

reaction has been estimated in several ways (4). The results seem to suggest that the clathrate is first formed in the liquid state, and it subsequently undergoes a phase transition and solidifies.

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## Relative Viscosities of Some Aqueous Rare Earth Chloride Solutions at 25°C

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**The relative viscosities of aqueous solutions of PrCl<sub>3</sub>, EuCl<sub>3</sub>, GdCl<sub>3</sub>, TmCl<sub>3</sub>, YbCl<sub>3</sub>, and LuCl<sub>3</sub> were determined over the concentration range of approximately 0.05*m* to saturation at 25°C. The Jones-Dole B-coefficients were determined for all of these salts, and the variation of this parameter across the rare earth series is discussed in terms of ion-solvent interactions. The concentration dependence of the relative viscosity is briefly discussed in terms of various quasi theoretical models and in terms of ion-solvent interactions and the modification of the solvent structure.**

Aqueous rare earth salt solutions differ in their transport and thermodynamic properties mainly because of a slight change in the cation radius across the rare earth series. The rare earth chlorides, perchlorates, and nitrates form good series of salts to study the variation of these properties as a function of the cation size. This laboratory is involved in the study of these properties from dilute solution to saturation, and one of these studies is reported here.

Transport (13-15, 17, 19-21), thermodynamic (16, 18), and spectral (9, 10) properties indicate that in aqueous electrolyte solutions, the light and heavy rare earth cations have different inner sphere hydration numbers, whereas Nd to Tb are mixtures of these two hydrated forms. Little concentrated electrolyte solution transport data are available for higher valence salt solutions except for the viscosity of seven rare earth chlorides (17) and conductance data for 11 rare earth perchlorates (20) and 13 rare earth chlorides (21). This paper deals with the viscosity of six additional rare earth chlorides.

One of the earliest significant equations dealing with the viscosity of electrolyte solutions was the two-parameter Jones-Dole equation (4, 6). This equation accurately represents dilute solution relative viscosity behavior, and the *A* parameter of this equation was later shown to be theoretically calculable for many electrolyte systems including the aqueous rare earth chlorides (5, 7). Although a completely theoretical justification for the B-coefficient is lacking, it is generally found to be an additive parameter for the ions in the system, and its sign and magnitude

are considered a measure of the effect of the electrolyte on the solvent structure (2, 8).

The next major viscosity equation was that of Vand (25) who originally derived his equation, assuming hard spheres in a viscous continuum. In fact, Vand first tested his theory with glass beads of variable sizes (26). His equation allowed the effect of the size and shape of these "obstructions to flow" to be related to the concentration dependence of the viscosity. Although not strictly applicable to electrolyte solutions in terms of its physical model, Robinson and Stokes (12, 23) have shown that a slight modification of the Vand equation gives a fair representation of the concentration dependence of electrolyte solution viscosities, provided one or both of the ions are strongly hydrated. They interpreted the validity of the modified Vand equation as indicating that the interference of the hydrated ions with the streamlines of the flowing solvent was the most important factor in viscosity behavior at moderate concentrations.

Spedding and Pikal (17) reasoned that although the modified Vand equation represented viscosity behavior moderately well, its major defect was the absence of an ion-ion interaction term. Consequently, they added a term taken from Pitts' viscosity theory (17). While the justification for this procedure was nonrigorous, the resulting Pitts-Vand equation represented rare earth chloride aqueous solution viscosity data up to saturation well within experimental error.

Although the above approach may seem reasonable for dilute and moderately concentrated electrolyte solutions, the application of this "theory" to highly concentrated electrolyte solutions where little, if any, free solvent remains is clearly unjustified. Angell and Bressel (1) have tackled this problem from the concentrated solution end, using equations based on those derived for transport properties in glass-forming liquids. Their derivation involved a number of empirical correlations and resulted in the basic functional form of the Vand portion of the Pitts-Vand equation. The main importance of their work, as it concerns us here, is that it justifies the use of Vand-type equations over the entire concentration range experimentally obtainable. In addition, the parameters of the Vand-type equations should be interpreted with caution since they may represent different physical effects at different concentrations.

