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

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The relative viscosities of aqueous solutions of the trivalent perchlorates of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were measured over the concentration range of 0.05*m* to saturation at 25°C. The relative viscosities of the aqueous rare earth chlorides were reported previously. With the perchlorate and chloride viscosity data, a best set of rare earth ionic Jones-Dole *B*-coefficients was calculated. A distinct two-series effect appears in the viscosities, across the rare earth series, from about 3.0*m* to saturation. The concentration dependence of the relative viscosities and trends across the rare earth series are discussed in terms of a change in the inner sphere cation hydration number, changes in overall hydration, and in terms of water sharing between the various ions.

The major differences in the solution properties of rare earth salts having the same monovalent inorganic anion are due to the decrease in the cation radius across the rare earth series. The rare earths form series of these trivalent salts which can be used to study aqueous solution transport and thermodynamic properties as a function of cation size. Previous reports have presented the electrical conductances of the rare earth chlorides (*15*) and perchlorates (*14*) and the viscosities of the rare earth chlorides (*12, 19*). This paper extends these measurements to include the viscosities of the aqueous rare earth perchlorates.

It has been suggested from apparent molal volume data (*13*) that the light rare earth ions exist in aqueous solution with a higher inner sphere hydration number than the heavy rare earths, whereas the rare earth ions between Nd and Tb are mixtures of the two hydrated forms. In addition, an overall increase in cation hydration occurs in dilute and moderately concentrated solutions as the lanthanide contraction gives rise to an increase in the cation surface charge density across the rare earth series. There is also evidence from thermodynamic properties for the systems discussed here that the cations retain their inner sphere water up to saturation. At high concentrations where ion-pairing and water sharing should be extensive, Spedding and Rard (*14*) found that the inner sphere hydration change manifests itself in a very prominent fashion in the electrical conductances of the rare earth perchlorates, but the two-series effect is much less marked in the conductances and viscosities of the chlorides (*12, 15, 19*) at these high concentrations. This study was conducted to see whether other rare earth perchlorate transport properties behave similar to the conductances at high concentrations.

Experimental

The viscosities were measured at 25.00 ± 0.01°C by use of the same suspended level Ubbelohde viscometers used for the determination of the rare earth chloride viscosities (*12, 19*). This experimental procedure has been described in detail elsewhere (*12*). Each solution was run in two separate viscometers, and at least three determinations were made with each of these viscometers. Solutions of the stoichiometric salts were prepared by the method of Spedding et al. (*13*). All dilutions were prepared by weight from samples of the corresponding stock solutions and conductivity water, and all weights were corrected to vacuum. Each stock solution was analyzed by EDTA (*10*) and sulfate methods (*13*). The analyses for each stock agreed to ±0.1% or better in all cases.

Errors and Data Treatment

The densities of the solutions studied in this research were measured pycnometrically and will be reported in a separate paper along with the apparent and partial molal volumes (*17*). The kinetic energy corrections were negligible for the viscometers used in this research; therefore, the relative viscosities were calculated from the equation

$$\eta_R = dt/d_0t_0 \qquad (1)$$

where d is the density of the solution of interest, d_0 is the density of water, t is the efflux time for the solution, and t_0 is the efflux time for water. In Table I the experimental relative viscosities are given along with the corresponding molalities. The highest concentration listed for each salt is for the saturated solution.

The total error in each experimental viscosity is due to errors in the viscosity measurement and to the error in the solution concentration. The density errors are negligible compared to the other errors. The errors in the experimental determination of the viscosity were estimated to be 0.05% or less over the entire concentration range. The solution concentration uncertainties were 0.1% or less in all cases. The maximum total probable error in the viscosity is then 0.12% at 1.0*m* 0.22% at 2.0*m*, 0.34% at 3.0*m*, 0.57% at 4.0*m*, and 0.74% at 4.6*m*. These errors were calculated by using the maximum concentration uncertainty, and the actual errors may be somewhat smaller in many cases. All dilutions for each separate salt were prepared by weight dilution from conductivity water and the corresponding stock. Consequently, the data for each salt should be self-consistent to 0.05%, except for the saturated solution which was analyzed separately. Because of this self-consistency, the data in Table I are given to five figures.

