Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 2. The Rare Earth Perchlorates

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The osmotic coefficients of the aqueous triperchlorates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu have been measured from 0.1 *m* to saturation at 25 °C. These data were fitted to semiempirical least-squares equations, and these equations were used to calculate water activities and mean molal activity coefficients for each electrolyte. The water activities of these solutions are much lower than for the corresponding rare earth chlorides at the same molalities, whereas the activity coefficients of the rare earth perchlorates are much larger. This behavior and changes in these properties across the rare earth series are discussed in terms of differences in interactions between anions, cations, and water, including the effect of the rare earth ionic radius upon cation hydration.

Recently the water activities and electrolyte activity coefficients of the rare earth chlorides have been determined up to saturation at 25 °C (*16*). These properties were found to depend mainly on total hydration of the rare earth ion, as influenced by changes in the ionic radii and the inner sphere hydration number. Thermodynamic (*9, 10, 14*) and transport (*13, 15*) properties have been reported for the rare earth perchlorates and significant differences were found for these properties from those reported for the corresponding rare earth chlorides. In both cases, only outer sphere ion pairs are believed to form (*1, 13*). Transport data (*13, 15*) at high concentrations indicate that water may be bound more strongly in the rare earth perchlorate systems than in the rare earth chlorides. Isopiestic measurements give direct information about hydration differences between these systems, so the activity measurements were extended to include the rare earth perchlorates.

Experimental Section

The isopiestic equilibrations were performed in the same stainless steel isopiestic chambers that were used for the rare earth chloride (*16*) and calcium chloride (*6*) studies. The measurements were made at 25.00 ± 0.01 °C. All samples were equilibrated in cups made of tantalum metal. The isopiestic reference solutions were KCl, $CaCl_2$, and H_2SO_4. The concentrated solutions were equilibrated for 3–4 days or longer while those with rare earth perchlorate concentrations below 0.5 *m* were equilibrated for 2–6 weeks. Equilibrium was considered to occur when the molalities of duplicate samples of each electrolyte agreed to within ±0.1% of the average above 0.5 *m* and ±0.15% below this concentration. In many cases the equilibrations were more accurate than these limits indicate. Equilibrium was approached from higher and lower concentrations in all cases. All sample weights were converted to mass. The rare earth perchlorate densities were obtained from Spedding et al. (*14*), and the densities of KCl, $CaCl_2$, and H_2SO_4 solutions were taken from the International Critical Tables.

Stock solutions of the rare earth perchlorates were prepared from reagent grade $HClO_4$ and oxides made from ion-exchange purified rare earths. The purity of each of the rare earth oxides was better than 99.85% by weight, with the principal impurities being Ca, Fe, Si, and adjacent rare earths (most of the rare earth oxides were probably of much higher purity than this limit indicates). The stock solutions were adjusted to their equivalence pH values to ensure a three to one ratio of perchlorate to rare earth ions (*12*). The concentrated rare earth perchlorate stock solutions were analyzed by EDTA and gravimetric sulfate methods. The analyses agreed to at least ±0.1% in terms of the molality, for each salt. The preparation and analyses of the KCl, $CaCl_2$, and H_2SO_4 reference solutions have been previously described (*6, 16*). Conductivity water, distilled from a KOH–$KMnO_4$ solution, was used in all solution preparations and dilutions.

Calculations and Errors

The molal osmotic coefficient of a rare earth perchlorate solution is given by

$$\phi = -\frac{1000 \ln a_1}{\nu m M_1} \tag{1}$$

where m is the molality of the solution, $M_1 = 18.0154$ g mol^{-1} is the molecular weight of water, ν is the number of ions formed by the complete dissociation of one molecule of solute into its component ions, and a_1 is the activity of water in the solution. All concentrations are in terms of the IUPAC-69 atomic weights. If the rare earth perchlorate solution is in isopiestic equilibrium with a standard solution whose osmotic coefficient is accurately known as a function of concentration, the osmotic coefficient of the rare earth perchlorate solution is given by

$$\phi = \frac{\nu^* \phi^* m^*}{\nu m} \tag{2}$$

where the asterisk refers to the standard. The osmotic coefficients of H_2SO_4 and $CaCl_2$ were taken from Rard, Habenschuss, and Spedding (*4, 5*), while those of KCl were from Hamer and Wu (*2*) with a small correction applied as described earlier (*4*). The experimental isopiestic molalities and the rare earth perchlorate osmotic coefficients are given in Table I. The highest concentration listed for each salt is the saturated solution.

The rare earth perchlorate osmotic coefficients were fitted to equations of the form

$$\phi = 1 - (A/3)(m^{1/2}) + \sum_i A_i m^{r_i} \tag{3}$$

where $A = (0.5108)(3)(6^{1/2})(2.302\ 585) = 8.6430$ and the r_i were not required to form a consecutive sequence of powers. Application of the Gibbs–Duhem relation to eq 3 yields

$$\ln \gamma_{\pm} = -A(m^{1/2}) + \sum_i A_i\left(\frac{r_i + 1}{r_i}\right) m^{r_i} \tag{4}$$

where $\gamma_{\pm}$ is the mean molal activity coefficient of the solute. This equation is just the Debye–Hückel limiting law with a series of terms containing powers of the molality. The experimental isopiestic data of this research extend from 0.1 *m* to saturation. Data below 0.1 *m* are desirable for obtaining reliable activity coefficients. Spedding and Jaffe (*11*) have obtained approximate

Table I. Isopiestic Molalities and Osmotic Coefficients of Some Rare Earth Perchlorates

m, $Re(ClO_4)_3$	m, standard	ϕ, $Re(ClO_4)_3$	$10^3\ \Delta\phi$
	$La(ClO_4)_3$ (from conductance)		
0.005 00	—	0.8764	−3.3
0.010 00	—	0.8526	−1.0
0.015 00	—	0.8399	0.8
0.020 00	—	0.8319	2.0
	$La(ClO_4)_3$ vs. KCl		
0.092 643	0.174 79	0.8631[a]	39.0
0.182 25	0.351 58	0.8713	1.9
0.280 49	0.580 24	0.9289	0.6
0.372 55	0.818 43	0.9850	−2.4
0.388 98	0.863 73	0.9957	−2.7
	$La(ClO_4)_3$ vs. $CaCl_2$		
0.479 71	0.703 06	1.0586	−2.0
0.511 44	0.757 77	1.0855	2.4
0.642 28	0.977 07	1.1822	1.2
0.764 48	1.188 0	1.2802	0.8
0.865 82	1.367 0	1.3675	1.2
0.946 34	1.509 9	1.4384	−0.3
1.046 7	1.691 8	1.5329	0.1
1.157 9	1.895 9	1.6424	0.5
1.243 7	2.054 7	1.7297	0.6
1.343 8	2.241 0	1.8341	0.1
1.448 0	2.436 2	1.9457	−0.6
1.552 7	2.634 0	2.0612	−0.4
1.646 5	2.811 5	2.1660	−0.9
1.740 0	2.989 4	2.2723	−0.6
1.823 4	3.147 6	2.3670	−1.3
1.909 8	3.312 2	2.4663	−1.3
2.006 7	3.497 8	2.5792	0.0
2.106 5	3.688 1	2.6943	0.3
2.237 4	3.937 4	2.8442	0.5
2.314 0	4.084 2	2.9325	1.8
2.412 4	4.269 6	3.0407	−0.6
2.481 6	4.401 6	3.1180	−0.4
2.561 6	4.557 1	3.2096	3.1
2.646 8	4.719 8	3.3018	2.5
2.750 7	4.919 1	3.4123	1.7
2.850 3	5.110 4	3.5148	−0.7
2.952 3	5.309 3	3.6188	−2.3
3.047 0	5.499 2	3.7163	−1.2
3.151 2	5.710 7	3.8200	−1.7
3.251 4	5.919 6	3.9183	−2.2
3.351 0	6.138 9	4.0170	−2.2
3.424 3	6.298 5	4.0862	−1.3
3.513 6	6.507 2	4.1734	1.1
3.618 0	6.761 1	4.2723	1.7
3.688 8	6.942 4	4.3393	2.5
3.775 1	7.174 6	4.4208	3.8
3.857 2	7.402 0	4.4940	1.1
3.927 2	7.602 8	4.5547	−2.6
3.933 9	7.624 4	4.5618	−1.6
4.006 0	7.839 7	4.6238	−5.7
4.114 3	8.188 9	4.7243	−3.8
4.188 5	8.439 2	4.7940	−1.2
	$La(ClO_4)_3$ vs. H_2SO_4		
3.969 1	11.978	4.6014	5.7
4.061 7	12.341	4.6840	3.6
4.165 3	12.753	4.7752	0.9
4.254 1	13.115	4.8543	0.3
4.385 8	13.660	4.9698	−0.6
4.493 8	14.117	5.0641	0.9
4.583 6	14.491	5.1364	−1.4
4.658 3	14.809	5.1975	0.0
4.684 0	14.918	5.2178	0.5
4.750 0	15.201	5.2705	3.7
4.775 9	15.293	5.2823	−3.1
	$Pr(ClO_4)_3$ (from conductance)		
0.005 00	—	0.8764	−3.6
0.010 00	—	0.8526	−1.1
0.015 00	—	0.8399	1.0
0.020 00	—	0.8319	2.4
	$Pr(ClO_4)_3$ vs. KCl		
0.097 658	0.179 65	0.8411[a]	18.1
0.181 27	0.347 59	0.8663	1.7
0.288 81	0.596 91	0.9278	−1.0
0.367 64	0.802 02	0.9782	−1.5
0.374 89	0.821 75	0.9829	−1.6
	$Pr(ClO_4)_3$ vs. $CaCl_2$		
0.460 74	0.670 11	1.0416	−1.4
0.520 06	0.769 57	1.0875	2.2
0.604 33	0.910 21	1.1493	1.2
0.686 37	1.049 1	1.2115	−0.8
0.767 35	1.190 2	1.2786	−0.2
0.858 45	1.352 1	1.3586	1.5
0.961 42	1.533 8	1.4479	−2.0
1.037 0	1.675 6	1.5256	4.6
1.134 2	1.849 2	1.6147	−1.1
1.219 7	2.009 0	1.7035	1.3
1.323 5	2.201 3	1.8104	−0.2
1.414 1	2.371 3	1.9075	−0.4
1.513 5	2.558 7	2.0162	−1.0
1.604 9	2.732 4	2.1189	−0.9
1.698 4	2.909 5	2.2239	−2.4
1.776 2	3.059 7	2.3155	−0.6
1.863 8	3.226 8	2.4163	−1.5
1.958 8	3.410 4	2.5286	−0.2
2.047 8	3.581 3	2.6332	0.1
2.156 7	3.791 6	2.7620	1.3
2.281 5	4.031 9	2.9077	1.6
2.377 2	4.217 0	3.0194	2.5
2.473 5	4.402 5	3.1293	2.1
2.555 2	4.559 9	3.2211	1.2
2.664 7	4.771 6	3.3422	−0.2
2.774 8	4.987 3	3.4635	−0.1
2.877 0	5.188 6	3.5728	−1.4
3.012 3	5.458 7	3.7137	−4.2
3.088 0	5.617 2	3.7960	−1.1
3.211 4	5.877 3	3.9230	−1.3
3.311 7	6.096 4	4.0248	−1.5
3.384 6	6.262 0	4.0990	−0.8
3.484 8	6.501 8	4.2030	2.9
3.566 2	6.702 6	4.2838	2.5
3.652 9	6.927 2	4.3695	1.9
3.736 7	7.158 4	4.4537	2.7
3.810 9	7.373 6	4.5277	2.7
3.892 5	7.616 0	4.6045	−2.2
3.969 9	7.858 6	4.6785	−6.0
4.049 8	8.123 5	4.7577	−7.4
4.133 5	8.415 4	4.8431	−6.8
4.211 6	8.706 2	4.9261	−3.2
	$Pr(ClO_4)_3$ vs. H_2SO_4		
4.026 7	12.390	4.7502	8.4
4.099 6	12.695	4.8220	6.4
4.200 4	13.118	4.9179	0.0
4.291 2	13.518	5.0098	−0.3
4.391 1	13.971	5.1127	1.9
4.492 6	14.444	5.2185	7.0
4.596 2	14.895	5.3070	−4.0
4.633 5	15.070	5.3436	−2.0
4.703 1	15.396	5.4101	2.3
4.718 2	15.457	5.4199	−0.9
	$Nd(ClO_4)_3$ (from conductance)		
0.005 00	—	0.8764	−3.6
0.010 00	—	0.8526	−1.5
0.015 00	—	0.8399	0.1
0.020 00	—	0.8319	1.2
	$Nd(ClO_4)_3$ vs. KCl		
0.109 47	0.200 47	0.8354	3.0
0.109 91	0.201 49	0.8362	3.6
0.191 13	0.369 79	0.8732	−1.7
0.280 57	0.577 75	0.9247	−3.1
0.372 39	0.816 29	0.9829	−2.8