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**Table I. Experimental Relative Viscosities at 25°C**

<i>m</i>	<i>d</i>	$\eta_R$	$\Delta, \%$	<i>m</i>	<i>d</i>	$\eta_R$	$\Delta, \%$
PrCl <sub>3</sub>				TmCl <sub>3</sub>			
0.062808	1.0116	1.0426	+0.09	0.050588	1.0103	1.0394	+0.05
0.098519	1.0197	1.0644	+0.08	0.087370	1.0197	1.0654	+0.03
0.24614	1.0530	1.1572	0.00	0.10495	1.0242	1.0780	+0.03
0.48193	1.1050	1.3242	-0.04	0.24731	1.0605	1.1833	-0.03
0.82159	1.1774	1.6206	-0.02	0.49598	1.1226	1.3949	-0.06
1.0092	1.2163	1.8206	-0.02	0.82134	1.2015	1.7445	-0.01
1.4537	1.3048	2.4388	+0.04	1.0153	1.2473	2.0046	+0.06
1.7123	1.3544	2.924	+0.04	1.4710	1.3512	2.8207	+0.01
1.9836	1.4047	3.572	+0.02	1.7124	1.4044	3.418	+0.03
2.1601	1.4366	4.090	-0.05	1.9612	1.4577	4.194	-0.11
2.5708	1.5083	5.718	-0.08	2.2716	1.5223	5.494	-0.07
2.9010	1.5635	7.637	-0.06	2.5915	1.5865	7.369	-0.03
3.2339	1.6170	10.417	+0.02	2.9278	1.6516	10.227	+0.04
3.5595	1.6672	14.371	+0.17	3.2822	1.7174	14.788	+0.15
3.7936	1.7020	18.294	+0.24	3.7003	1.7914	23.694	+0.33
3.8940	1.7163	20.219	-0.32	3.8794	1.8215	29.170	-0.39
EuCl <sub>3</sub>				YbCl <sub>3</sub>			
0.057281	1.0108	1.0408	+0.01	0.047009	1.0095	1.0373	+0.10
0.079184	1.0160	1.0560	+0.09	0.075372	1.0170	1.0570	+0.05
0.10159	1.0214	1.0700	+0.02	0.10509	1.0248	1.0779	+0.02
0.24163	1.0543	1.1648	-0.01	0.24286	1.0606	1.1800	0.00
0.48637	1.1107	1.3542	+0.18	0.50114	1.1263	1.4003	0.00
0.72859	1.1651	1.5663	-0.31	0.79222	1.1984	1.7118	+0.15
0.97157	1.2183	1.8376	+0.11	0.87518	1.2185	1.8065	-0.31
1.2607	1.2798	2.2272	+0.10	1.0150	1.2521	2.0045	+0.07
1.5483	1.3393	2.7192	+0.06	1.4611	1.3561	2.8045	+0.08
1.8362	1.3969	3.352	+0.02	1.6991	1.4096	3.391	+0.09
2.1221	1.4524	4.162	-0.17	1.9771	1.4705	4.272	+0.01
2.4056	1.5057	5.225	-0.12	2.1682	1.5112	5.038	-0.11
2.6914	1.5576	6.654	+0.06	2.5892	1.5981	7.421	-0.05
2.8909	1.5927	7.927	+0.14	2.8899	1.6577	9.975	-0.01
3.5864	1.7087	15.220	-0.04	3.2712	1.7304	14.903	+0.05
GdCl <sub>3</sub>				LuCl <sub>3</sub>			
0.051018	1.0096	1.0382	+0.07	0.051950	1.0110	1.0408	+0.08
0.076695	1.0158	1.0558	+0.08	0.087120	1.0204	1.0658	+0.06
0.099125	1.0212	1.0707	+0.05	0.10054	1.0239	1.0752	+0.04
0.15933	1.0358	1.1122	+0.06	0.25369	1.0640	1.1886	-0.07
0.24836	1.0570	1.1751	+0.01	0.49699	1.1267	1.3879 <sup>a</sup>	-0.78
0.35899	1.0832	1.2580	-0.02	0.81360	1.2060	1.7399	-0.03
0.44484	1.1032	1.3280	-0.06	1.0084	1.2535	2.0026	+0.05
0.63895	1.1479	1.5010	-0.02	1.4663	1.3618	2.8344	+0.03
0.80874	1.1862	1.6754	+0.09	1.7189	1.4193	3.475	+0.01
0.97562	1.2233	1.8722	+0.05	1.9822	1.4777	4.340	-0.04
1.2093	1.2741	2.1921	-0.02	2.2850	1.5429	5.684	-0.06
1.4956	1.3346	2.6783	+0.05	2.5862	1.6056	7.555	-0.03
1.5239	1.3405	2.7353	-0.04	2.9136	1.6714	10.508	+0.09
1.8584	1.4087	3.499	-0.03	3.3110	1.7480	16.153	+0.07
2.1480	1.4680	4.380	-0.05	3.6023	1.8020	22.678	-0.05
2.5512	1.5422	6.093	+0.01	4.1202	1.8929	44.326	-0.02
2.8683	1.5999	8.030	+0.09				
3.2006	1.6580	10.897	+0.10				
3.4360	1.6976	13.665	+0.10				
3.5906	1.7229	15.898	-0.13				

<sup>a</sup> This point given a weight of zero.