The data below 0.1*M* were used to calculate the Jones-Dole *B*-coefficients by a least-squares method using the inverse square of the probable error as the weighting factors. The Jones-Dole equation is of the form

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

where c is the molar concentration. The *A*-coefficients were calculated from theory with equations given in Harned and Owen (*4*) and the ionic conductances recommended by Spedding et al. (*11*). These Jones-Dole coefficients are given in Table II along with the 90% confidence limits for the *B*-coefficients. The differences between the rare earth chloride (*12, 19*) and perchlorate *B*-coefficients are also given in this table. Assuming that

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Table I. Experimental Relative Viscosities at 25°C

m	η_R	Δ, %
	$La(ClO_4)_3$	
0.050169	1.0246	−0.30
0.077468	1.0370	−0.32
0.094054	1.0456	−0.42
0.25881	1.1225	−0.04
0.33227	1.1608	+0.09
0.72708	1.4193	+0.20
0.96463	1.6206	+0.19
1.2555	1.9286	+0.05
1.6080	2.4166	−0.09
1.8468	2.8384	0.00
2.1048	3.4159	−0.04
2.4116	4.3200	+0.02
2.7250	5.6135	0.00
2.9492	6.8854	−0.13
3.2705	9.4246	+0.20
3.5404	12.682	−0.21
4.1892	27.764	+0.09
4.7601	60.096	−0.04
	$Pr(ClO_4)_3$	
0.051174	1.0272	−0.47
0.080146	1.0398	−0.41
0.096110	1.0466	−0.36
0.24998	1.1200	−0.08
0.49752	1.2604	+0.29
0.76397	1.4516	+0.34
0.99984	1.6630	+0.14
1.3046	2.0053	−0.10
1.6078	2.4446	−0.20
1.9037	3.0042	+0.18
2.2111	3.7720	+0.14
2.5028	4.7512[a]	(+0.84)
2.8063	6.2749	+0.08
3.0862	8.2659	+0.01
3.4088	11.760	−0.05
3.7052	16.820	−0.01
4.0161	25.382	+0.12
4.3083	38.177	+0.02
4.5068	50.731	−0.21
4.6956	66.944	+0.16
	$Nd(ClO_4)_3$	
0.053516	1.0280	−0.41
0.082089	1.0408	−0.37
0.098806	1.0484	−0.35
0.25182	1.1210	+0.04
0.50247	1.2688	+0.08
0.74612	1.4398	+0.39
1.0255	1.6911	+0.18
1.3289	2.0402	−0.11
1.6237	2.4756	−0.23
1.9186	3.0374	−0.06
2.2394	3.8685	−0.01
2.4626	4.6354	+0.08
2.8122	6.3241	+0.07
3.0833	8.2670	−0.02
3.4675	12.657	−0.08
3.7084	17.019	+0.11
4.1152	29.692	−0.04
4.6849	68.864	+0.01
	$Sm(ClO_4)_3$	
0.049127	1.0287	−0.55
0.077369	1.0418	−0.50
0.094875	1.0504	−0.50
0.24058	1.1224	−0.08
0.48974	1.2710	+0.21
0.73861	1.4548	+0.22
0.96752	1.6577	+0.29
1.2520	1.9744	+0.04
1.5269	2.3573	−0.03
1.8269	2.8958	−0.09
2.1037	3.5476	−0.15
2.3863	4.4238	0.00
2.6548	5.5558	+0.05
2.9406	7.2518	−0.07
3.2201	9.6251	+0.16
3.4966	13.183	−0.18
3.7525	18.022	+0.04
3.9761	24.200	+0.06
4.6400	62.552	−0.02
	$Eu(ClO_4)_3$	
0.045347	1.0268	−0.50
0.077863	1.0418	−0.38
0.10206	1.0540	−0.37
0.24892	1.1294	+0.03
0.50198	1.2850	+0.44
0.75204	1.4842	0.00
1.0047	1.7198	+0.12
1.3117	2.0843	−0.10
1.6123	2.5411	−0.28
1.9151	3.1188	+0.19
2.2112	3.8842	+0.06
2.5018	4.8937	+0.02
2.8265	6.4934	−0.05
3.1150	8.5733	−0.05
3.4097	11.737	+0.08
3.7345	17.334	−0.10
4.1724	30.990	+0.06
4.6334	60.496	−0.03
	$Gd(ClO_4)_3$	
0.049515	1.0290	−0.42
0.077568	1.0432	−0.39
0.097904	1.0538	−0.39
0.25314	1.1365	+0.01
0.50305	1.2958	+0.32
0.74893	1.4908	+0.24
1.0027	1.7374	+0.02
1.3167	2.1165	−0.07
1.6527	2.6474	−0.18
1.9075	3.1604	−0.04
2.2097	3.9542	−0.03
2.5422	5.1529	+0.07
2.8149	6.5273	+0.07
3.1182	8.7088	0.00
3.3880	11.551	−0.07
3.7602	17.827	+0.04
4.0613	26.377	+0.08
4.4321	44.485	−0.18
4.6088	57.252	+0.14
	$Tb(ClO_4)_3$	
0.051878	1.0306	−0.39
0.077438	1.0444	−0.42
0.099820	1.0552	−0.29
0.25549	1.1418	+0.02
0.50897	1.3102	+0.49
0.76231	1.5194	+0.23
1.0177	1.7790	+0.04
1.3354	2.1822	−0.08
1.6294	2.6620	−0.26
1.9443	3.3120	+0.02