Table I (continued)

m, $Re(ClO_4)_3$	m, standard	ϕ, $Re(ClO_4)_3$	$10^3\ \Delta\phi$
0.445 70	1.026 0	1.0330	−1.3
0.536 51	1.038 7	1.0978	−0.2
0.541 57	1.325 8	1.1020	0.4
0.547 70	1.346 7	1.1071	1.1
$Nd(ClO_4)_3$ vs. $CaCl_2$			
0.574 40	0.858 26	1.1243	−1.3
0.672 95	1.025 7	1.2004	−0.6
0.756 15	1.170 1	1.2685	0.3
0.825 63	1.293 3	1.3290	2.0
0.906 15	1.437 6	1.4016	3.5
1.002 3	1.609 7	1.4888	1.6
1.089 1	1.768 6	1.5731	2.1
1.158 5	1.895 7	1.6413	0.9
1.232 1	2.032 9	1.7174	1.3
1.320 0	2.196 7	1.8092	0.1
1.401 1	2.349 4	1.8967	−0.3
1.466 3	2.472 4	1.9679	−1.2
1.531 8	2.597 0	2.0413	−1.4
1.609 2	2.744 0	2.1282	−2.7
1.695 5	2.909 5	2.2277	−2.7
1.775 0	3.062 6	2.3208	−2.4
1.862 3	3.231 0	2.4236	−2.1
1.929 7	3.361 5	2.5039	−1.4
1.949 8	3.400 4	2.5278	−1.2
2.012 3	3.520 9	2.6016	−1.4
2.088 9	3.669 2	2.6928	−0.9
2.179 7	3.846 4	2.8023	1.3
2.258 7	3.999 6	2.8959	1.9
2.313 3	4.105 5	2.9602	2.3
2.341 7	4.159 8	2.9926	1.4
2.401 9	4.277 9	3.0644	3.2
2.432 3	4.335 1	3.0974	1.0
2.525 5	4.517 0	3.2056	1.8
2.611 4	4.685 7	3.3047	2.9
2.645 9	4.753 0	3.3433	2.5
2.712 5	4.882 3	3.4159	0.3
2.822 7	5.101 3	3.5384	0.5
2.919 3	5.294 7	3.6429	−0.9
3.005 3	5.469 6	3.7346	−2.2
3.104 7	5.677 6	3.8402	−2.9
3.199 7	5.879 4	3.9395	−4.0
3.288 7	6.077 7	4.0341	−2.7
3.385 6	6.302 7	4.1369	−0.5
3.468 3	6.502 0	4.2232	0.3
3.555 7	6.720 6	4.3121	−0.6
3.652 7	6.981 6	4.4142	1.9
3.726 9	7.189 4	4.4894	1.1
3.807 3	7.427 1	4.5712	0.5
3.913 9	7.761 8	4.6796	−0.7
4.004 3	8.061 9	4.7717	−1.9
4.018 5	8.115 2	4.7894	1.1
4.095 5	8.389 5	4.8719	4.0
4.104 3	8.419 7	4.8802	3.1
4.143 7	8.568 0	4.9242	6.3
4.188 8	8.739 3	4.9721	7.2
4.195 7	8.765 6	4.9790	7.0
4.248 7	8.967 6	5.0269	−0.3
4.314 4	9.235 7[b]	—	—
$Nd(ClO_4)_3$ vs. H_2SO_4			
4.095 3	12.761	4.8609	−6.9
4.158 5	13.040	4.9280	−5.4
4.234 0	13.375	5.0064	−5.5
4.312 9	13.737	5.0913	−2.8
4.335 8	13.850	5.1192	1.3
4.359 3	13.950	5.1398	−2.6
4.398 5	14.136	5.1829	−0.3
4.441 1	14.344	5.2269	−0.6
4.446 5	14.357	5.2315	−1.7
4.472 5	14.478	5.2579	−2.2
4.506 1	14.639	5.2938	−1.1
4.568 9	14.942	5.3603	0.8
4.627 5	15.222	5.4195	0.3
4.682 2	15.490	5.4763	1.9
$Sm(ClO_4)_3$ (from conductance)			
0.005 00	—	0.8764	−4.1
0.010 00	—	0.8526	−1.4
0.015 00	—	0.8399	0.7
0.020 00	—	0.8319	2.3
$Sm(ClO_4)_3$ vs. KCl			
0.097 296	0.179 65	0.8442[a]	21.5
0.180 56	0.347 59	0.8697	4.5
0.288 18	0.596 91	0.9299	−1.6
0.366 60	0.802 02	0.9810	−2.5
0.373 88	0.821 75	0.9855	−2.9
$Sm(ClO_4)_3$ vs. $CaCl_2$			
0.458 59	0.670 11	1.0465	−1.1
0.517 49	0.769 57	1.0929	2.5
0.601 38	0.910 21	1.1549	0.9
0.682 86	1.049 1	1.2178	−0.9
0.763 36	1.190 2	1.2853	−0.1
0.854 38	1.352 1	1.3650	0.8
0.956 68	1.533 8	1.4551	−2.0
1.032 0	1.675 6	1.5330	4.7
1.128 8	1.849 2	1.6225	−0.7
1.214 1	2.009 0	1.7114	1.6
1.317 4	2.201 3	1.8187	0.6
1.407 9	2.371 3	1.9159	0.1
1.507 2	2.558 7	2.0247	−1.0
1.598 4	2.732 4	2.1275	−1.1
1.691 2	2.909 5	2.2334	−1.8
1.768 6	3.059 7	2.3254	0.3
1.856 5	3.226 8	2.4258	−2.4
1.950 8	3.410 1	2.5390	−0.6
2.039 1	3.581 3	2.6444	0.2
2.148 0	3.791 6	2.7731	−0.3
2.271 4	4.031 9	2.9206	1.2
2.366 8	4.217 0	3.0326	1.0
2.461 9	4.402 5	3.1440	1.4
2.542 9	4.559 9	3.2366	0.4
2.649 3	4.771 6	3.3616	3.6
2.759 4	4.987 3	3.4828	0.6
2.861 1	5.188 6	3.5927	−2.6
2.993 6	5.458 7	3.7369	−3.3
3.069 3	5.617 2	3.8191	−2.7
3.187 4	5.877 3	3.9525	4.8
3.289 2	6.096 4	4.0523	−2.6
3.360 6	6.262 0	4.1283	−1.2
3.459 4	6.501 8	4.2338	1.7
3.539 1	6.702 6	4.3166	2.0
3.624 5	6.927 2	4.4037	0.8
3.707 0	7.158 4	4.4894	1.2
3.781 6	7.373 6	4.5628	−2.7
3.859 2	7.616 0	4.6442	−2.0
3.933 4	7.858 6	4.7219	−1.8
4.011 5	8.123 5	4.8031	−2.6
4.094 8	8.415 4	4.8889	−4.9
4.170 7	8.706 2	4.9744	0.0
$Sm(ClO_4)_3$ vs. H_2SO_4			
3.992 2	12.390	4.7914	6.0
4.064 9	12.695	4.8632	1.2
4.160 3	13.118	4.9654	2.1
4.248 9	13.518	5.0598	1.9
4.346 8	13.971	5.1649	2.3
4.447 9	14.444	5.2710	0.4
4.544 7	14.895	5.3673	−5.8
4.644 6	15.396	5.4783	1.6
4.662 1	15.480	5.4956	1.1
$Gd(ClO_4)_3$ (from conductance)			
0.005 00	—	0.8764	−3.3
0.010 00	—	0.8526	−1.6

Table I *(continued)*

m, Re(ClO$_4$)$_3$	m, standard	ϕ, Re(ClO$_4$)$_3$	$10^3\ \Delta\phi$
0.015 00	—	0.8399	−0.4
0.020 00	—	0.8319	0.3
	Gd(ClO$_4$)$_3$ vs. KCl		
0.108 83	0.200 47	0.8403	3.4
0.109 29	0.201 49	0.8410	3.9
0.189 63	0.369 79	0.8801	−1.3
0.277 84	0.577 75	0.9337	−2.6
0.368 16	0.816 29	0.9942	−2.3
0.440 27	1.026 0	1.0458	−1.4
0.529 34	1.308 7	1.1127	−0.4
0.534 45	1.325 8	1.1167	−0.3
0.540 43	1.346 7	1.1220	0.5
	Gd(ClO$_4$)$_3$ vs. CaCl$_2$		
0.566 21	0.858 26	1.1406	−0.9
0.662 88	1.025 7	1.2186	−0.4
0.744 55	1.170 1	1.2882	0.1
0.812 83	1.293 3	1.3500	1.7
0.891 93	1.437 6	1.4240	3.4
0.986 83	1.609 7	1.5121	1.1
1.072 7	1.768 6	1.5972	1.0
1.141 3	1.895 7	1.6661	−0.2
1.214 0	2.032 9	1.7431	0.7
1.300 7	2.196 7	1.8360	0.6
1.381 1	2.349 4	1.9242	0.3
1.445 8	2.472 4	1.9958	−0.4
1.510 7	2.597 0	2.0698	−0.2
1.587 5	2.744 0	2.1573	−1.1
1.673 3	2.909 5	2.2573	−1.1
1.752 7	3.062 6	2.3503	−1.8
1.839 3	3.231 0	2.4539	−1.1
1.906 3	3.361 5	2.5346	−0.7
1.926 6	3.400 4	2.5582	−1.4
1.988 5	3.520 9	2.6327	−1.3
2.065 0	3.669 2	2.7239	−2.3
2.155 1	3.846 4	2.8343	−0.6
2.232 9	3.999 6	2.9294	0.8
2.287 0	4.105 5	2.9943	0.6
2.313 7	4.159 8	3.0288	3.1
2.375 5	4.277 9	3.0985	−1.2
2.403 1	4.335 1	3.1351	2.5
2.494 9	4.517 0	3.2449	3.2
2.580 1	4.685 7	3.3448	2.6
2.615 3	4.753 0	3.3824	−1.0
2.678 5	4.882 3	3.4593	2.2
2.787 4	5.101 3	3.5833	0.6
2.882 1	5.294 7	3.6899	−0.6
2.966 4	5.469 6	3.7836	−1.7
3.063 4	5.676 6	3.8919	−1.0
3.157 1	5.879 4	3.9927	−2.8
3.245 1	6.077 7	4.0883	−2.3
3.340 5	6.302 7	4.1928	0.4
3.422 9	6.502 0	4.2792	−0.2
3.509 2	6.720 6	4.3693	−0.3
3.606 2	6.981 6	4.4711	1.0
3.679 6	7.189 4	4.5471	1.4
3.760 0	7.427 1	4.6287	0.7
3.866 8	7.761 8	4.7366	−0.6
3.957 0	8.061 9	4.8288	−0.6
3.972 8	8.115 2	4.8445	−1.1
4.049 7	8.389 5	4.9270	2.7
4.057 2	8.419 7	4.9369	4.8
4.098 3	8.568 0	4.9788	4.5
4.142 0	8.739 3	5.0283	8.8
4.149 7	8.765 6	5.0342	6.8
4.200 9	8.967 6	5.0841	3.6
4.266 9	9.235 7[b]	—	—
	Gd(ClO$_4$)$_3$ vs. H$_2$SO$_4$		
4.049 5	12.761	4.9159	−8.3
4.111 9	13.040	4.9838	−4.5
4.175 8	13.320	5.0485	−5.9
4.187 3	13.375	5.0623	−4.1
4.265 5	13.732	5.1454	−2.5
4.266 7	13.737	5.1464	−2.7
4.312 7	13.950	5.1954	−2.2
4.357 1	14.159	5.2433	−1.3
4.398 0	14.357	5.2891	1.0
4.424 3	14.478	5.3152	−1.1
4.444 8	14.580	5.3389	0.6
4.487 9	14.790	5.3859	1.0
4.573 9	15.215	5.4798	0.8
4.621 5	15.453	5.5315	−0.2
	Tb(ClO$_4$)$_3$ (from conductance)		
0.005 00	—	0.8764	−3.5
0.010 00	—	0.8526	−1.4
0.015 00	—	0.8399	0.2
0.020 00	—	0.8319	1.2
	Tb(ClO$_4$)$_3$ vs. KCl		
0.091 948	0.174 79	0.8696[a]	41.8
0.180 40	0.351 58	0.8803	3.6
0.276 92	0.580 24	0.9409	1.4
0.367 08	0.818 43	0.9997	−2.4
0.383 05	0.863 73	1.0111	−2.4
	Tb(ClO$_4$)$_3$ vs. CaCl$_2$		
0.471 54	0.703 06	1.0769	−2.1
0.502 36	0.757 77	1.1051	2.6
0.630 08	0.977 07	1.2051	0.3
0.749 39	1.188 0	1.3060	−0.9
0.848 03	1.367 0	1.3962	0.0
0.926 41	1.509 9	1.4694	−1.0
1.024 3	1.691 8	1.5664	−0.2
1.133 2	1.895 9	1.6782	0.0
1.216 9	2.054 7	1.7678	0.8
1.314 8	2.241 0	1.8746	0.6
1.416 6	2.436 2	1.9889	0.4
1.519 1	2.634 0	2.1068	0.4
1.610 5	2.811 5	2.2144	0.6
1.701 5	2.989 4	2.3237	1.5
1.783 2	3.147 6	2.4204	−0.4
1.866 9	3.312 2	2.5230	0.5
1.961 7	3.497 8	2.6384	−0.1
2.058 6	3.688 1	2.7570	−0.6
2.185 0	3.937 4	2.9124	−0.7
2.259 2	4.084 2	3.0036	−0.6
2.353 2	4.269 6	3.1172	−2.0
2.417 9	4.401 6	3.2001	2.2
2.496 2	4.557 1	3.2937	1.0
2.577 3	4.719 8	3.3908	0.8
2.676 6	4.919 1	3.5067	−1.3
2.769 6	5.110 4	3.6172	0.1
2.866 8	5.309 3	3.7267	−2.9
2.956 0	5.499 2	3.8307	−0.6
3.054 8	5.710 7	3.9406	−1.7
3.148 1	5.919 6	4.0469	1.4
3.244 7	6.138 9	4.1512	0.5
3.314 0	6.298 5	4.2222	−3.0
3.397 9	6.507 2	4.3155	1.1
3.497 7	6.761 1	4.4193	0.1
3.564 4	6.942 4	4.4907	2.2
3.645 9	7.174 6	4.5774	4.9
3.723 8	7.402 0	4.6549	2.6
3.789 4	7.602 8	4.7203	1.1
3.798 5	7.624 4	4.7244	−4.0
3.865 4	7.839 7	4.7920	−4.4
3.969 2	8.188 9	4.8970	−4.6
4.038 5	8.439 2	4.9720	0.2
	Tb(ClO$_4$)$_3$ vs. H$_2$SO$_4$		
3.827 8	11.978	4.7713	13.1
3.919 2	12.341	4.8543	3.3
3.950 8	12.444	4.8702	−12.8
4.015 9	12.753	4.9528	3.9
4.040 9	12.854	4.9747	0.5