**Experimental**

The viscosities of stoichiometric rare earth chloride solutions were measured with suspended level Ubbelohde-type viscometers. The preparation and analyses of such solutions, the experimental setup, and the viscometer calibration procedure have been described elsewhere (17, 18). Each solution viscosity was measured in two separate viscometers, and the mean viscosity is reported as the experimental viscosity.

**Errors and Data Treatment**

For the viscometers used in this research, the kinetic energy correction is negligible so the relative viscosity of each solution is given by

$$\eta_R = dt/d_0t_0 \tag{1}$$

where *d* is the density of the solution of interest, *d*<sub>0</sub> is the density of water at the same temperature and pressure, *t* is the efflux time for the solution, and *t*<sub>0</sub> is the efflux time

for water. The density data used in these calculations are that of Spedding and coworkers (22). The experimental values of the relative viscosities as a function of the molality are given in Table I. For each salt the highest concentration listed is the saturated solution.

The absolute error in each experimental viscosity is due to the error in the viscosity measurement and to the uncertainty in the solution concentration. The error in each experimental viscosity is due to a  $\pm 0.01^\circ\text{C}$  fluctuation in the temperature bath and uncertainties in the efflux times. This was estimated to produce a  $\pm 0.05\%$  uncertainty in the viscosity. The stock solution probable errors in the molalities were estimated to be about  $\pm 0.05\%$ . This second uncertainty does not contribute to significant relative errors for each separate salt, since the dilutions for each salt series were prepared by weight dilution from the same concentrated stock solution. However, the concentration uncertainty does contribute to the absolute errors and must be considered when comparing different salt solution viscosities. The probable error in the viscosity due to the solution concentration uncertainty was estimated to be  $\pm 0.1\%$  at  $2m$ ,  $\pm 0.16\%$  at  $3m$ , and  $\pm 0.3\%$  at  $4m$ . Clearly, this error goes to zero as the molality goes to zero.

The Jones-Dole equation is of the form:

$$\eta_R = 1 + Ac^{1/2} + Bc \quad (2)$$

where  $c$  is the molar concentration. The  $A$  parameter was calculated from theory with equations given by Harned and Owen (3) and the conductance data tabulated in Spedding and Atkinson (13). The  $B$ -coefficients were calculated from the data below  $0.1m$  by a least-squares method using the inverse square of the probable error as the weighting factors. The probable error in each of the  $B$ -coefficients is about  $\pm 0.005$  l./mol. The Jones-Dole coefficients are given in Table II.

The relative viscosity data, up to saturation, were fitted to a combination of the Pitts and Vand equations. The functional form of the resulting equation is:

$$\eta_R = Am^{1/2}[1 + P(4.831 m^{1/2})] + \exp\left\{\frac{Ym}{1 - 0.24375 Ym}\right\} \quad (3)$$

where  $A$  is the same as in the Jones-Dole equation,  $P$  is a function of the square root of the molality, and  $Y$  and  $P$  are defined elsewhere (17). In this equation,  $Y$  was fitted to the power series

$$Y = B_0 (1 + B_1 m + B_2 m^2 + B_3 m^3) \quad (4)$$

by use of a least-squares method. These parameters are also given in Table II. The experimental values of the relative viscosities and the percent differences between the calculated and experimental results are given in Table I.

The precision of the viscosity data is much greater than could be shown directly on graphs of the size allowed here. The reason for obtaining the above viscosity fitting equations is to allow one to easily calculate various

combinations of the viscosity data which can be used to graphically illustrate the small but real differences between adjacent rare earth chlorides.

## Results

The Jones-Dole  $B$ -coefficients for the total salt are given as a function of the cation radius (24) in Figure 1. The  $B$ -coefficients of Spedding and Pikal (17), Jones and Stauffer (5), and Kaminsky (7) are also shown on this graph. The error bars represent the 90% confidence limit for the data. The  $B$ -coefficients clearly show a two-series effect, and the values for the heavy rare earth ions are about 0.1 l./mol greater than for the light rare earths. Since the  $B$ -coefficients are additive for the ions within experimental error, the rare earth ionic  $B$ -coefficients will also change by this amount across the rare earth series.