(Continued on page 68)

Table I. Continued

m	η_R	Δ, %
	$Tb(ClO_4)_3$	
2.2591	4.1819	+0.08
2.5551	5.2883	+0.02
2.8957	7.0806	−0.02
3.2061	9.4714	+0.03
3.5399	13.416	−0.07
3.8425	18.980	+0.10
4.0952	26.078	−0.05
4.6072	53.428	0.00
	$Dy(ClO_4)_3$	
0.049765	1.0306	−0.44
0.082070	1.0475	−0.37
0.10734	1.0604	−0.26
0.24872	1.1408	+0.01
0.49659	1.3056	+0.37
0.74606	1.5142	+0.17
0.97757	1.7464	+0.07
1.2990	2.1485	−0.06
1.5991	2.6334	−0.21
1.8991	3.2551	−0.20
2.2027	4.0695	+0.06
2.4931	5.1076	+0.21
2.7969	6.6100	−0.04
3.0816	8.5486	+0.04
3.4054	11.801	−0.11
3.7055	16.374	+0.11
4.0038	23.570	+0.07
4.3576	38.135	−0.18
4.6016	53.898	+0.12
	$Ho(ClO_4)_3$	
0.046969	1.0299	−0.49
0.077322	1.0458	−0.42
0.10230	1.0590	−0.34
0.23906	1.1367	+0.01
0.49425	1.3106	+0.29
0.74173	1.5196	+0.32
0.98891	1.7781	+0.08
1.2766	2.1518	−0.19
1.5741	2.6346	−0.11
1.8725	3.2608	−0.11
2.1613	4.0422	+0.04
2.4568	5.1030	+0.08
2.7295	6.4206	+0.02
3.0385	8.4887	+0.01
3.2906	10.870	−0.04
3.5405	14.156	+0.01
3.8251	19.657	+0.04
4.2744	35.217	−0.03
4.6241	59.188	+0.02
	$Er(ClO_4)_3$	
0.047792	1.0280	−0.28
0.081976	1.0470	−0.32
0.10297	1.0584	−0.29
0.25203	1.1438	+0.03
0.50804	1.3194	+0.34
0.74731	1.5256	+0.22
1.0113	1.8070	−0.02
1.2959	2.1844	−0.14
1.5896	2.6810	−0.27
1.8986	3.3455	+0.02
2.1906	4.1776	+0.08
2.4923	5.3277	+0.07
2.7869	6.8628	+0.06
3.0731	8.9523	−0.02
3.3924	12.373	−0.06
3.6740	16.937	0.00
3.9791	24.640	+0.15
4.4216	45.724	−0.32
4.6185	61.419	+0.21
	$Tm(ClO_4)_3$	
0.040490	1.0263	−0.48
0.077060	1.0468	−0.53
0.097533	1.0571	−0.41
0.25008	1.1443	−0.01
0.49390	1.3126	+0.27
0.74549	1.5290	+0.27
0.99006	1.7898	+0.10
1.2886	2.1889	−0.11
1.5883	2.7012	−0.14
1.8931	3.3774	−0.09
2.1754	4.1934	+0.05
2.4702	5.3297	+0.08
2.7825	7.0010	+0.01
3.0881	9.3486	−0.06
3.3772	12.587	+0.02
3.6636	17.422	+0.03
3.9643	25.433	−0.05
4.1899	34.640	+0.02
4.6172	67.427	−0.01
	$Yb(ClO_4)_3$	
0.039757	1.0259	−0.48
0.083360	1.0481	−0.31
0.086986	1.0500	−0.30
0.22545	1.1284	+0.02
0.49177	1.3090	+0.38
0.73704	1.5224	+0.11
0.98584	1.7822	+0.15
1.3047	2.2155	−0.30
1.5713	2.6679	−0.15
1.8635	3.3006	+0.08
2.1455	4.1112	−0.06
2.4221	5.1452	+0.07
2.7148	6.6329	+0.07
3.0205	8.7828[a]	(+0.58)
3.2962	11.699	−0.06
3.5914	16.267	−0.07
3.8786	23.121	+0.23
4.2377	38.034	−0.21
4.6044	65.488	+0.10
	$Lu(ClO_4)_3$	
0.043756	1.0290	−0.57
0.074066	1.0451	−0.52
0.094990	1.0556	−0.41
0.24664	1.1423	0.00
0.48972	1.3094	+0.36
0.72797	1.5162	+0.23
0.96943	1.7726	+0.09
1.2675	2.1864[a]	(−0.80)
1.5464	2.6492	−0.26
1.8363	3.2804	−0.13
2.1296	4.1166	+0.03
1.4016	5.1448	+0.09
2.6957	6.6563	+0.02
2.9611	8.5326	+0.04
3.2514	11.470	−0.07
3.5368	15.748	+0.06
3.8075	21.983	−0.01
4.6334	76.334	0.00