Table I (continued)

m, Re(ClO$_4$)$_3$	m, standard	ϕ, Re(ClO$_4$)$_3$	$10^3 \Delta\phi$
4.096 7	13.115	5.0408	10.0
4.127 3	13.212	5.0528	−9.0
4.213 5	13.593	5.1396	−10.0
4.224 6	13.660	5.1594	−1.5
4.303 1	14.005	5.2338	−7.3
4.324 3	14.117	5.2626	−0.2
4.399 4	14.474	5.3434	3.3
4.402 1	14.491	5.3482	5.3
4.465 6	14.809	5.4218	13.4
4.491 0	14.918	5.4421	7.4
4.512 3	14.987	5.4485	−8.2
4.552 0	15.201	5.4997	1.8
4.619 6	15.513	5.5610	−7.1
	Dy(ClO$_4$)$_3$ (from conductance)		
0.005 00	—	0.8764	−2.4
0.010 00	—	0.8526	−0.7
0.015 00	—	0.8399	0.4
0.020 00	—	0.8319	0.9
	Dy(ClO$_4$)$_3$ vs. KCl		
0.091 684	0.174 79	0.8721^a	40.7
0.179 85	0.351 58	0.8830	2.0
0.275 84	0.580 24	0.9445	1.5
0.365 85	0.818 43	1.0031	−2.1
0.381 72	0.863 73	1.0146	−1.9
	Dy(ClO$_4$)$_3$ vs. CaCl$_2$		
0.470 50	0.703 06	1.0793	−2.6
0.501 26	0.757 77	1.1076	2.1
0.628 41	0.977 07	1.2083	0.8
0.747 29	1.188 0	1.3097	−0.3
0.845 55	1.367 0	1.4003	0.4
0.923 60	1.509 9	1.4739	−0.7
1.020 9	1.691 8	1.5717	0.2
1.129 1	1.895 9	1.6843	0.5
1.212 3	2.054 7	1.7745	1.2
1.309 8	2.241 0	1.8817	0.4
1.411 1	2.436 2	1.9966	0.0
1.512 7	2.634 0	2.1157	0.6
1.603 9	2.811 5	2.2235	−0.1
1.694 3	2.989 4	2.3336	0.9
1.775 6	3.147 6	2.4307	−1.3
1.859 0	3.312 2	2.5337	−0.9
1.952 7	3.497 8	2.6505	−0.3
2.048 7	3.688 1	2.7703	0.0
2.174 1	3.937 4	2.9270	0.3
2.248 2	4.084 2	3.0183	−0.8
2.341 0	4.269 6	3.1335	−0.9
2.406 0	4.401 6	3.2159	1.1
2.484 2	4.557 1	3.3096	−1.5
2.563 2	4.719 8	3.4095	1.8
2.661 4	4.919 1	3.5268	0.2
2.753 5	5.110 4	3.6384	1.4
2.849 5	5.309 3	3.7493	−1.3
2.938 4	5.499 2	3.8537	−0.7
3.035 8	5.710 7	3.9652	−1.3
3.129 4	5.919 6	4.0710	−1.7
3.223 4	6.138 9	4.1786	0.7
3.291 0	6.298 5	4.2517	−0.8
3.373 5	6.507 2	4.3467	4.2
3.472 6	6.761 1	4.4512	2.0
3.539 1	6.942 4	4.5228	2.8
3.621 7	7.174 6	4.6080	0.8
3.698 9	7.402 0	4.6863	−1.6
3.763 2	7.602 8	4.7532	−1.5
3.770 9	7.624 4	4.7590	−3.7
3.839 8	7.839 7	4.8240	−9.9
3.941 6	8.188 9	4.9313	−7.2
4.012 8	8.439 2	5.0039	−7.7
	Dy(ClO$_4$)$_3$ vs. H$_2$SO$_4$		
3.802 0	11.978	4.8037	8.8
3.889 6	12.341	4.8912	6.1
3.986 4	12.753	4.9894	5.0
4.070 6	13.115	5.0731	2.4
4.194 8	13.660	5.1961	−2.2
4.291 0	14.117	5.3035	6.0
4.373 8	14.491	5.3828	−0.6
4.438 6	14.809	5.4547	3.5
4.451 7	14.879	5.4717	6.8
4.466 0	14.918	5.4725	−7.4
4.521 9	15.201	5.5363	−2.7
4.604 2	15.616	5.6266	−0.1
	Ho(ClO$_4$)$_3$ (from conductance)		
0.005 00	—	0.8764	−3.4
0.010 00	—	0.8526	−1.0
0.015 00	—	0.8399	0.8
0.020 00	—	0.8319	2.1
	Ho(ClO$_4$)$_3$ vs. KCl		
0.101 51	0.192 55	0.8660^a	36.7
0.210 57	0.427 63	0.9148^a	21.7
0.325 35	0.705 31	0.9723	0.9
0.436 16	1.023 8	1.0533	0.6
0.534 40	1.339 2	1.1283	−1.0
0.602 07	1.578 6	1.1849	0.4
0.665 93	1.814 6	1.2368	−1.5
0.729 82	2.068 5	1.2935	−0.7
0.798 53	2.354 5	1.3548	−1.4
0.872 55	2.683 5	1.4252	−0.1
0.944 29	3.019 0	1.4955	0.9
0.985 29	3.215 6	1.5354	0.3
1.059 9	3.588 7	1.6111	0.4
1.077 5	3.674 0	1.6268	−2.0
1.094 1	3.769 3	1.6486	2.5
1.140 6	4.012 5	1.6964	1.6
1.178 3	4.217 1	1.7373	2.3
	Ho(ClO$_4$)$_3$ vs. CaCl$_2$		
1.138 9	1.911 3	1.6905	−2.6
1.177 5	1.985 3	1.7327	−1.4
1.214 5	2.056 6	1.7739	−0.1
1.320 1	2.259 1	1.8910	0.7
1.407 9	2.428 1	1.9904	0.7
1.493 4	2.593 8	2.0895	0.9
1.578 2	2.758 0	2.1884	0.0
1.665 5	2.928 3	2.2926	−0.3
1.751 8	3.098 0	2.3979	0.3
1.833 9	3.260 3	2.4996	1.4
1.934 2	3.455 6	2.6202	−2.0
2.037 3	3.658 8	2.7473	−3.2
2.112 1	3.811 0	2.8456	1.7
2.203 7	3.992 6	2.9591	0.6
2.299 9	4.184 9	3.0793	0.7
2.372 2	4.328 9	3.1680	−0.6
2.463 8	4.513 9	3.2820	−0.2
2.568 0	4.726 7	3.4117	1.4
2.672 9	4.940 6	3.5380	0.0
2.784 1	5.168 4	3.6678	−3.8
2.857 1	5.326 7	3.7598	1.5
2.989 1	5.605 8	3.9087	−3.8
3.090 1	5.832 9	4.0287	0.3
3.185 8	6.049 7	4.1352	−1.1
3.318 6	6.367 2	4.2835	0.3
3.385 3	6.536 0	4.3586	2.9
3.438 3	6.673 8	4.4172	4.4
3.524 7	6.906 3	4.5106	5.9
3.693 3	7.388 8	4.6834	2.4
3.761 3	7.593 9	4.7491	−2.0
3.773 9	7.636 3	4.7638	−0.3
3.840 5	7.849 2	4.8297	−2.5
3.913 9	8.089 9	4.9006	−6.3
3.915 8	8.099 9	4.9048	−4.0
3.941 1	8.183 8	4.9286	−5.9
3.982 4	8.331 9	4.9733	−3.1