In Figure 2 the viscosities of two of the salts are shown as a function of the molality. In Figure 3 the percent differences between the calculated and experimental results are shown for two of the salts studied. The solid curves represent the total probable percent error in the measurements. The fits are within experimental error of the measured values. To show graphically the real differences between adjacent rare earth chloride viscosities, the viscosities relative to lanthanum were calculated with the Pitts-Vand equation. These ratios are thus defined as:

$$R = \eta_{RECl_3} / \eta_{LaCl_3} \quad (5)$$

where  $RE$  represents the rare earth of interest. These ratios are shown in Figure 4 up to  $3.6m$ ; above this concentration the rare earth chlorides begin to saturate out.

To clarify the trends occurring across the rare earth chloride series as a function of the molality, isomolal plots of  $R$  are given in Figures 5 and 6. The data of Spedding and Pikal (17) are included on the ratio graphs without further identification.

In Figure 5, ratio plots are given at  $0.4$  and  $1.2m$ . These curves have a distinct S shape with the values for the heavy rare earths being greater than for the light ones. In Figure 6 the same type of plots is given at  $2.0$  and  $3.6m$ . The S shape is still present at  $2.0m$  (27.8 waters per rare earth ion), but at higher concentrations a major modification in shape has occurred. At low concentrations the inner sphere two-series effect can be seen indirectly. The S shape of the ratio curves indicates that the net hydration is not a smooth function of the cation radius, and significant changes occur for the intermediate rare earths for which the inner sphere hydration change is believed to occur. The differences in behavior can be clearly seen in Figure 4 where the initial slopes for the light rare earths are similar to each other but differ from those for the heavy ones with the curves for the intermediate rare earths falling in between.

At  $3.6m$  (15.4 waters per rare earth ion) La through Nd form one series, and Eu through Lu form a second series with Sm having an intermediate value. Similar effects were found in the rare earth chloride equivalent conductances (21), but the high concentration modification in behavior was less pronounced. The perchlorate conductances (20) show the same type of low concentration behavior, but at higher concentrations a new two-series effect appears and is considerably enhanced over that for the chlorides. Spedding and Rard (20) and Spedding et al. (21) have attributed the onset of this high concentration two-series effect as due to the occurrence of water sharing between anions and cations. Since most of the water should be bound directly to one or more ions at high concentrations, net hydration can no longer be the dominant factor in transport phenomena since little but

Table II. Parameters for Viscosity Equations

Salt	A	B	B <sub>0</sub>	B <sub>1</sub> × 10 <sup>3</sup>	B <sub>2</sub> × 10 <sup>3</sup>	B <sub>3</sub> × 10 <sup>3</sup>
PrCl <sub>3</sub>	0.0285	0.567	0.52315	-18.732	0.32140	-0.16081
EuCl <sub>3</sub>	0.0290	0.602	0.56231	-34.533	1.8717	-0.14276
GdCl <sub>3</sub>	0.0293	0.626	0.58058	-40.521	2.1830	-0.07220
TmCl <sub>3</sub>	0.0298	0.655	0.60881	-34.741	-1.1749	0.35869
YbCl <sub>3</sub>	0.0299	0.652	0.60771	-33.536	-1.2499	0.36600
LuCl <sub>3</sub>	0.0300	0.659	0.61070	-33.854	-0.92062	0.32278

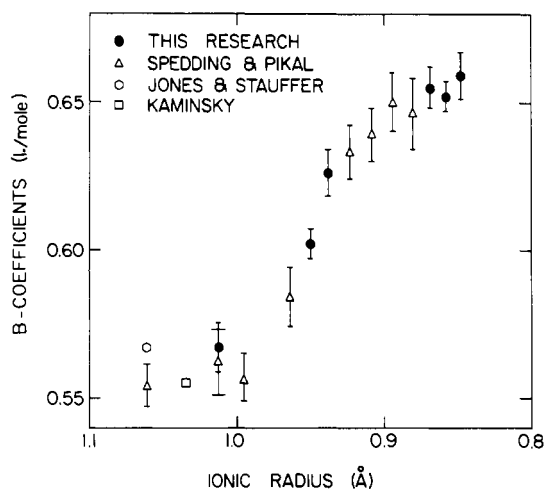


Figure 1. Viscosity B-coefficient at 25°C as function of cation radius for aqueous rare earth chloride solutions