[a] This point given a weight of zero.

the B-coefficients are additive, these differences give the result that

$$\Delta B/3 = \tfrac{1}{3}(B_{\mathrm{RECl_3}} - B_{\mathrm{RE(ClO_4)_3}}) = B_{\mathrm{Cl^-}} - B_{\mathrm{ClO_4^-}} = 0.055 \pm 0.002 \quad (3)$$

where RE represents the rare earth of interest. With $B_{\mathrm{Cl^-}} = -0.007$ l./mol (*7*), then $B(\mathrm{ClO_4^-}) = -0.062 \pm 0.002$ l./mol. This value is in good agreement with Nightingale's value (*9*) of -0.056 ± 0.005 but not with a more recent tabulation (*5*). With these anion B-coefficients, a best set of rare earth cation B-coefficients was calculated and are reported in Table II along with the 90% confidence limits. The data for Sm were not used in obtaining the perchlorate ionic B-coefficient since the deviation from additivity is outside experimental error. The ionic B-coefficient for Sm is based solely on the chloride data, and the result for Ce is based on the data of Kaminsky (*6*).

The Pitts-Vand equation, used to represent the rare earth chloride viscosity data (*12, 19*), was inadequate for the rare earth perchlorate viscosities. The rare earth perchlorate viscosity data were instead fitted to the equation

$$\frac{\eta_R - 1}{\eta_R} = \sum_{i=1}^{6} A_i m^i \quad (4)$$

by use of statistical weighting factors. In this equation m is the molality. These coefficients are listed in Table III. In Table I the experimental viscosities and the percent differences between the experimental and calculated viscosities are listed. Above 1.0*m* these polynomials represent the data well within experimental error, but below 1.0*m* systematic deviations occur between the experimental and calculated viscosities. That is, the polynomials do not represent the data within experimental error for the initial flat portion of the viscosity curves. If a precision of better than 0.5% is desired at low concentrations, the viscosity should be calculated from the Jones-Dole equation up to 0.1*m* and estimated graphically between 0.1 and 1.0*m*.

Table II. Jones-Dole Equation Parameters

Salt	A	$B_{\mathrm{RE(ClO_4)_3}}$	ΔB	$B_{\mathrm{RE^{3+}}}$
$\mathrm{La(ClO_4)_3}$	0.0295	0.384 ± 0.011	0.170	0.573 ± 0.006
$\mathrm{Ce(ClO_4)_3}$	...	...	...	0.576 ± 0.008
$\mathrm{Pr(ClO_4)_3}$	0.0295	0.398 ± 0.005	0.167	0.585 ± 0.004
$\mathrm{Nd(ClO_4)_3}$	0.0295	0.400 ± 0.005	0.157	0.582 ± 0.005
$\mathrm{Sm(ClO_4)_3}$	0.0299	0.440 ± 0.007	(0.144)	0.605 ± 0.010
$\mathrm{Eu(ClO_4)_3}$	0.0301	0.440 ± 0.007	0.162	0.625 ± 0.005
$\mathrm{Gd(ClO_4)_3}$	0.0303	0.456 ± 0.006	0.170	0.645 ± 0.004
$\mathrm{Tb(ClO_4)_3}$	0.0304	0.465 ± 0.005	0.168	0.653 ± 0.005
$\mathrm{Dy(ClO_4)_3}$	0.0305	0.477 ± 0.003	0.162	0.662 ± 0.004
$\mathrm{Ho(ClO_4)_3}$	0.0306	0.489 ± 0.005	0.161	0.673 ± 0.005
$\mathrm{Er(ClO_4)_3}$	0.0307	0.473 ± 0.009	0.173	0.663 ± 0.007
$\mathrm{Tm(ClO_4)_3}$	0.0308	0.496 ± 0.005	0.159	0.679 ± 0.004
$\mathrm{Yb(ClO_4)_3}$	0.0310	0.478 ± 0.007	0.174	0.669 ± 0.005
$\mathrm{Lu(ClO_4)_3}$	0.0311	0.497 ± 0.013	0.162	0.682 ± 0.007

Results

In Figure 1 the rare earth ionic B-coefficients are plotted against the ionic radii of Templeton and Dauben (*20*). The ionic B-coefficients are approximately constant from La to Nd, rise to around Ho, and then increase slightly to Lu. The B-coefficients are usually considered to be a measure of ion-solvent interactions (*3*); therefore, the larger positive values for the heavy rare earth ions should indicate that they are affecting more solvent molecules than the light rare earth ions. This is compatible with the idea that the heavy rare earth ions have a greater amount of overall hydration than the light ones, owing to the smaller size of the heavy rare earth ions (*14, 15, 19*).