Table I (continued)

m, $Re(ClO_4)_3$	m, standard	ϕ, $Re(ClO_4)_3$	$10^3\ \Delta\phi$
	$Ho(ClO_4)_3$ vs. H_2SO_4		
3.983 1	12.722	4.9772	0.1
4.005 8	12.818	4.9994	−0.8
4.009 7	12.853	5.0129	8.8
4.102 4	13.245	5.1004	2.4
4.166 5	13.537	5.1693	6.2
4.218 1	13.750	5.2122	−3.3
4.335 1	14.290	5.3334	−2.0
4.471 1	14.936	5.4748	−2.1
4.475 8	14.969	5.4845	2.7
4.577 0	15.484	5.5995	10.3
4.631 4	15.717	5.6393	−8.5
	$Er(ClO_4)_3$ *(from conductance)*		
0.005 00	—	0.8764	−3.8
0.010 00	—	0.8526	−1.3
0.015 00	—	0.8399	0.8
0.020 00	—	0.8319	2.1
	$Er(ClO_4)_3$ vs. KCl		
0.101 43	0.192 55	0.8667^a	38.5
0.210 43	0.427 63	0.9154^a	22.9
0.324 84	0.705 31	0.9738	2.1
0.435 75	1.023 8	1.0543	0.0
0.533 48	1.339 2	1.1302	−1.0
0.601 01	1.578 6	1.1870	0.2
0.664 52	1.814 6	1.2395	−1.3
0.728 52	2.068 5	1.2958	−1.2
0.796 99	2.354 5	1.3574	−1.6
0.870 63	2.683 5	1.4284	0.3
0.942 59	3.019 0	1.4982	0.5
0.983 16	3.215 6	1.5388	0.8
1.057 5	3.588 7	1.6148	1.3
1.075 1	3.674 0	1.6304	−1.3
1.092 7	3.769 3	1.6507	0.7
1.138 4	4.012 5	1.6997	1.6
1.175 7	4.217 1	1.7411	3.2
	$Er(ClO_4)_3$ vs. $CaCl_2$		
1.136 8	1.911 3	1.6936	−2.8
1.175 2	1.985 3	1.7361	−1.3
1.212 2	2.056 6	1.7772	−0.2
1.318 0	2.259 1	1.8940	−0.5
1.405 2	2.428 1	1.9942	0.4
1.490 7	2.593 8	2.0933	−0.1
1.575 0	2.758 0	2.1929	−0.5
1.661 5	2.928 3	2.2981	0.4
1.747 6	3.098 0	2.4037	0.5
1.829 7	3.260 3	2.5053	0.6
1.927 3	3.455 6	2.6295	2.8
2.031 3	3.658 8	2.7554	−2.2
2.106 6	3.811 0	2.8530	0.2
2.196 8	3.992 6	2.9684	1.4
2.292 5	4.184 9	3.0892	1.2
2.364 8	4.328 9	3.1779	−1.4
2.455 7	4.513 9	3.2928	−0.7
2.559 5	4.726 7	3.4231	0.2
2.663 6	4.940 6	3.5503	−1.0
2.773 4	5.186 4	3.6820	−3.2
2.847 4	5.326 7	3.7726	−1.5
2.976 3	5.605 8	3.9255	−1.3
3.078 3	5.832 9	4.0441	−1.3
3.173 0	6.049 7	4.1519	−1.9
3.304 0	6.367 2	4.3024	1.6
3.369 5	6.536 0	4.3790	5.9
3.423 6	6.673 8	4.4361	3.8
3.508 8	6.906 3	4.5311	6.5
3.676 8	7.388 8	4.7044	1.0
3.743 5	7.593 9	4.7717	−1.8
3.755 3	7.636 3	4.7874	1.5
3.822 6	7.849 2	4.8523	−3.9
3.894 2	8.089 9	4.9254	−5.3
3.896 5	8.099 9	4.9291	−3.9
3.920 5	8.183 8	4.9545	−3.5
3.962 7	8.331 9	4.9980	−3.7
	$Er(ClO_4)_3$ vs. H_2SO_4		
3.963 5	12.722	5.0018	−0.7
3.984 2	12.818	5.0265	2.5
3.991 1	12.853	5.0362	5.1
4.083 0	13.245	5.1246	−1.7
4.146 2	13.537	5.1946	2.7
4.194 3	13.750	5.2418	0.0
4.310 9	14.290	5.3633	−0.1
4.446 7	14.936	5.5048	−1.4
4.449 8	14.969	5.5165	7.1
4.557 6	15.484	5.6233	−0.5
4.622 1	15.804	5.6901	−2.5
	$Tm(ClO_4)_3$ (from conductance)		
0.005 00	—	0.8764	−2.0
0.010 00	—	0.8526	−0.5
0.015 00	—	0.8399	0.4
0.020 00	—	0.8319	0.9
	$Tm(ClO_4)_3$ vs. KCl		
0.096 434	0.179 65	0.8517^a	19.4
0.178 29	0.347 59	0.8807	3.8
0.284 29	0.596 91	0.9426	−2.3
0.361 14	0.802 02	0.9958	−2.4
0.368 34	0.821 75	1.0003	−3.0
	$Tm(ClO_4)_3$ vs. $CaCl_2$		
0.451 10	0.670 11	1.0639	−0.6
0.508 43	0.769 57	1.1124	3.5
0.590 10	0.910 21	1.1770	1.9
0.669 66	1.049 1	1.2418	−1.0
0.747 58	1.190 2	1.3124	0.3
0.835 91	1.352 1	1.3952	1.0
0.935 43	1.533 8	1.4882	−2.8
1.008 4	1.675 6	1.5689	4.2
1.102 7	1.849 2	1.6609	−2.2
1.184 6	2.009 0	1.7540	2.6
1.285 8	2.201 3	1.8634	−0.3
1.373 7	2.371 3	1.9636	−0.4
1.470 1	2.558 7	2.0758	−0.8
1.559 0	2.732 4	2.1813	−1.2
1.649 4	2.909 5	2.2900	−2.0
1.724 9	3.059 7	2.3843	−0.4
1.809 7	3.226 8	2.4885	−1.4
1.901 4	3.410 1	2.6049	0.1
1.986 9	3.581 3	2.7139	1.1
2.091 8	3.791 6	2.8477	1.8
2.211 3	4.031 9	3.0000	2.0
2.303 2	4.217 0	3.1164	1.4
2.395 1	4.402 5	3.2317	0.0
2.471 1	4.559 9	3.3307	2.8
2.575 2	4.771 6	3.4584	−0.5
2.679 6	4.987 3	3.5865	−2.5
2.775 3	5.188 6	3.7038	−3.3
2.901 3	5.458 7	3.8558	−4.4
2.972 7	5.617 2	3.9432	−2.5
3.086 5	5.877 3	4.0817	1.6
3.180 9	6.096 4	4.1903	0.6
3.250 1	6.262 0	4.2686	−0.1
3.344 0	6.501 8	4.3799	5.4
3.421 5	6.702 6	4.4650	4.4
3.505 2	6.927 2	4.5536	1.5
3.584 6	7.158 4	4.6427	4.9
3.658 4	7.373 6	4.7164	0.0
3.736 5	7.616 0	4.7967	−2.1
3.811 2	7.858 6	4.8733	−3.6
3.890 0	8.123 5	4.9531	−5.6
3.972 9	8.415 4	5.0389	−5.6
4.048 4	8.706 2	5.1246	2.2

Table I (continued)

m, Re(ClO_4)$_3$	m, standard	ϕ, Re(ClO_4)$_3$	$10^3\ \Delta\phi$
Tm(ClO_4)$_3$ vs. H_2SO_4			
3.902 8	12.514	4.9677	−4.3
3.982 4	12.866	5.0541	−0.2
4.055 0	13.189	5.1310	1.7
4.133 7	13.542	5.2128	2.1
4.185 9	13.782	5.2684	3.3
4.239 9	14.029	5.3238	2.0
4.301 0	14.308	5.3845	−2.0
4.327 2	14.438	5.4150	0.6
4.368 4	14.639	5.4606	1.8
4.420 5	14.894	5.5175	1.7
4.503 0	15.302	5.6066	−1.2
4.621 5	15.922	5.7444	−1.4
Yb(ClO_4)$_3$ (from conductance)			
0.005 00	—	0.8764	−3.7
0.010 00	—	0.8526	−1.2
0.015 00	—	0.8399	0.8
0.020 00	—	0.8319	2.2
Yb(ClO_4)$_3$ vs. KCl			
0.101 25^c	0.192 55	0.8683^a	39.7
0.210 05	0.427 63	0.9170^a	23.7
0.324 38	0.705 31	0.9752	2.2
0.435 27	1.023 8	1.0555	−0.5
0.532 40	1.339 2	1.1325	−0.2
0.600 61	1.578 6	1.1877	−1.2
0.663 78	1.814 6	1.2408	−2.0
0.727 41	2.068 5	1.2977	−1.1
0.795 07	2.354 5	1.3607	0.4
0.869 73	2.683 5	1.4298	−0.6
0.941 41	3.019 0	1.5001	0.1
0.982 03	3.215 6	1.5405	0.1
1.056 1	3.588 7	1.6169	1.1
1.073 8	3.674 0	1.6324	−1.8
1.090 3	3.769 3	1.6543	2.9
1.136 8	4.012 5	1.7021	1.7
1.174 1	4.217 1	1.7435	3.1
Yb(ClO_4)$_3$ vs. $CaCl_2$			
1.135 2	1.911 3	1.6960	−2.8
1.173 4	1.985 3	1.7388	−0.9
1.210 5	2.056 6	1.7797	−0.2
1.316 4	2.259 1	1.8964	−1.1
1.403 1	2.428 1	1.9972	0.8
1.488 1	2.593 8	2.0970	1.3
1.572 4	2.758 0	2.1965	0.5
1.658 7	2.928 3	2.3020	1.5
1.745 1	3.098 0	2.4071	0.5
1.827 6	3.260 3	2.5082	−1.0
1.926 1	3.455 6	2.6312	−1.8
2.027 8	3.658 8	2.7602	−1.5
2.103 3	3.811 0	2.8575	−0.2
2.193 1	3.992 6	2.9734	1.2
2.288 9	4.184 9	3.0941	−0.2
2.360 1	4.328 9	3.1842	−0.6
2.450 9	4.513 9	3.2992	−0.6
2.554 0	4.726 7	3.4304	0.8
2.658 0	4.940 6	3.5578	−1.5
2.765 6	5.168 4	3.6923	0.5
2.840 1	5.326 7	3.7823	−0.3
2.969 3	5.605 8	3.9348	−2.9
3.069 8	5.832 9	4.0553	−0.8
3.163 7	6.049 7	4.1641	−1.1
3.294 4	6.367 2	4.3149	0.7
3.358 7	6.536 0	4.3931	6.6
3.412 2	6.673 8	4.4510	4.9
3.497 6	6.906 3	4.5456	5.4
3.665 7	7.388 8	4.7187	−3.9
3.730 1	7.593 9	4.7889	−2.8
3.741 0	7.636 3	4.8057	2.4
3.809 9	7.849 2	4.8684	−8.4
3.878 6	8.089 9	4.9452	−4.7
3.880 2	8.099 9	4.9498	−1.7
3.905 7	8.183 8	4.9733	−5.4
3.948 7	8.331 9	5.0157	−8.5
Yb(ClO_4)$_3$ vs. H_2SO_4			
3.945 0	12.722	5.0253	5.0
3.966 5	12.818	5.0489	5.8
3.973 8	12.853	5.0581	7.3
4.064 0	13.245	5.1486	2.0
4.128 0	13.537	5.2175	2.7
4.174 8	13.750	5.2663	1.5
4.294 8	14.290	5.3835	−10.3
4.422 8	14.936	5.5345	1.4
4.426 0	14.969	5.5462	9.5
4.532 6	15.484	5.6543	−0.3
4.596 4	15.810	5.7247	−1.3
4.640 0	16.037	5.7735	−1.7
Lu(ClO_4)$_3$ (from conductance)			
0.005 00	—	0.8764	−2.7
0.010 00	—	0.8526	−1.2
0.015 00	—	0.8399	−0.2
0.020 00	—	0.8319	0.2
Lu(ClO_4)$_3$ vs. KCl			
0.108 52	0.200 47	0.8427	3.2
0.108 97	0.201 49	0.8434	3.7
0.188 91	0.369 79	0.8835	−1.5
0.276 59	0.577 75	0.9380	−2.9
0.366 11	0.816 29	0.9998	−2.2
0.437 53	1.026 0	1.0523	−1.3
0.525 39	1.308 7	1.1210	0.4
0.530 47	1.325 8	1.1250	0.4
0.536 49	1.346 7	1.1303	0.9
Lu(ClO_4)$_3$ vs. $CaCl_2$			
0.562 17	0.858 26	1.1488	−1.2
0.657 70	1.025 7	1.2282	−1.1
0.738 19	1.170 1	1.2993	−0.6
0.805 23	1.293 3	1.3627	1.5
0.883 10	1.437 6	1.4382	3.0
0.976 39	1.609 7	1.5283	0.6
1.060 7	1.768 6	1.6153	0.6
1.127 7	1.895 7	1.6861	0.3
1.199 2	2.032 9	1.7646	0.8
1.284 4	2.196 7	1.8593	0.2
1.363 3	2.349 4	1.9493	−0.3
1.426 2	2.472 4	2.0233	0.1
1.489 9	2.597 0	2.0987	0.0
1.565 0	2.744 0	2.1883	−0.9
1.648 8	2.909 5	2.2908	−0.9
1.725 9	3.062 6	2.3868	−0.5
1.810 1	3.231 0	2.4935	0.8
1.875 9	3.361 5	2.5757	−0.2
1.895 7	3.400 4	2.5999	−1.1
1.956 0	3.520 9	2.6765	−1.3
2.029 6	3.669 2	2.7714	−0.5
2.117 8	3.846 4	2.8842	−0.9
2.193 5	3.999 6	2.9820	−0.5
2.245 3	4.105 5	3.0499	0.8
2.271 5	4.159 8	3.0850	2.2
2.330 3	4.277 9	3.1586	0.2
2.357 9	4.335 1	3.1952	1.3
2.446 6	4.517 0	3.3090	1.4
2.528 4	4.685 7	3.4132	1.2
2.561 6	4.753 0	3.4533	−0.8
2.622 9	4.882 3	3.5326	0.9
2.727 3	5.101 3	3.6622	−0.6
2.818 2	5.294 7	3.7735	−2.3
2.898 5	5.469 6	3.8722	−2.3
2.991 7	5.676 6	3.9852	−2.5
3.080 5	5.879 4	4.0919	−2.2
3.164 4	6.077 7	4.1925	−0.7
3.256 3	6.302 7	4.3012	1.0