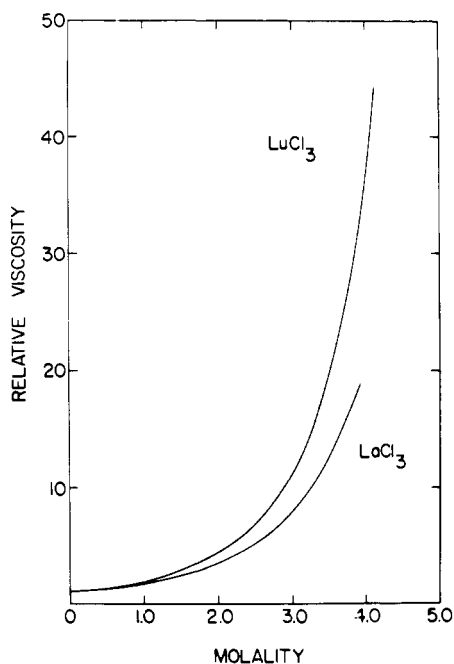


Figure 2. Relative viscosities of aqueous LaCl<sub>3</sub> and LuCl<sub>3</sub> at 25°C as function of molality

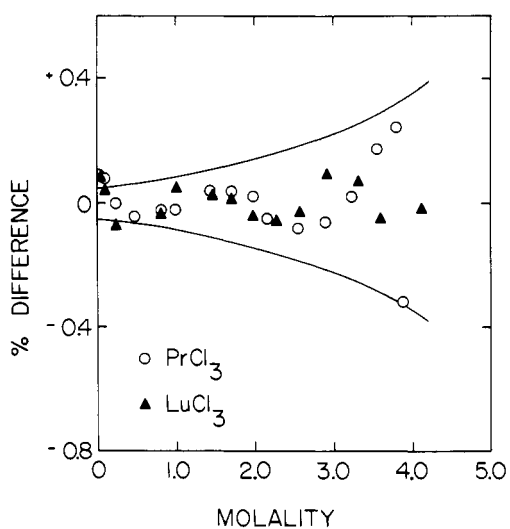


Figure 3. Percent differences between calculated and experimental viscosities. Solid curves represent total probable errors

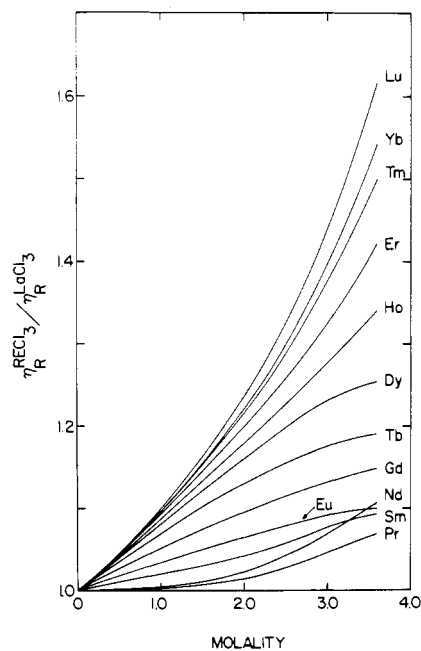


Figure 4. Ratios of aqueous rare earth chloride viscosities to that of LaCl<sub>3</sub> at 25°C as function of molality

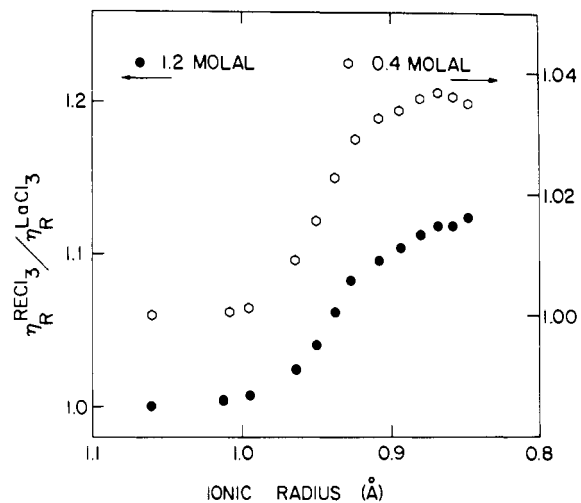


Figure 5. Ratio plots for rare earth chlorides at constant molality as function of cation radius