In Figure 1 the heavy rare earth ionic B-coefficients show an even-odd alternation with Dy, Er, and Yb being lower and Ho, Tm, and Lu being higher than expected. The size of this alternation is just at the limit of the experimental error. A few other properties such as the activity coefficients of the rare earth chlorides (*18*) and, to a certain extent, the pH's of concentrated rare earth chloride and perchlorate solutions of the stoichiometric salts (*14, 15*) seem to show alternating behavior. This alternation may possibly be real, but we will postpone discussing it until more data are available.

In Figure 2 the relative viscosities of the chlorides and perchlorates of La and Lu are compared as a function of the molality. Each perchlorate viscosity is lower than that of the corresponding chloride, although the La curves cross by saturation. Since the rare earth perchlorates are more soluble than the chlorides, they eventually become more viscous. The increase in viscosity with concentration is quite large, and the viscosities of the saturated solutions are as high as 53–76 times that of water. For the light rare earths the corresponding chloride and perchlorate curves either intersect near saturation or appear that they would do so if the rare earth chlorides were more soluble. The viscosity curves do not, however, appear to approach each other for the heavier rare earths.

In Figure 3 the percent differences between the viscosities calculated from Equation 4 and the experimental viscosities are shown for two of the salts studied. This equation accurately represents the data above 1*m*

Table III. Parameters for Viscosity Polynomial

Salt	$A_1 \times 10$	$A_2 \times 10^2$	$A_3 \times 10^2$	$A_4 \times 10^2$	$A_5 \times 10^3$	$A_6 \times 10^4$
$\mathrm{La(ClO_4)_3}$	4.198034	1.292955	−5.084808	1.717395	−2.690584	1.663007
$\mathrm{Pr(ClO_4)_3}$	4.274560	0.311120	−4.335413	1.446875	−2.239512	1.377183
$\mathrm{Nd(ClO_4)_3}$	4.343465	−0.727880	−3.683433	1.239904	−1.910819	1.170274
$\mathrm{Sm(ClO_4)_3}$	4.589504	−2.962075	−2.867395	1.093003	−1.788711	1.139737
$\mathrm{Eu(ClO_4)_3}$	4.703547	−2.744468	−3.835054	1.548987	−2.620257	1.682229
$\mathrm{Gd(ClO_4)_3}$	4.888488	−5.033832	−2.353664	1.018627	−1.678078	1.039772
$\mathrm{Tb(ClO_4)_3}$	5.013251	−5.119927	−2.884693	1.259541	−2.088686	1.296748
$\mathrm{Dy(ClO_4)_3}$	5.147128	−7.026950	−1.496619	0.736150	−1.139310	0.641608
$\mathrm{Ho(ClO_4)_3}$	5.194303	−6.190986	−2.522401	1.150477	−1.883018	1.145612
$\mathrm{Er(ClO_4)_3}$	5.149004	−5.369942	−2.925422	1.229580	−1.935913	1.140320
$\mathrm{Tm(ClO_4)_3}$	5.194047	−5.516342	−2.947065	1.254057	−1.997822	1.193820
$\mathrm{Yb(ClO_4)_3}$	5.200177	−5.969304	−2.428548	1.031144	−1.577713	0.899402
$\mathrm{Lu(ClO_4)_3}$	5.192251	−5.085597	−3.187722	1.302071	−2.032581	1.195831