Table I (continued)

m, $Re(ClO_4)_3$	m, standard	ϕ, $Re(ClO_4)_3$	$10^3\ \Delta\phi$	m, $Re(ClO_4)_3$	m, standard	ϕ, $Re(ClO_4)_3$	$10^3\ \Delta\phi$
3.334 6	6.502 0	4.3925	2.5	$Lu(ClO_4)_3$ vs. H_2SO_4			
3.418 6	6.720 6	4.4850	0.0	3.945 3	12.761	5.0457	−8.0
3.511 5	6.981 6	4.5917	3.2	4.007 9	13.040	5.1132	−6.1
3.583 5	7.189 4	4.6690	1.5	4.082 7	13.375	5.1920	−5.7
3.661 3	7.427 1	4.7535	1.5	4.161 2	13.737	5.2769	−3.2
3.765 8	7.761 8	4.8637	−0.4	4.206 9	13.950	5.3260	−2.3
3.854 5	8.061 9	4.9572	−1.0	4.292 2	14.357	5.4195	0.3
3.869 3	8.115 2	4.9741	0.3	4.297 9	14.377	5.4221	−3.2
3.945 5	8.389 5	5.0571	3.3	4.317 3	14.478	5.4469	0.7
3.954 1	8.419 7	5.0656	2.7	4.349 3	14.628	5.4793	−1.5
3.993 7	8.568 0	5.1092	4.8	4.453 7	15.148	5.5961	0.3
4.037 5	8.739 3	5.1584	8.1	4.481 0	15.286	5.6267	0.1
4.045 1	8.765 6	5.1644	6.1	4.520 5	15.488	5.6713	−0.2
4.097 2	8.967 6	5.2128	−0.1	4.577 5	15.785	5.7368	−0.8
4.162 4	9.235 7[b]	—	—	4.631 3	16.082	5.8047	3.0

[a] This point given a weight of zero in the least-squares fit. [b] The osmotic coefficients of $CaCl_2$ solutions are not highly reliable above 9.0 m so this point was not included in the least-squares fit. [c] The molalities of the $Yb(ClO_4)_3$ solutions in equilibrium with KCl solutions were adjusted a small amount (see text for discussion).

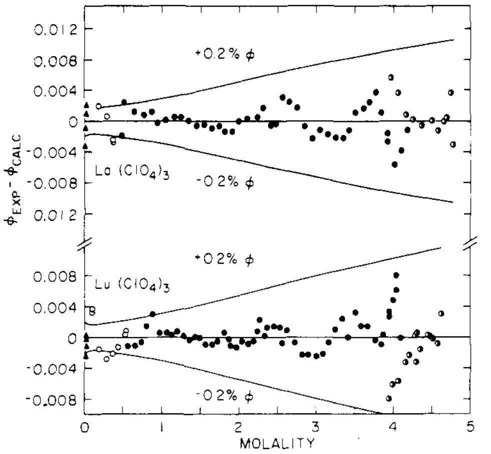

Figure 1. Differences between experimental and calculated osmotic coefficients of $La(ClO_4)_3$ and $Lu(ClO_4)_3$ at 25 °C. ▲, estimated from conductances; O, isopiestic vs. KCl; ●, isopiestic vs. $CaCl_2$; ◑, isopiestic vs. H_2SO_4.

Debye–Hückel ion-size parameters from electrical conductance data. These å values were used to calculate approximate osmotic coefficients for the rare earth perchlorates at 0.005, 0.010, 0.015, and 0.020 m. The Debye–Hückel equation would not be expected to apply to higher concentrations than these, and may already be breaking down by 0.020 m. Since the dilute solution ϕ values for the rare earth perchlorates are only approximate, they were averaged (Nd data were not included since they are much different than results for the other salts). The average values were included in the least-squares fits for each salt, along with the experimental isopiestic data. It was found that good fits could be obtained by fixing the first three powers at $r_1 = 0.75$, $r_2 = 0.875$, and $r_3 = 1$ while the other four powers were allowed to vary in increments of $m^{1/2}$. Similar series also worked for the rare earth chlorides (*16*). The coefficient of the $r_1 = 0.75$ term was much smaller for each rare earth perchlorate than for the corresponding rare earth chloride, while the percent error of this coefficient was larger. However, this term was retained since we felt that it would be best to utilize power series with the dominant terms having the same powers, to allow a more meaningful comparison with the rare earth chloride data. The differences between the experimental and calculated values of ϕ are given in Table I while the coefficients, powers, and standard deviations for the best fits are given in Table II. Table III contains values of ϕ, a_1, and $\gamma_\pm$ at various even molalities.

Fifteen points out of nearly 800 points were given weights of zero in the least-squares fits to eq 3 (one or two points were weighted zero for each salt), 12 of these from low concentrations where the isopiestic measurements are of lower accuracy. The other three points that were dropped were measured relative to a 9.24 m $CaCl_2$ standard solution. The osmotic coefficients of $CaCl_2$ solutions are not known as accurately above 9 m as they are below this concentration (*5*) so these three rare earth perchlorate osmotic coefficients were not included in the least-squares fits, although the isopiestic molalities should be reliable. All other osmotic coefficients were given unit weights.

The standard deviations of eq 3 are slightly larger for the rare earth perchlorates than for the rare earth chlorides. This occurs, in part, because three different electrolytes were used as isopiestic standards for the perchlorates, whereas only two were used for the chlorides. Also, the osmotic coefficients of the rare earth perchlorates become much larger than for the chlorides, so a similar percentage scatter in the data at high concentrations would result in a larger standard deviation for the perchlorates. The largest standard deviation was obtained for $Tb(ClO_4)_3$, mainly due to scatter in the H_2SO_4–$Tb(ClO_4)_3$ data. The original determination exhibited significant scatter so new samples were weighed out and the equilibrations repeated. The second run had less scatter than the first but was otherwise in agreement with it, so both determinations are reported.

The data for $Yb(ClO_4)_3$ measured with the KCl standard had a small mismatch with data obtained using the $CaCl_2$ standard. The samples that were equilibrated with the $CaCl_2$ and H_2SO_4 standards were weighed directly from the concentrated stock solution, while those for the KCl equilibrations were weighed from a dilution prepared from the concentrated stock solution. The $Yb(ClO_4)_3$ stock concentration was remeasured and found to agree with earlier determinations, but too little of the dilution remained to perform an analysis on it. We assumed the concentration of this dilution was slightly in error and adjusted the $Yb(ClO_4)_3$ molality to bring the dilute data in agreement with the data at higher concentrations. This adjustment was about 0.37% in terms of the molality. As will be seen below in series plots of the results for the various perchlorates, $Yb(ClO_4)_3$ shows no unusual behavior after this is done. While this adjustment has only a small effect on the thermodynamic properties of $Yb(ClO_4)_3$, we do feel that the KCl–$Yb(ClO_4)_3$ isopiestic ratio should be redetermined as a check on our results.

The errors due to isopiestic measurements have been discussed in detail elsewhere (*16*), so they need only be summa-

Table II. Coefficients and Powers for Osmotic Coefficient Polynomials

i	r_i	A_i	r_i	A_i
		$La(ClO_4)_3$		$Pr(ClO_4)_3$
1	0.75	−0.611 630 77	0.75	−0.146 035 90
2	0.875	18.317 344	0.875	16.897 710
3	1	−16.714 981	1	−15.644 464
4	1.5	2.394 006 4	1.5	2.275 663 6
5	4.5	−1.803 527 3 × 10^{-2}	4	−1.607 634 9 × 10^{-2}
6	6	4.046 763 3 × 10^{-3}	7.5	1.893 456 6 × 10^{-4}
7	6.5	−1.236 527 1 × 10^{-3}	8	−7.115 862 2 × 10^{-5}
S.D.		0.002 2		0.003 1
		$Nd(ClO_4)_3$		$Sm(ClO_4)_3$
1	0.75	−0.746 856 38	0.75	0.380 496 16
2	0.875	18.861 635	0.875	15.252 927
3	1	−17.215 278	1	−14.325 377
4	1.5	2.480 681 9	1.5	2.078 200 0
5	5	−3.679 963 1 × 10^{-2}	5	−9.956 881 0 × 10^{-3}
6	5.5	2.812 904 0 × 10^{-2}	6	2.541 543 6 × 10^{-3}
7	6	−5.544 187 3 × 10^{-3}	7.5	−7.213 008 8 × 10^{-5}
S.D.		0.002 7		0.002 5
		$Gd(ClO_4)_3$		$Tb(ClO_4)_3$
1	0.75	−1.457 932 1	0.75	−0.680 663 35
2	0.875	21.195 040	0.875	18.553 762
3	1	−19.144 330	1	−16.886 070
4	1.5	2.883 278 3	1.5	2.465 672 2
5	3	−7.116 128 3 × 10^{-2}	3.5	−2.942 224 9 × 10^{-2}
6	7.5	5.695 923 4 × 10^{-5}	7.5	8.998 206 9 × 10^{-5}
7	8	−2.034 539 5 × 10^{-5}	8	−3.281 851 7 × 10^{-5}
S.D.		0.002 7		0.004 6
		$Dy(ClO_4)_3$		$Ho(ClO_4)_3$
1	0.75	−2.022 008 0	0.75	−0.296 580 52
2	0.875	22.744 091	0.875	17.276 361
3	1	−20.217 441	1	−15.849 718
4	1.5	2.999 298 2	1.5	2.326 829 3
5	3	−7.268 664 9 × 10^{-2}	3.5	−2.609 925 7 × 10^{-2}
6	7.5	5.345 460 0 × 10^{-5}	7.5	6.042 826 9 × 10^{-5}
7	8	−1.901 983 6 × 10^{-5}	8	−2.091 373 7 × 10^{-5}
S.D.		0.003 4		0.003 2
		$Er(ClO_4)_3$		$Tm(ClO_4)_3$
1	0.75	0.251 990 08	0.75	−3.242 212 0
2	0.875	15.545 931	0.875	27.177 141
3	1	−14.460 745	1	−24.409 996
4	1.5	2.111 251 7	1.5	4.591 455 8
5	4	−1.263 187 3 × 10^{-2}	2	−0.677 669 99
6	7.5	1.044 566 0 × 10^{-4}	5	−2.022 785 2 × 10^{-3}
7	8	−3.717 907 8 × 10^{-5}	6	3.453 460 1 × 10^{-4}
S.D.		0.002 6		0.002 6
		$Yb(ClO_4)_3$		$Lu(ClO_4)_3$
1	0.75	0.190 743 89	0.75	−2.233 923 1
2	0.875	15.706 882	0.875	23.609 845
3	1	−14.563 775	1	−21.048 795
4	1.5	2.117 994 8	1.5	3.118 743 5
5	4	−1.241 458 6 × 10^{-2}	2	0.232 459 01
6	7.5	9.925 877 6 × 10^{-5}	2.5	−0.245 605 76
7	8	−3.499 638 9 × 10^{-5}	8	2.487 236 6 × 10^{-6}
S.D.		0.003 5		0.002 5

rized here. The stock and standard solution concentration uncertainties, together with the maximum error in the equilibrium molalities, result in a maximum error in the experimental rare earth perchlorate osmotic coefficients of about 0.4% above 4 *m*, 0.3% between 0.5 and 4 *m*, and about 0.34% below 0.5 *m*. The probable errors are about two-thirds of these values. The relative errors in the osmotic coefficients as a function of concentration are somewhat smaller than these values. The errors in the osmotic coefficients of the isopiestic standards have been discussed elsewhere (*4*, *5*). Due to the absence of experimental dilute solution activity coefficients (approximate values were used), the activity coefficients reported here are uncertain by about 1–2%.