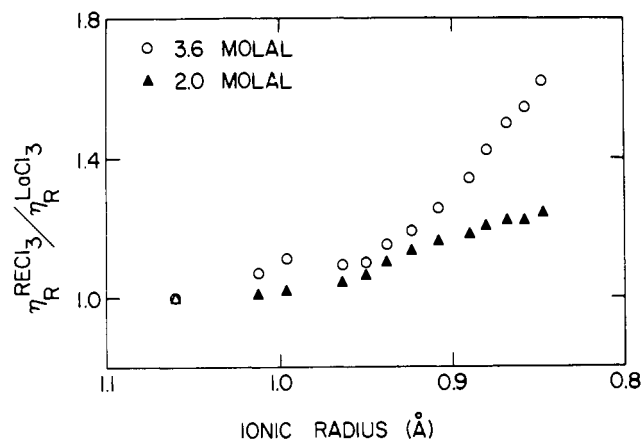


Figure 6. Ratio plots for rare earth chlorides at constant molality as function of cation radius

inner sphere water will remain. Consequently, the inner sphere two-series effect observed for the partial molal volumes (18) is then also observed for the transport properties at high concentrations. Even in dilute solutions the inner sphere two-series effect is reflected in the net hydration.

From conductance and other data, Spedding and Rard (20) deduced that water sharing is more important in the perchlorate system than in the chloride system at the same molal concentrations, and water sharing should just be starting to dominate in the chlorides when saturation occurs. If the rare earth chloride solubilities were greater, then one would expect the complete two-series effect to show up with La to Nd forming one series and Tb to Lu forming a second series and with the remaining rare earth chlorides being intermediate in behavior.

Spedding et al. (21) have discussed the effect of complexation on the conductance behavior of the rare earth chlorides. They conclude that outer sphere complexation gives rise to very little distinctive behavior for individual rare earth chlorides, and complexation may be affecting all of the rare earths by about equal amounts. Similar considerations hold for the relative viscosities.

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The rare earth oxides used in preparing the rare earth chloride solutions were purified by J. E. Powell's rare earth separation group at the Ames Laboratory.

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## Electrical Conductances of Some Aqueous Rare Earth Electrolyte Solutions at 25°C. II. Rare Earth Chlorides

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The electrical conductances of aqueous solutions of LaCl<sub>3</sub>, PrCl<sub>3</sub>, NdCl<sub>3</sub>, SmCl<sub>3</sub>, EuCl<sub>3</sub>, GdCl<sub>3</sub>, TbCl<sub>3</sub>, DyCl<sub>3</sub>, HoCl<sub>3</sub>, ErCl<sub>3</sub>, TmCl<sub>3</sub>, YbCl<sub>3</sub>, and LuCl<sub>3</sub> were measured over the concentration range of approximately 0.02*m* to saturation at 25°C. The equivalent conductances of the rare earth chlorides at each molality decreased smoothly from SmCl<sub>3</sub> to LuCl<sub>3</sub>, and LaCl<sub>3</sub> through NdCl<sub>3</sub> had very similar conductances. By 0.16*m*, the equivalent conductances of the rare earth chlorides dropped below those of the corresponding perchlorates. The differences between the chloride and perchlorate systems were discussed in terms of ionic hydration, anion-cation complex formation, the degree of cation hydrolysis, and the effect of these electrolytes on the hydrogen-bonded water structure.

The lanthanides form the most complete series of trivalent cations available for the study of aqueous solution properties. This paper is one of a series reporting accurate transport data for aqueous solutions of the rare earth

perchlorates (26), chlorides (23, 29), and nitrates (16) up to saturation at 25°C.

A moderate amount of data exists concerning the nature of the rare earth ion-chloride ion interaction. Fluorescent (18) and visible spectra (3) measurements show little evidence for complex formation even at moderately high concentrations, but the formation of outer sphere complexes would probably not appreciably affect transitions within the 4*f* subshell. Nmr (13) and ultrasonic absorption (6) measurements also indicate the absence of strong complex formation between the rare earth and chloride ions.

Thermodynamic evidence does indicate the formation of weak, outer sphere complexes. There has been some success in determining the formation constants for the rare earth chloride complexes by thermodynamic (4, 14), electrochemical (7), and spectral (11) methods. Ahrland (1) has discussed some of the evidence for outer sphere complex formation.

Spectral (32) and solution viscosity (31) measurements have been interpreted as giving evidence for the greater disruption of the hydrogen-bonded water structure by the perchlorate ion than by the chloride ion. The disruption of the water structure should tend to enhance the

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