cells with transference. The cell potentials were measured with a Rubicon Type B high-precision potentiometer. A Leeds and Northrup Type E galvanometer was used as a nullpoint indicator. Four separate matched silver-silver halide electrodes were used in eight pairwise combinations, and the average cell potential was used in the calculations. The cell potentials typically ranged from 20 to 60 mV with an average deviation for each concentration of about 0.03 mV or less.

Calculations

The electrical conductances were corrected for solvent and hydrogen ion contributions. The limiting conductance of each salt, λ°, was then obtained by extrapolation with Onsager's equation in the form:

$$\lambda^\circ = \lambda + \left[3.3150\,\lambda^\circ\left(\frac{p}{1+p^{1/2}}\right) + 170.25\right]N^{1/2} \tag{1}$$

where

$$p = \frac{0.75\,\lambda^\circ}{\lambda^\circ + 2\,\lambda_-^\circ} \tag{2}$$

In this equation λ is the experimental equivalent conductance at a normality of N, and λ_-° is the limiting anion conductance. The values for λ_-° were taken from Robinson and Stokes (*6*). λ° is obtained from the experimental data by successive approximations. A plot of λ° vs. $N^{1/2}$ has zero slope as N approaches zero for the best value of λ°. This extrapolation equation was suggested by Shedlovsky (*7*).

The cation transference numbers were corrected for the solvent conductivity and volume changes during electrolysis. The equation used was

$$t_+\,(1 - L^\circ/L) = \frac{FNV}{1000\,It} - \frac{N\Delta V}{1000} \tag{3}$$

where F is Faraday's constant, V is the volume swept out by the moving boundary in time t, I is the average current during this time, ΔV is the volume change in the electrode compartments, L° is the solvent conductivity, and L is the solution conductivity. The volume corrections were made with the density data reported here and the cadmium halide density data of Longsworth (*3*).

The activity coefficients were calculated by the method of Shedlovsky and MacInnes (*9*), by use of the transference numbers reported here. Mean molar activity coefficients were calculated from the equation:

$$\ln\left(\frac{y_\pm}{y_\pm'}\right) = \ln\left(\frac{c'}{c}\right) - \frac{3\,FE}{4\,RT}\left\{\frac{1}{t_+'} + \int_0^E\left(\frac{1}{t_+} - \frac{1}{t_+'}\right)dE\right\} \tag{4}$$

where $y_\pm$ is the mean molar activity coefficient at a molarity c, R is the gas constant, T is the absolute temperature, and E is the observed emf. The primed symbols

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Table I. $TbCl_3$ Data at 25°C

N	λ	t_+	d	$\gamma_\pm$	m
0.00018628	139.5	...	...	...	...
0.00037243	138.1	...	...	...	...
0.00074529	135.5	...	...	...	...
0.0011179	134.1	...	...	...	...
0.0014906	132.8	...	...	...	...
0.0018628	132.0	...	...	0.8121[a]	0.0006227
0.0037243	127.6	...	...	0.7716	0.001245
0.0074529	122.3	...	...	0.7118	0.002492
0.011179	118.8	0.4494	0.99801	0.6625	0.003737
0.014906	116.2	0.4472	...	0.6344	0.004983
0.018632	114.2	0.4457	0.99864	0.6148	0.006229
0.037265	107.5	0.4381	1.0002	0.5345	0.01246
0.074529	100.5	0.4285	1.0033	0.4535	0.02493
0.11179	96.5	0.4223	...	0.4170	0.03740
0.14906	93.6	0.4139	1.0095	0.3926	0.04988

[a] Reference solution activity coefficient obtained from Debye-Hückel equation.

Table II. $TbBr_3$ Data at 25°C

N	λ	t_+	d	$\gamma_\pm$	m
0.00025059	140.6	...	...	...	...
0.00037594	139.3	...	...	...	...
0.00062660	138.0	...	...	...	...
0.00087724	136.7	...	...	...	...
0.0012532	135.4	...	...	...	...
0.0025059	132.3	...	...	0.8033[a]	0.0008377
0.0037594	129.7	...	...	0.7726	0.001257
0.0062660	126.0	...	...	0.7258	0.002095
0.0087724	123.3	...	0.99815	0.6968	0.002933
0.012532	120.4	0.4443	0.99859	0.6583	0.004190
0.025064	114.4	0.4393	1.0001	0.5876	0.008382
0.037596	110.6	0.4348	1.0017	0.5440	0.01258
0.062661	105.7	0.4286	1.0046	0.4898	0.02097
0.087724	102.7	0.4228	1.0076	0.4584	0.02936
0.12532	99.5	0.4145	1.0120	0.4248	0.04197

[a] Reference solution activity coefficient obtained from Debye-Hückel equation.