The molal solubilities of six of the rare earth perchlorates, determined isopiestically in this study, are within 0.2% of those determined by direct analyses (*13*), and all of the solubilities are within 0.5% except for $Yb(ClO_4)_3$. The saturated solution isopiestic measurements were performed by equilibrating samples of the rare earth perchlorate solutions with other samples that contained both solution and the corresponding hydrated solid rare earth perchlorates. The solid hydrated rare earth perchlorates had been prepared by concentrating samples of the stock solutions over a $Mg(ClO_4)_2$ desiccant. The resulting solid rare earth perchlorates form on the surface of the solution and they are glassy in appearance. Zinov'ev and Shchirova (*20*) studied the H_2O–$HClO_4$–$Ce(ClO_4)_3$ phase system and found that both eight and nine hydrated $Ce(ClO_4)_3$ can exist in the solid phase. The fact that the solid phases were glassy in appearance suggests that more than one hydrate may have been present. If so, the solubility differences found between the direct analyses

Table III. Osmotic Coefficients, Water Activities, and Activity Coefficients at Even Molalities

m	ϕ	a_1	$\gamma_\pm$
	$La(ClO_4)_3$		
0.1	0.8270	0.994 06	0.3793
0.2	0.8796	0.987 40	0.3600
0.3	0.9406	0.979 87	0.3686
0.4	1.0057	0.971 43	0.3902
0.5	1.0749	0.962 01	0.4218
0.6	1.1485	0.951 56	0.4632
0.7	1.2266	0.940 00	0.5154
0.8	1.3093	0.927 30	0.5801
0.9	1.3967	0.913 40	0.6599
1.0	1.4885	0.898 3	0.7578
1.2	1.6844	0.864 5	1.025
1.4	1.8942	0.826 1	1.427
1.6	2.1145	0.783 7	2.033
1.8	2.3415	0.738 1	2.947
2.0	2.5715	0.690 3	4.324
2.2	2.8011	0.641 4	6.387
2.4	3.0275	0.592 4	9.460
2.6	3.2485	0.544 1	14.00
2.8	3.4627	0.497 2	20.65
3.0	3.6698	0.452 3	30.33
3.2	3.8700	0.409 7	44.30
3.4	4.0642	0.369 4	64.39
3.6	4.2538	0.331 7	93.23
3.8	4.4400	0.296 5	134.6
4.0	4.6240	0.263 7	193.9
4.2	4.8055	0.233 5	278.7
4.4	4.9827	0.206 0	398.8
4.6	5.1511	0.181 3	565.4
4.7759	5.2854	0.162 2	757.7
	$Pr(ClO_4)_3$		
0.1	0.8238	0.994 08	0.3775
0.2	0.8752	0.987 47	0.3570
0.3	0.9359	0.979 97	0.3647
0.4	1.0013	0.971 55	0.3856
0.5	1.0709	0.962 15	0.4166
0.6	1.1448	0.951 71	0.4574
0.7	1.2233	0.940 16	0.5089
0.8	1.3064	0.927 45	0.5727
0.9	1.3940	0.913 56	0.6514
1.0	1.4859	0.898 5	0.7479
1.2	1.6821	0.864 6	1.012
1.4	1.8926	0.826 2	1.409
1.6	2.1142	0.783 7	2.010
1.8	2.3436	0.737 9	2.920
2.0	2.5771	0.689 8	4.301
2.2	2.8112	0.640 4	6.387
2.4	3.0431	0.590 8	9.522
2.6	3.2702	0.541 9	14.20
2.8	3.4910	0.494 4	21.13
3.0	3.7050	0.448 9	31.30
3.2	3.9126	0.405 7	46.18
3.4	4.1152	0.364 9	67.88
3.6	4.3149	0.326 5	99.60
3.8	4.5141	0.290 5	146.2
4.0	4.7148	0.256 9	215.1
4.2	4.9175	0.225 8	317.3
4.4	5.1197	0.197 2	468.2
4.6	5.3145	0.171 8	686.3
4.7182	5.4208	0.158 3	852.7
	$Nd(ClO_4)_3$		
0.1	0.8283	0.994 05	0.3808
0.2	0.8800	0.987 40	0.3614
0.3	0.9397	0.979 89	0.3695
0.4	1.0037	0.971 48	0.3905
0.5	1.0719	0.962 11	0.4215
0.6	1.1447	0.951 71	0.4622
0.7	1.2224	0.940 20	0.5138
0.8	1.3051	0.927 52	0.5779
0.9	1.3926	0.913 64	0.6572
1.0	1.4850	0.898 5	0.7548
1.2	1.6829	0.864 6	1.023
1.4	1.8958	0.825 9	1.428
1.6	2.1203	0.783 1	2.044
1.8	2.3524	0.737 0	2.981
2.0	2.5884	0.688 6	4.406
2.2	2.8249	0.639 0	6.567
2.4	3.0590	0.589 2	9.826
2.6	3.2888	0.540 0	14.71
2.8	3.5129	0.492 2	21.99
3.0	3.7311	0.446 4	32.77
3.2	3.9438	0.402 8	48.69
3.4	4.1523	0.361 6	72.15
3.6	4.3582	0.322 8	106.8
3.8	4.5633	0.286 6	158.0
4.0	4.7691	0.252 9	234.3
4.2	4.9765	0.221 8	348.2
4.4	5.1848	0.193 2	518.5
4.6	5.3913	0.167 4	771.3
4.6822	5.4744	0.157 7	906.6
	$Sm(ClO_4)_3$		
0.1	0.8238	0.994 08	0.3782
0.2	0.8766	0.987 45	0.3583
0.3	0.9392	0.979 90	0.3671
0.4	1.0064	0.971 41	0.3893
0.5	1.0776	0.961 92	0.4218
0.6	1.1530	0.951 37	0.4644
0.7	1.2326	0.939 72	0.5179
0.8	1.3166	0.926 91	0.5843
0.9	1.4051	0.912 90	0.6659
1.0	1.4978	0.897 7	0.7661
1.2	1.6953	0.863 6	1.040
1.4	1.9072	0.825 0	1.453
1.6	2.1305	0.782 2	2.081
1.8	2.3619	0.736 1	3.036
2.0	2.5978	0.687 7	4.492
2.2	2.8350	0.638 0	6.705
2.4	3.0705	0.588 0	10.06
2.6	3.3018	0.538 7	15.09
2.8	3.5276	0.490 8	22.62
3.0	3.7471	0.444 8	33.80
3.2	3.9610	0.401 2	50.32
3.4	4.1705	0.359 9	74.72
3.6	4.3776	0.321 2	110.8
3.8	4.5846	0.285 0	164.5
4.0	4.7936	0.251 1	245.0
4.2	5.0056	0.219 8	366.3
4.4	5.2195	0.191 1	549.3
4.6	5.4308	0.165 3	822.3
4.6621	5.4945	0.157 9	930.5
	$Gd(ClO_4)_3$		
0.1	0.8328	0.994 02	0.3835
0.2	0.8877	0.987 29	0.3666
0.3	0.9508	0.979 66	0.3775
0.4	1.0186	0.971 07	0.4020
0.5	1.0910	0.961 45	0.4373
0.6	1.1681	0.950 75	0.4835
0.7	1.2500	0.938 89	0.5419
0.8	1.3368	0.925 83	0.6145
0.9	1.4281	0.911 54	0.7042
1.0	1.5239	0.896 0	0.8147
1.2	1.7276	0.861 2	1.119
1.4	1.9449	0.821 8	1.580
1.6	2.1728	0.778 4	2.285
1.8	2.4082	0.731 7	3.366
2.0	2.6479	0.682 8	5.023
2.2	2.8890	0.632 5	7.565
2.4	3.1289	0.582 1	11.45
2.6	3.3655	0.532 3	17.36
2.8	3.5971	0.483 9	26.31
3.0	3.8227	0.437 6	39.74
3.2	4.0420	0.393 7	59.79

Table III (continued)

m	ϕ	a_1	$\gamma_\pm$
3.4	4.2553	0.352 5	89.57
3.6	4.4637	0.314 1	133.7
3.8	4.6690	0.278 4	199.0
4.0	4.8734	0.245 4	296.3
4.2	5.0796	0.214 9	442.0
4.4	5.2902	0.186 9	662.9
4.6	5.5078	0.161 1	1002
4.6215	5.5317	0.158 5	1048
		$Tb(ClO_4)_3$	
0.1	0.8314	0.994 03	0.3825
0.2	0.8889	0.987 27	0.3665
0.3	0.9551	0.979 56	0.3790
0.4	1.0258	0.970 86	0.4054
0.5	1.1007	0.961 12	0.4430
0.6	1.1800	0.950 26	0.4919
0.7	1.2638	0.938 24	0.5534
0.8	1.3522	0.925 01	0.6298
0.9	1.4451	0.910 53	0.7242
1.0	1.5423	0.894 8	0.8406
1.2	1.7489	0.859 7	1.162
1.4	1.9696	0.819 8	1.653
1.6	2.2013	0.775 8	2.408
1.8	2.4411	0.728 6	3.574
2.0	2.6855	0.679 1	5.379
2.2	2.9315	0.628 3	8.172
2.4	3.1762	0.577 3	12.48
2.6	3.4171	0.527 2	19.08
2.8	3.6524	0.478 6	29.13
3.0	3.8809	0.432 1	44.30
3.2	4.1022	0.388 3	67.05
3.4	4.3166	0.347 3	100.9
3.6	4.5253	0.309 1	151.2
3.8	4.7300	0.273 8	225.7
4.0	4.9328	0.241 3	336.5
4.2	5.1358	0.211 3	501.9
4.4	5.3407	0.183 9	750.2
4.6	5.5477	0.159 0	1124
4.6196	5.5681	0.156 7	1170
		$Dy(ClO_4)_3$	
0.1	0.8354	0.994 00	0.3835
0.2	0.8936	0.987 20	0.3689
0.3	0.9594	0.979 47	0.3820
0.4	1.0297	0.970 76	0.4089
0.5	1.1044	0.960 99	0.4472
0.6	1.1840	0.950 10	0.4969
0.7	1.2684	0.938 02	0.5597
0.8	1.3577	0.924 72	0.6380
0.9	1.4517	0.910 15	0.7350
1.0	1.5503	0.894 3	0.8551
1.2	1.7599	0.858 8	1.187
1.4	1.9839	0.818 6	1.698
1.6	2.2189	0.774 3	2.487
1.8	2.4619	0.726 6	3.712
2.0	2.7096	0.676 7	5.619
2.2	2.9590	0.625 6	8.586
2.4	3.2074	0.574 2	13.19
2.6	3.4524	0.523 7	20.31
2.8	3.6922	0.474 7	31.23
3.0	3.9255	0.428 0	47.87
3.2	4.1518	0.383 9	73.03
3.4	4.3712	0.342 7	110.8
3.6	4.5844	0.304 4	167.3
3.8	4.7928	0.269 2	251.6
4.0	4.9984	0.236 7	377.3
4.2	5.2036	0.207 0	565.8
4.4	5.4108	0.179 9	850.5
4.6	5.6222	0.155 1	1284
4.6042	5.6267	0.154 6	1295
		$Ho(ClO_4)_3$	
0.1	0.8287	0.994 05	0.3803
0.2	0.8862	0.987 31	0.3638
0.3	0.9535	0.979 60	0.3762
0.4	1.0256	0.970 87	0.4029
0.5	1.1020	0.961 07	0.4409
0.6	1.1827	0.950 15	0.4904
0.7	1.2679	0.938 05	0.5528
0.8	1.3575	0.924 72	0.6303
0.9	1.4516	0.910 15	0.7261
1.0	1.5498	0.894 3	0.8444
1.2	1.7583	0.859 0	1.171
1.4	1.9807	0.818 9	1.671
1.6	2.2144	0.774 7	2.443
1.8	2.4565	0.727 1	3.642
2.0	2.7040	0.677 3	5.508
2.2	2.9538	0.626 1	8.416
2.4	3.2031	0.574 7	12.94
2.6	3.4494	0.524 0	19.94
2.8	3.6906	0.474 9	30.69
3.0	3.9251	0.428 0	47.10
3.2	4.1522	0.383 9	71.91
3.4	4.3716	0.342 6	109.1
3.6	4.5839	0.304 5	164.6
3.8	4.7908	0.269 3	247.1
4.0	4.9943	0.237 0	369.8
4.2	5.1971	0.207 4	553.1
4.4	5.4026	0.180 3	829.6
4.6	5.6139	0.155 5	1252
4.6314	5.6477	0.151 8	1337
		$Er(ClO_4)_3$	
0.1	0.8275	0.994 05	0.3802
0.2	0.8857	0.987 32	0.3636
0.3	0.9540	0.979 59	0.3764
0.4	1.0271	0.970 83	0.4036
0.5	1.1044	0.960 99	0.4423
0.6	1.1859	0.950 02	0.4926
0.7	1.2717	0.937 87	0.5559
0.8	1.3618	0.924 50	0.6345
0.9	1.4562	0.909 88	0.7316
1.0	1.5549	0.894 0	0.8515
1.2	1.7642	0.858 5	1.183
1.4	1.9879	0.818 3	1.692
1.6	2.2234	0.773 9	2.481
1.8	2.4679	0.726 1	3.711
2.0	2.7181	0.675 9	5.637
2.2	2.9710	0.624 4	8.652
2.4	3.2236	0.572 6	13.37
2.6	3.4730	0.521 7	20.70
2.8	3.7172	0.472 3	32.02
3.0	3.9546	0.425 3	49.37
3.2	4.1844	0.381 0	75.73
3.4	4.4066	0.339 7	115.5
3.6	4.6221	0.301 5	175.1
3.8	4.8326	0.266 2	264.4
4.0	5.0404	0.233 9	398.3
4.2	5.2477	0.204 3	599.9
4.4	5.4569	0.177 2	905.3
4.6	5.6690	0.152 7	1371
4.6221	5.6926	0.150 2	1435
		$Tm(ClO_4)_3$	
0.1	0.8339	0.994 01	0.3819
0.2	0.8902	0.987 25	0.3660
0.3	0.9555	0.979 56	0.3783
0.4	1.0263	0.970 85	0.4047
0.5	1.1023	0.961 06	0.4428
0.6	1.1833	0.950 12	0.4927
0.7	1.2694	0.937 97	0.5559
0.8	1.3604	0.924 57	0.6349
0.9	1.4560	0.909 89	0.7329
1.0	1.5561	0.893 9	0.8543
1.2	1.7682	0.858 2	1.191
1.4	1.9944	0.817 7	1.709