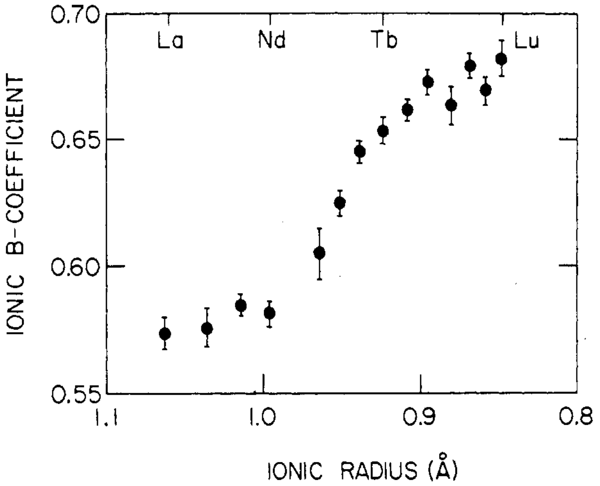

Figure 1. Ionic viscosity *B*-coefficient as function of rare earth ionic radius

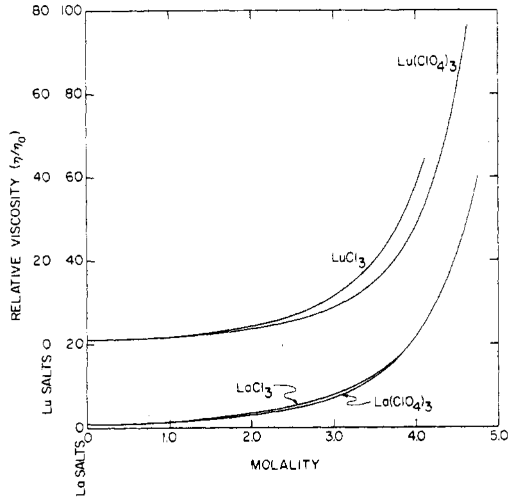

Figure 2. Relative viscosities of aqueous La and Lu electrolytes at 25°C as function of molality

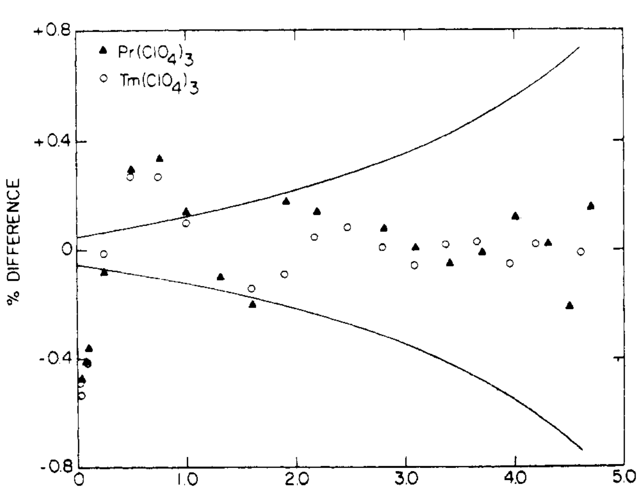

Figure 3. Percent differences between calculated and experimental viscosities. Solid curves represent total probable errors

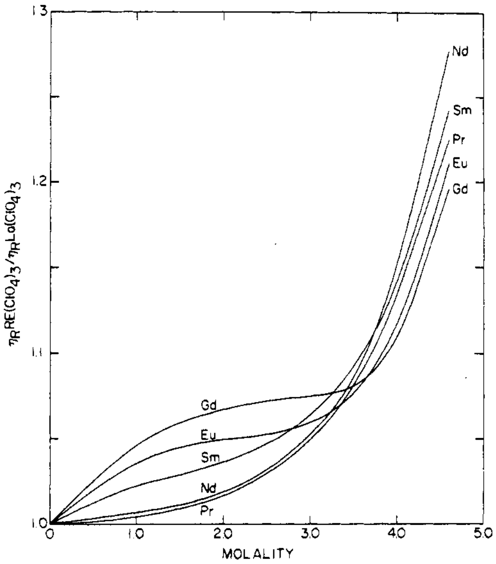

Figure 4. Ratios of aqueous rare earth perchlorate viscosities to those of La(ClO$_4$)$_3$ at 25°C for some light and middle rare earths

but gives calculated values which differ systematically from the experimental data below 1*m*.

To the size of graphs allowed here, the full accuracy of the data cannot be seen on a direct plot of the viscosities. To graphically present the data so that the real differences between adjacent rare earth perchlorates will appear, the ratios of the viscosities of interest to those of lanthanum perchlorate

$$R = \eta_R^{\mathrm{RE(ClO_4)_3}}/\eta_R^{\mathrm{La(ClO_4)_3}} \qquad (5)$$

were calculated as a function of the molality and these ratios are shown in Figures 4 and 5. The Gd data are shown on both graphs as a common reference. Below 3.0*m* (18.5 water molecules per rare earth perchlorate) the trends across the rare earth perchlorate series are quite similar to those for the chlorides (*12, 19*). That is, the isomolal viscosity increases with the atomic number of the cation.

At very high concentrations the viscosity increases rapidly with concentration. A small error in the analysis of a saturated solution could raise or lower the end of the viscosity curve appreciably. Therefore, the crossing of the Tm and Yb curves near saturation may not be real since there may be a small error in the saturation molality of either salt. The data for the saturated Yb(ClO$_4$)$_3$ probably contains the major error since other properties measured on this solution also exhibit irregularities.