Table III. $DyCl_3$ Equivalent Conductances at 25°C

N	λ	N	λ
0.00019506	139.1	0.0068271	122.2
0.00029259	137.8	0.0097530	119.4
0.00048765	136.6	0.019506	113.0
0.00068271	135.3	0.029259	109.0
0.00097530	134.1	0.048765	104.0
0.0019506	130.7	0.068271	100.7
0.0029259	128.0	0.097530	97.1
0.0048765	124.9	...	...

refer to the most dilute solution for each salt, which was used as a reference solution. The integrations were performed graphically. The data were then fitted to the Debye-Hückel equation:

$$\log y_\pm = \frac{-Ac^{1/2}}{1 + åBc^{1/2}} \tag{5}$$

with A = 3.7446 and B = 0.8049. This equation was rearranged into the form:

$$\log \left(\frac{y_\pm}{y_\pm{}'}\right) + Ac^{1/2} = -\log y_\pm{}' - åB\left\{\left[\log \frac{y_\pm}{y_\pm{}'} + \log y_\pm{}'\right]c^{1/2}\right\} \tag{6}$$

Table IV. Rare Earth Limiting Ionic Conductances at 25°C

Rare earth	Cl^-	Br^-	ClO_4^-	NO_3^-	SO_4^{-2}	Av
La^{+3}	69.7	69.5	69.6	69.1	69.5	69.5
Ce^{+3}	69.8	...	...	...	69.5	69.7
Pr^{+3}	69.6	69.5	69.4	...	69.5	69.5
Nd^{+3}	69.3	69.5	69.8	69.8	69.5	69.6
Sm^{+3}	68.5	68.8	68.4	68.6	68.5	68.6
Eu^{+3}	67.8	...	...	...	...	67.8
Gd^{+3}	67.3	67.5	67.1	67.2	67.4	67.3
Tb^{+3}	66.9	66.8	...	...	...	66.9
Dy^{+3}	66.3	...	...	...	...	66.3
Ho^{+3}	66.2	...	66.4	66.4	66.3	66.3
Er^{+3}	65.9	65.9	66.1	65.5	65.9	65.9
Tm^{+3}	65.4	...	...	...	...	65.4
Yb^{+3}	65.1	65.6	66.0	65.1	65.2	65.4
Lu^{+3}	64.7	...	...	...	...	64.7

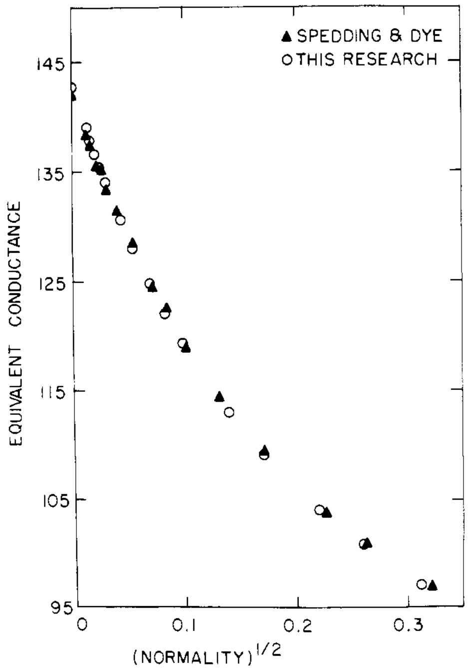

Figure 1. Equivalent conductances of $DyCl_3$ at 25°C

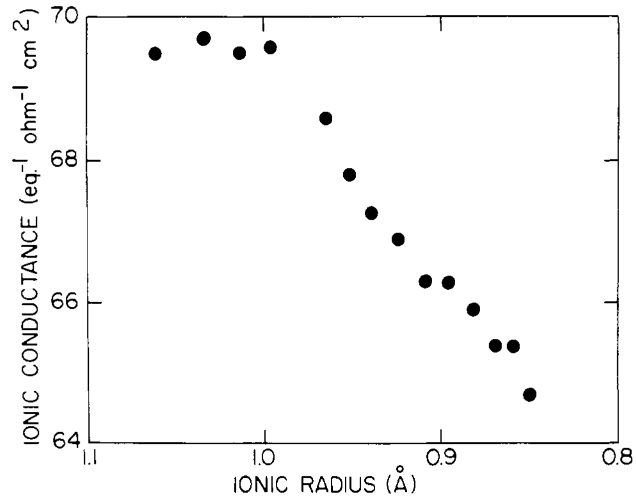

Figure 2. Limiting rare earth ionic conductances at 25°C as function of cation radius