Table III (continued)

m	ϕ	a_1	$\gamma_\pm$
1.6	2.2319	0.773 1	2.514
1.8	2.4778	0.725 1	3.769
2.0	2.7293	0.674 8	5.738
2.2	2.9836	0.623 1	8.829
2.4	3.2380	0.571 2	13.68
2.6	3.4899	0.520 0	21.26
2.8	3.7372	0.470 4	33.05
3.0	3.9782	0.423 2	51.21
3.2	4.2116	0.378 6	78.97
3.4	4.4368	0.337 2	121.0
3.6	4.6542	0.299 0	184.2
3.8	4.8653	0.263 9	278.7
4.0	5.0724	0.231 7	420.2
4.2	5.2799	0.202 3	633.9
4.4	5.4932	0.175 2	962.3
4.6	5.7202	0.150 1	1482
4.6215	5.7458	0.147 6	1554
		$Yb(ClO_4)_3$	
0.1	0.8280	0.994 05	0.3803
0.2	0.8867	0.987 30	0.3641
0.3	0.9555	0.979 56	0.3773
0.4	1.0290	0.970 77	0.4049
0.5	1.1066	0.960 91	0.4441
0.6	1.1884	0.949 91	0.4950
0.7	1.2745	0.937 73	0.5589
0.8	1.3649	0.924 33	0.6384
0.9	1.4596	0.909 68	0.7366
1.0	1.5585	0.893 8	0.8579
1.2	1.7684	0.858 2	1.193
1.4	1.9928	0.817 9	1.710
1.6	2.2292	0.773 4	2.511
1.8	2.4748	0.725 4	3.762
2.0	2.7264	0.675 1	5.726
2.2	2.9810	0.623 4	8.811
2.4	3.2354	0.571 5	13.65
2.6	3.4871	0.520 3	21.21
2.8	3.7339	0.470 8	32.93
3.0	3.9741	0.423 5	50.99
3.2	4.2069	0.379 0	78.56
3.4	4.4325	0.337 6	120.4
3.6	4.6517	0.299 2	183.5
3.8	4.8663	0.263 8	278.7
4.0	5.0787	0.231 3	422.5
4.2	5.2917	0.201 6	641.2
4.4	5.5082	0.174 4	976.9
4.6	5.7301	0.149 7	1498
4.6400	5.7752	0.145 0	1632
		$Lu(ClO_4)_3$	
0.1	0.8354	0.994 00	0.3843
0.2	0.8918	0.987 23	0.3688
0.3	0.9564	0.979 54	0.3810
0.4	1.0261	0.970 86	0.4073
0.5	1.1008	0.961 11	0.4450
0.6	1.1808	0.950 23	0.4944
0.7	1.2660	0.938 14	0.5571
0.8	1.3564	0.924 79	0.6355
0.9	1.4517	0.910 15	0.7330
1.0	1.5515	0.894 2	0.8540
1.2	1.7647	0.858 5	1.190
1.4	1.9924	0.817 9	1.711
1.6	2.2318	0.773 1	2.520
1.8	2.4800	0.724 9	3.788
2.0	2.7340	0.674 3	5.783
2.2	2.9908	0.622 4	8.926
2.4	3.2479	0.570 2	13.88
2.6	3.5028	0.518 8	21.65
2.8	3.7533	0.468 9	33.80
3.0	3.9977	0.421 4	52.62
3.2	4.2349	0.376 6	81.57
3.4	4.4641	0.335 0	125.7
3.6	4.6856	0.296 5	192.4
3.8	4.9004	0.261 3	292.8
4.0	5.1110	0.229 2	443.8
4.2	5.3211	0.199 8	672.6
4.4	5.5363	0.172 8	1025
4.6	5.7642	0.148 0	1583
4.6313	5.8017	0.144 2	1697

and isopiestic methods may be due to slight differences in the composition of the solid phases.

In Figure 1 the differences between the experimental and calculated osmotic coefficients, for $La(ClO_4)_3$ and $Lu(ClO_4)_3$, are shown as a function of the molality. Deviation plots of this type have the advantage of simultaneously showing mismatches between data sets when the isopiestic standards are changed, the scatter in the experimental data, and systematic differences between the experimental data and the equation used to represent it. It can be seen that nearly all of the data fall within ±0.2% of eq 3, with most of the data within ±0.1%. The mismatches that occurred when the isopiestic standards were changed are well within the uncertainty of the standard solutions' osmotic coefficients.

Results

Figures 2–4 show the concentration dependence of ln $\gamma_\pm$, ϕ, and a_1 for $La(ClO_4)_3$, $Lu(ClO_4)_3$, $LaCl_3$, and $LuCl_3$. These thermodynamic properties have many qualitative similarities for the rare earth perchlorates and chlorides, but there are large quantitative differences. These differences are most extreme for the activity coefficients. For example, the activity coefficient of $LuCl_3$ is about 14 at 4.0 m whereas it is 444 for $Lu(ClO_4)_3$. At this concentration the water activity of $LuCl_3$ is 0.385 while it is 0.229 for $Lu(ClO_4)_3$. This indicates that water is bound much more tightly in the rare earth perchlorates than in the chlorides, in agreement with deductions from transport property measurements (*13*, *15*).

Series plots of these same properties are given for the rare earth perchlorates in Figures 5–7, at 0.4, 1.4, 2.4, 3.4, and 4.4 m, as a function of the ionic radius (*18*). These constant molality series plots all have a distinct S shape from dilute solutions to over 2.4 m, but modifications do occur at higher concentrations. At low concentrations the water activities at constant molality decrease gradually from La to Nd–Sm, more rapidly to Tb–Dy, and then decrease gradually again to Lu. At higher concentrations the water activities decrease from La to Nd, and from Sm to Lu, with the trend for the middle and heavy rare earths displaced from the trend for the light rare earths. The osmotic and activity coefficients show similar series behavior, except that these properties increase from La to Lu.

There are experimental activity data for the dilute rare earth chloride solutions and these were used with isopiestic data to yield activity coefficients for the rare earth chlorides at higher concentrations. Since activity data for very dilute rare earth perchlorate solutions were not available, values of ϕ were estimated from conductance data for concentrations from 0.005 to 0.020 m. The differences between the actual dilute solution ϕ values for the various rare earth perchlorates are probably smaller than the uncertainty introduced by using $\mathring{a}$ values from conductance data, so average values of ϕ were used for all of the rare earth perchlorates. The rare earth chlorides and perchlorates exhibit very similar series trends for ϕ, a_1, and $\gamma_\pm$. This suggests that little error arises for $\gamma_\pm$ due to using constant ϕ values for the perchlorates at low concentrations.

The ionic radius of the rare earth ion decreases from La to

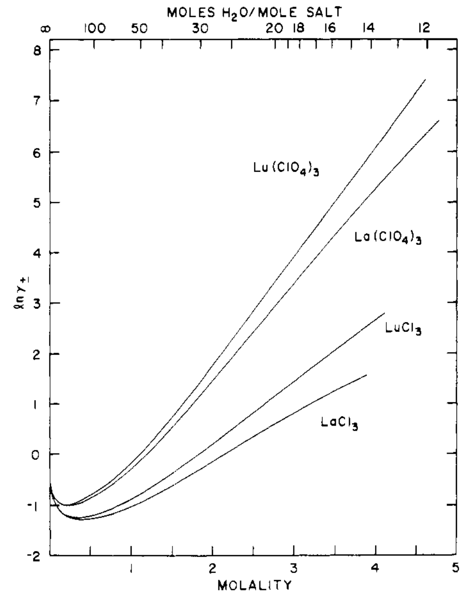

Figure 2. Natural log of the mean molal activity coefficients of $LaCl_3$, $LuCl_3$, $La(ClO_4)_3$, and $Lu(ClO_4)_3$ solutions at 25 °C.

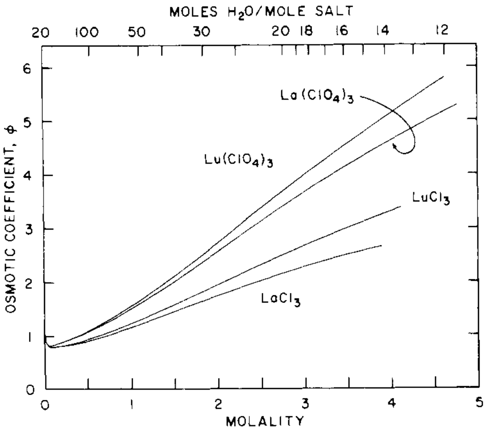

Figure 3. Osmotic coefficients of $LaCl_3$, $LuCl_3$, $La(ClO_4)_3$, and $Lu(ClO_4)_3$ solutions at 25 °C.

Lu(*18*) and this decrease results in an increase in the electrical charge density at the surface of the rare earth ion. This surface charge density increase across the rare earth series should result in an increase in the total number of water molecules affected by the rare earth ion, at least up to concentrations where water sharing between ions becomes important. This can account for the gradual decrease in a_1, at constant molality, from La to Nd–Sm and from Tb–Dy to Lu. It has been proposed that the inner sphere hydration number of the rare earth ion decreases by one between Nd and Tb, due to the decreasing ion size (*12*). The net result of this inner sphere hydration decrease is to cause the total rare earth ionic hydration to increase more rapidly, with ionic radius, than it would if the inner sphere hydration number remained constant (as it does for La to Nd and for Tb to Lu). This same argument has been used to explain series trends in the rare earth chloride water activities (*16*) and rare earth chloride and perchlorate transport properties (*13, 15*) at low and moderate concentrations. Only outer sphere ion pairs are believed to form in these solutions (*1, 13*), or at least the amount of inner sphere chloride or perchlorate–rare earth complex is small enough as to have been undetected up to now. Thus the inner hydration sphere should contain only water and remain intact even up to saturation for the chlorides and perchlorates.