To clarify the trends occurring across the rare earth series, plots of *R* are given as a function of the ionic radius, at various constant molalities, in Figure 6. At 1.2*m* (46.3 water molecules per rare earth perchlorate) the series curve is S-shaped. This increase in viscosity across the series indicates an increase in overall hydration as the lanthanide contraction causes an increase in the surface charge density of the cations. Changes in the inner sphere hydration number between Nd and Tb cause the overall hydration to change more rapidly with atomic number and give rise to the S-shaped curves. The same considerations apply to the ionic *B*-coefficients.

Because of the large solubilities of the rare earth chlorides and perchlorates, concentrations are reached at

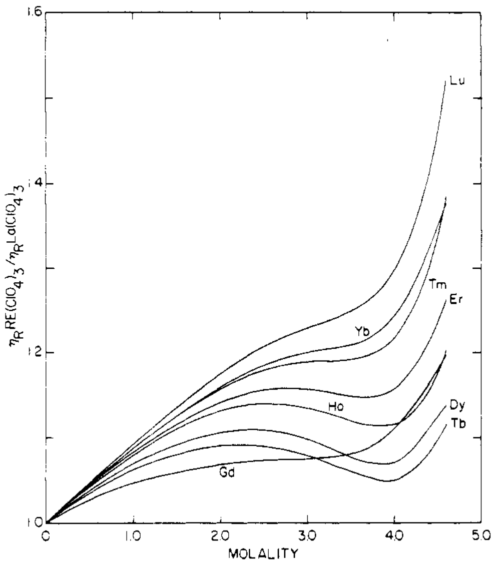

Figure 5. Ratios of aqueous rare earth perchlorate viscosities to those of $La(ClO_4)_3$ at 25°C for some middle and heavy rare earths

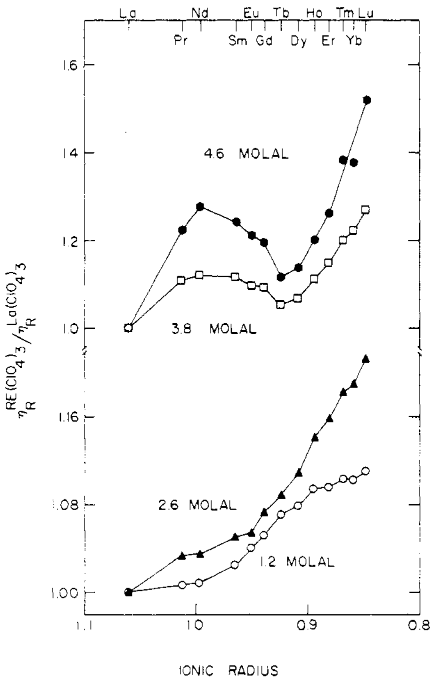

Figure 6. Ratio plots for rare earth perchlorates as function of cation radius

which water sharing between ions becomes important. When this occurs, there will no longer be sufficient water present in the rare earth perchlorate systems to allow all of the ions to separately satisfy their hydration needs; therefore, the dependence of viscosity on overall hydration will begin to break down. However, the new mechanism for transport, involving the breaking and reforming of outer sphere ion-pairs and ion-water bonds, should produce the same trend since the increasing surface charge density across the rare earth series should cause the strength of the water sharing ion-pairs to increase across the series. As mentioned in the conductance papers (*14, 15*), only outer sphere anion–cation complexes appear to be present in detectable amounts in the rare earth chloride and perchlorate systems.

By 3.6*m* (15.4 water molecules per rare earth perchlorate) the viscosities fall into two-series (Figure 6). The isomolal viscosity increases from La to Nd, decreases to Tb, and then increases again to Lu. The rare earth perchlorate conductance data show corresponding behavior in this concentration range (*14*). The plot of the perchlorate viscosities at 2.6*m* (21.4 water molecules per rare earth perchlorate) is transitional between the S shape at lower concentrations and the prominent two-series shape at higher concentrations and is similar in shape to the corresponding chloride curve at 3.6*m* (*19*).

As mentioned above, it has been suggested that the light rare earth ions have a larger inner sphere hydration number in aqueous solution than the heavy rare earth ions. Between Nd and Tb, mixtures of the two forms should exist with the amount of the lower coordinated form, at constant molality, increasing with increasing atomic number. The gradual release of this "extra" water into a system in which nearly all the water is shared between ions should reduce the amount of ion-pairing present and enhance the tendency to flow in this system, giving rise to the isomolal decrease in viscosity between Nd and Tb (Figure 6). The inner sphere hydration shift is complete at Tb, and the heavier rare earth perchlorates show the expected increase in viscosity with atomic number.