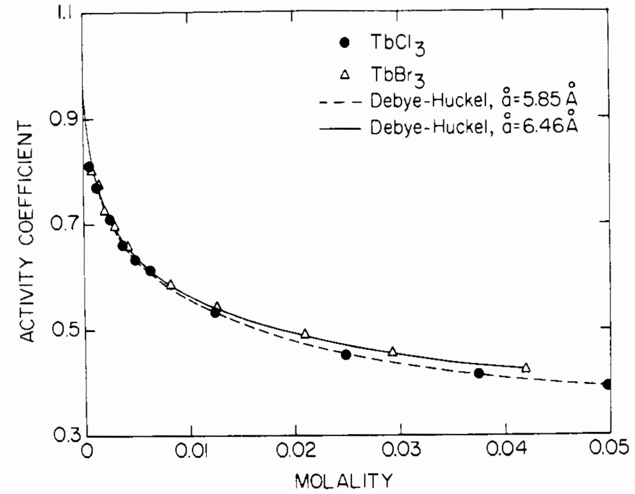

Figure 3. Mean molal activity coefficients of terbium halides at 25°C

The left-hand side of this equation was plotted vs. the term in parenthesis, and $y_{\pm}'$ was varied until the best least-squares straight line was obtained. å was then obtained from the least-squares slope. The $y_{\pm}$'s were converted to mean molal activity coefficients.

Results

The dilute solution electrical conductances of aqueous $TbCl_3$, $TbBr_3$, and $DyCl_3$ were measured at 25°C. These data are reported in Tables I-III. The units of the equivalent conductance are ohm^{-1} cm^2 $equivalent^{-1}$. In Figure 1 the $DyCl_3$ data reported here are compared to that of Spedding and Dye (*11*). These two sets of data are in fairly good agreement except for the four most dilute values. These dilute points are the most important ones for the extrapolation to obtain the limiting conductance. The new value of $\lambda°$ is 142.7 for $DyCl_3$, as compared to Spedding and Dye's value of 142.0. This new value is in better agreement with the data for other rare earth chlorides. It is possible that Spedding and Dye's $DyCl_3$ stock solution may have been slightly off from the equivalence pH, and this slight difference would be most important for the very dilute solutions. Consequently, their limiting conductance would have a larger error than their individual experimental values. A limiting conductance of 143.3 was obtained for $TbCl_3$, and a value of 144.9 for $TbBr_3$.

In Table IV the limiting ionic conductances, $\lambda_+°$, are given for the rare earth ions, based on the data reported here and that tabulated in Spedding and Atkinson (*10*). The anion conductances were taken from Robinson and Stokes (*6*). For Dy, the only value listed is the one based on the data reported here. Other measurements for $LaCl_3$ (*2, 4*) are in good agreement with the value reported in this table. The averages listed here are our recommended best values for the limiting rare earth ionic conductances. In most cases, the averages are reliable to ±0.2 ohm^{-1} cm^2 $equivalent^{-1}$. The value for *Yb* is reliable to about ±0.3 unit. In Figure 2 these average values are plotted against the ionic radii of Templeton and Dauben (*14*). This curve indicates that, for those salts for which the limiting ionic conductance is based on the data for a single salt, an uncertainty of 0.3 unit is a reasonable estimate.

The experimental values of the cation transference numbers, t_+, are given in Tables I and II. These cation transference numbers were represented by the least-squares equations

$$\begin{aligned} TbCl_3: t_+ &= 0.4624 - 0.1235\, N^{1/2} \\ TbBr_3: t_+ &= 0.4585 - 0.1221\, N^{1/2} \end{aligned} \qquad (7)$$

with an average deviation of 0.0004 unit which is also the probable error for each experimental value.

The mean molal activity coefficients, $\gamma_{\pm}$, of the Tb halides are reported in Tables I and II as a function of the molality *m*. These values are also plotted in Figure 3. The activity coefficients obey the Debye-Hückel equation over the concentration range studied, provided that the distance of closest approach, å, is included. A least-squares value of 5.85 Å was obtained for $TbCl_3$ and 6.46 Å was obtained for $TbBr_3$. The average difference between the experimental and Debye-Hückel values of $\gamma_{\pm}$ is 0.0027 for $TbCl_3$ and 0.0011 for $TbBr_3$. The å values are similar to those reported for other rare earth chlorides and bromides (*10*).

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