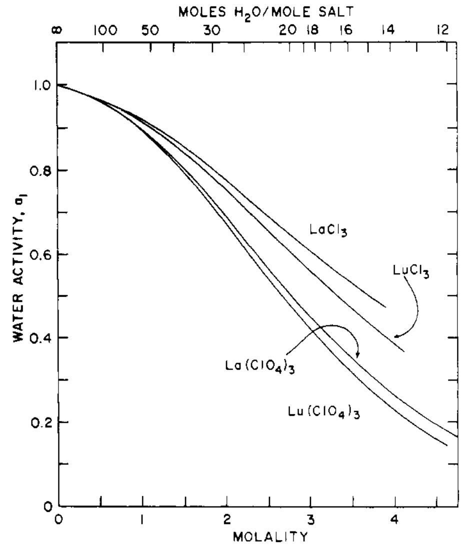

Figure 4. Water activities of $LaCl_3$, $LuCl_3$, $La(ClO_4)_3$, and $Lu(ClO_4)_3$ solutions at 25 °C.

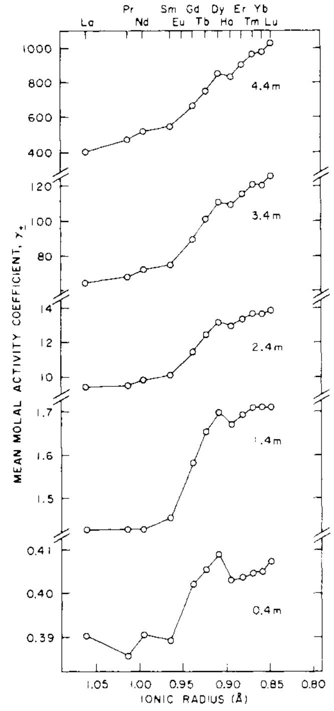

Figure 5. Mean molal activity coefficients of rare earth perchlorate solutions at constant molalities.

At high concentrations water sharing between ions becomes important and the increase in total hydration with radius becomes modified, resulting in a more nearly monotone dependence of total hydration on ionic radius. The displacement of the a_1 and ϕ trends for Sm–Lu above 3.4 *m*, from the trends for La–Nd, is probably due to the inner sphere hydration change. The water activities decrease more rapidly, with decreasing ionic radius, at high cocentrations than at low concentrations (except for the displacement due to the inner sphere hydration number change). This difference presumably occurs since the trends in the water activities are mainly due to overall cation hydration at low and moderate concentrations, whereas the binding of water by or between ion pairs should be important at higher concentrations.

The rare earth perchlorate transport data (*13, 15*) depend mainly on total cation hydration at low and moderate concentrations. Series curves for these transport properties have S

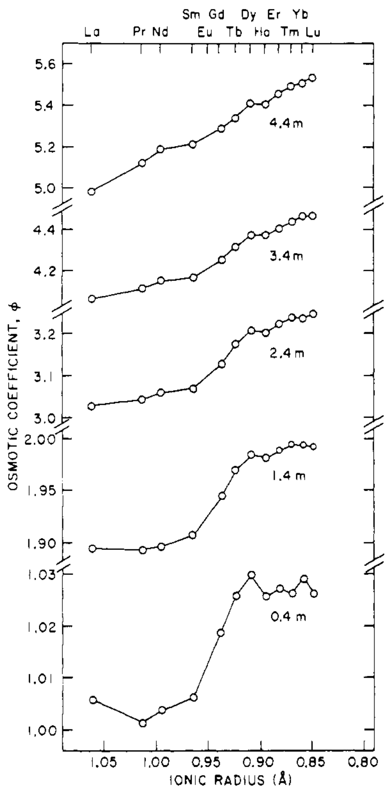

Figure 6. Osmotic coefficients of rare earth perchlorate solutions at constant molalities.

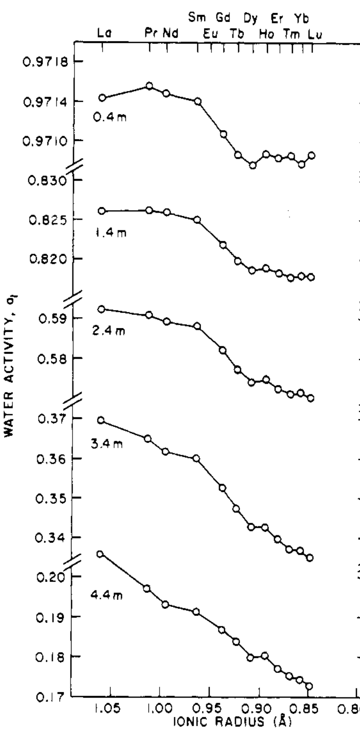

Figure 7. Water activities of rare earth perchlorate solutions at constant molalities.

shapes similar to the activity data at these concentrations. However, the rare earth perchlorate transport properties at constant molalities above 3.5–3.7 *m* exhibit a prominent two-series effect that is quite different from series trends present in the activity data (this new behavior is already starting to show up by about 2.5 *m*, but it does not occur in the complete form until the higher concentrations are reached). At high concentrations the electrical conductances decrease from La to Nd, rise to Tb, and then decrease to Lu. The perchlorate viscosity series curves undergo similar changes, except for a general increase across the rare earth series. This behavior occurs only when water sharing between ions becomes extensive. Similar modifications are also starting to occur in the transport properties of the rare earth chloride solutions, but the high concentration two-series behavior is not as well developed at 3.5 *m* as for the perchlorates.

The proposed transport mechanism at high concentrations (*13, 15*) involves the breaking and re-forming of the outer sphere ion pairs. The increasing strength of the ion pairs with decreasing ionic radius gives rise to the decreasing electrical conductances, and increasing viscosities, from La to Nd and from Tb to Lu. The gradual "release" of one inner sphere water to the rest of the solution at these high concentrations, as the inner sphere hydration decrease occurs, should slightly reduce the amount of ion pairing and enhance the tendency to flow in these perchlorate solutions, giving rise to the reversal in transport behavior between Nd and Tb. This "extra" water in the bulk of the solution is still surrounded by enough ions and ion pairs that it apparently cannot contribute very much to the water activity, although it probably causes the displacement in activity series trends between Nd and Sm.

The results tabulated in Table III indicate that the activity coefficients of the rare earth perchlorates reach very high values at high concentrations, the maximum being 1697 for $Lu(ClO_4)_3$ at saturation. Robinson and Lim (*7*) reported a value of 1510 for $UO_2(ClO_4)_2$ at 5.5 *m*. Examination of the activity coefficients tabulated by Robinson and Stokes (*8*) indicates that large activity coefficients occur for some other concentrated solutions of perchlorate electrolytes. Figure 4 illustrates the fact that the water activities of the rare earth perchlorates are appreciably lower than for the rare earth chlorides at equal molal concentrations. The osmotic coefficients tabulated by Robinson and Stokes (*8*), Hamer and Wu (*2*), and Libus and Sadowska (*3*) indicate that this order also holds at all concentrations for the acids and for the Li^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, and $UO_2{}^{2+}$ salts of these anions. The water activities for the perchlorate electrolytes are lower than for the corresponding chlorides, even for dilute solutions where anion–cation interactions are small and differences in cation hydration have only minimal dependence of the anion. This suggests that anion–water interactions may be involved (the larger size of the perchlorate anion will also contribute to these activity differences, especially at low concentrations). The only exceptions given in Robinson and Stokes' and Hamer and Wu's tables are the Na^+ and $NH_4{}^+$ salts.

It is usually assumed that the perchlorate ion is unhydrated in aqueous solution. This assumption is mainly based on spectral evidence. However, Symons and Waddington (*17*) noted that symmetrical hydration can explain at least part of the spectral results. They found that a hydration number of 4 was consistent with their data. It has been suggested that the chloride ion forms a single hydrogen bond with water (*19*). The thermodynamic differences noted above can be accounted for if the perchlorate ion is more extensively hydrated than the chloride ion. Additional investigations will be required before the existence of this perchlorate ion hydration can be ascertained.

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The Apparent Molal Volumes of Aqueous Solutions of NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ from 0 to 1000 Bars at 0, 25, and 50 °C†

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The densities of aqueous solutions of NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$ have been measured with a high pressure magnetic float densimeter from 0 to 1000 bars, 0.01 to 1.0 *m* ionic strength, and at 0, 25, and 50 °C. The relative apparent molal volumes, $\phi_V(P) - \phi_V(0)$, of these solutions have been fitted to an equation of the form $\phi_V(P) - \phi_V(0) = \phi_V^0(P) - \phi_V^0(0) + Sm^{1/2}$ where the relative infinite dilution partial molal volumes, $\phi_V^0(P) - \phi_V^0(0)$, and the slopes *S* are functions of applied pressure and temperature. The pressure, temperature, and concentration dependence of the apparent molal volumes are briefly discussed.

Although there are reliable density and apparent molal volume data for many electrolytes at 1 atm (*9*, *11*), little reliable data are available at high pressures. In our recent studies of the volume properties of multicomponent electrolyte solutions (*13*, *15*) we have been examining the use of Young's rule (*18*) in predicting the properties of seawater. In order to predict the apparent molal volumes of seawater at elevated pressures (*3*), we had a need for reliable volume data on sea salts (NaCl, KCl, $MgCl_2$, Na_2SO_4, and $MgSO_4$). The present paper contains results on the apparent molal volumes of these salts from 0 to 1000 bars applied pressure, 0.01 to 1.0 ionic strength (to 2.0 ionic strength for NaCl), and 0, 25, and 50 °C.

Experimental Section

The high pressure magnetic float densimeter used in this study is described in detail elsewhere (*12*). The high pressure densimeter consists essentially of a 1 atm densimeter (*8*) enclosed in a nonmagnetic bomb with optical ports to observe the motion of the float. The apparatus consists of a pressure bomb, a magnetic float, and auxiliary measuring and control systems.

The pressure bomb used in this study was machined from beryllium copper. The cylindrical bomb contains two plugs seated with O rings to form a vessel of 170 cm^3. The magnetic float is made of thick-wall (0.4 cm) Pyrex glass and contains an Alnico-5 bar magnet. The volume of the float is 58.7672 cm^3 at 0 °C and 1 atm.

The pressure bomb was completely immersed in a 30-L constant temperature bath controlled to ±0.001 °C with a Hallikainen Thermotrol. The temperature of the bath was set to ±0.005 °C with a platinum resistance thermometer (calibrated by the National Bureau of Standards, 1968 temperature scale). A 2800-bar Enerpac hand pump was used to generate pressure. A 1400-bar Heise Bourdon tube gauge was used to set the pressure. The Heise gauge was calibrated with a Harwood Engineering deadweight tester. The pressures were found to be reproducible to ±0.5 bars from 0 to 1000 bars and are thought to be accurate to 1.4 bars.

Ion-exchanged (18 MΩ) water (Millipore-Super Q system) was used in the calibration runs and in the preparation of the solutions. Reagent grade salts were used, without further purification, for preparation of the solutions. The solutions of NaCl, KCl, Na_2SO_4, and $MgSO_4$ were analyzed by evaporation to dryness. The $MgCl_2$ solutions were analyzed gravimetrically with $AgNO_3$.

The calibration of the densimeter (*2*, *3*) was made with ion-exchanged water using the densities of water from the sound-derived equation of state (*4*). The calibration results (*2*) indicate that the precision of the densities is ±3 ppm at a given temperature and ±8 ppm over the entire temperature range. The accuracy of the densities is thought to be ~30 ppm at 1000 bars applied pressure. An error of ±30 ppm in density is equivalent to an error of ±0.3 $cm^3\ mol^{-1}$ at 0.1 *m* and ±0.03 $cm^3\ mol^{-1}$ at 1.0 *m* in ϕ_V for 1–1 electrolytes.

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