Outer sphere ion-pairs have been suggested in both the aqueous rare earth chlorides and perchlorates, and the strength of these ion-pairs is believed to be greater in the case of the chlorides than the perchlorates (*2*). Inner sphere ion-pairs were found to be absent in detectable amounts in both cases (*1, 8*). Anion–water–rare earth bonds should therefore be more difficult to break in the rare earth chloride systems, and this, to a large extent, accounts for the lower conductances and higher viscosities of the chlorides compared to the corresponding perchlorates. At low concentrations the disruption of the hydrogen-bonded water structure by the different anions also contributes to the observed differences (*15*). In addition, the relative sizes of the equilibrium constants for the various complexes across each rare earth anion series also contribute to overall trends.

The activities of water in rare earth perchlorate solutions (*16*) at high concentrations are much lower than in the corresponding rare earth chloride solutions (*18*). Consequently, the tying up of water in the rare earth perchlorate systems will be more complete at high concentrations than in the chlorides at equal molalities. The high concentration two-series effect begins to appear when most of the water outside the rare earth ion's inner sphere is bound to ions; therefore, the two-series behavior appears at lower concentrations in the perchlorates. As mentioned above, the high concentration two-series effect is just beginning to appear in the chlorides at 3.6*m* and would presumably appear in the more complete form at higher concentrations if the chlorides were more soluble.

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Densities and Apparent Molal Volumes of Some Aqueous Rare Earth Solutions at 25°C. I. Rare Earth Chlorides

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The densities of aqueous solutions of $LaCl_3$, $PrCl_3$, $NdCl_3$, $SmCl_3$, $EuCl_3$, $GdCl_3$, $TbCl_3$, $DyCl_3$, $HoCl_3$, $ErCl_3$, $TmCl_3$, $YbCl_3$, $LuCl_3$, and YCl_3 were determined from approximately $0.02m$ to saturation at 25°C with an accuracy of $\pm 1 \times 10^{-5}$ g/ml by a pycnometric method. The densities of YCl_3 were also determined at 0°C. Empirical equations representing the densities were obtained. Apparent molal volumes calculated from the experimental densities were fitted to semiempirical equations. Available dilute solution data (less than $0.2m$) were included in these fits. The partial molal volumes of the salt and water were discussed in terms of the ion–water and ion–ion interactions. A two-series effect in the partial molal volumes of the salt across the rare earth chloride series reported earlier was confirmed in dilute solutions, and this effect persists to high concentrations.

The rare earth ions behave very similarly in solutions since they all exist in the trivalent state. Furthermore, the ionic radii of the rare earth ions decrease in a regular way across the series owing to the lanthanide contraction, forming an ideal group of ions for studying ion–ion and ion–solvent interactions as a function of ionic radii. For these reasons this laboratory is determining the thermodynamic and transport properties of aqueous rare earth salt solutions. This report is one in a series presenting such data.

The densities and apparent molal volumes of electrolytic solutions are frequently required as auxiliary data for the study of thermodynamic and transport properties. These include the expansibilities, compressibilities, viscosities, conductivities, and transference numbers. Over the past several years, precision pycnometric measurements of the densities of the rare earth chloride, perchlorate, and nitrate solutions have been made in this laboratory for the above purpose, in addition to their own intrinsic value. These data have been consolidated, and the results for the chlorides are presented in this report. Papers in preparation will cover the perchlorates and nitrates.

The volume changes accompanying the addition of electrolyte to water are presently only incompletely understood. It is becoming increasingly clear that the detailed molecular configuration of the ion–water aggregates must be considered for a successful understanding of the partial molal volumes of electrolytes. Reviews of the theory of molal volumes can be found in Redlich (*31*), Harned and Owen (*13*), and Redlich and Meyer (*32*). Particularly good discussions of partial molal volumes at infinite dilution and reviews of the literature are those of Millero (*21, 22*). Millero has also published a compilation of partial molal volume data (*22*).

Thermodynamic (*24, 35–37, 39, 41, 48*), transport (*40, 42–44*), and spectral (*15, 17, 19, 25, 27, 28*) properties of the rare earth cations in aqueous solutions indicate that these properties are not smooth functions of the ionic radii. The apparent molal volumes of dilute (less than $0.2m$) rare earth chloride, nitrate, and perchlorate solutions were reported by Spedding et al. (*37, 41*). From the trends in these data they suggested that the cations La to Nd and Tb to Lu have different inner sphere water coordination numbers, while for the cations from Nd to Tb there exist equilibrium mixtures of the two inner sphere water coordination numbers. It was of interest to examine the trends in the volume properties of these solutions at higher concentrations, where changes in hydration and various types of complexing may be important. This report presents the extension of these density measurements to saturation.

Experimental

Apparatus and procedure. The densities were measured with 40-ml Sprengel-Ostwald pycnometers. A description of the pycnometer and the general procedure can be found in Bauer and Lewin (*2*). The bath tempera-

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