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

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The densities of aqueous solutions of La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu perchlorate were determined from approximately 0.05*m* to saturation at 25°C with an accuracy of $\pm 5 \times 10^{-5}$ g/ml by a pycnometric method. The apparent molal volumes calculated from the experimental densities were fitted to semiempirical equations. Dilute apparent molal volume data (less than 0.2*m*) available in the literature for La, Nd, Gd, and Lu perchlorate were included in these fits. Apparent molal volumes at infinite dilution for the remaining perchlorates were obtained from the additivity relationships. A two-series effect in the partial molal volumes across the rare earth series, similar to the one found for the chlorides, persists to high concentrations in the perchlorates. This two-series effect is discussed in terms of a change in the inner sphere water coordination of the cations in the rare earth series.

Many of the thermodynamic and transport properties of rare earth salt solutions do not vary in a simple manner with the cationic rare earth radii (*17–21*). From dilute (less than 0.2*m*) apparent molal volume data on some rare earth chlorides and nitrates, Spedding et al. (*18*) suggested that a two-series effect in these data across the rare earth series is due to a decrease in the inner sphere water coordination of the cation as the radii decrease across the rare earth series.

Spedding et al. (*17*) have recently shown that this two-series effect also appears in the apparent molal volumes of the rare earth perchlorates in dilute solutions. Except for an anion shift, the two-series effect in the three anion series is the same within experimental error at infinite dilution, where the salts are completely ionized and the cation–anion interactions can be neglected. It was of interest to examine this two-series effect at higher concentrations where anion–cation interactions must be taken into account. In a previous paper reporting the extension of these measurements to saturation for the rare earth chlorides (*20*), the two-series effect persists to high concentrations, with only minor modifications owing to rare earth chloride interactions. In this report we present the results for the rare earth perchlorate systems up to saturation.

Experimental

The apparatus and experimental procedure were similar to the previous work (*20*). The densities of the solutions were determined with 20-ml Sprengel-Ostwald pycnometers, calibrated to about ±0.0005 ml with conductivity water. The temperature was held at 25.000° ± 0.005°C, and the density of water (0.997075 g/ml) was taken from Tilton and Taylor (*25*).

The preparation and analysis of the solutions have been described in detail (*17, 18, 20*). The stock solutions were prepared from ion-exchange purified oxides and reagent-grade $HClO_4$. The stock solutions were adjusted to the equivalence pH to insure a 1:3 ratio of rare earth ions to perchlorate ions. The stock and saturated solutions were analyzed by sulfate and EDTA methods (*17, 18*). These analyses agreed in most cases to ±0.1% in terms of molality. The dilutions were made by weight from the stock solutions.

Calculations and Results

Densities. The experimental densities and concentrations are listed in Table I. The error in the density owing to the density measurement itself is approximately $\pm 5 \times 10^{-5}$ g/ml. This is a somewhat larger error than the errors in the chloride densities (*20*), probably due to the smaller pycnometers used for the measurements in the present work. As discussed in the chloride paper, the absolute errors in the densities owing to the 0.1% analysis error in the stock and saturated solutions range from $\pm 1 \times 10^{-5}$ g/ml at 0.05*m* to $\pm 120 \times 10^{-5}$ g/ml at saturation. However, the experimental densities below the saturated value for each salt should be internally consistent to $\pm 5 \times 10^{-5}$ g/ml, since these solutions were prepared by weight dilution. The densities were therefore fitted to empirical equations

$$d - d^{\circ} = A_1 m + A_2 m^2 + A_3 m^3 + A_4 m^4 \qquad (1)$$

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

m	d, g/ml	$\Delta d \times 10^5$	ϕ_V, ml/mol	$\Delta\phi_V$
		$La(ClO_4)_3$		
0.050169	1.01403	−6	97.00	−0.10
0.077468	1.02311	−3	97.97	−0.46
0.094054	1.02862	−4	98.10	−0.29
0.25881	1.08198	1	100.04	−0.16
0.33227	1.10515	−5	100.48	0.10
0.72708	1.22221	8	103.67	−0.04
0.96463	1.28747	−4	105.11	0.07
1.2555	1.36211	3	106.94	−0.02
1.6080	1.44578	2	108.86	−0.03
1.8468	1.49855	0	110.06	−0.02
2.1048	1.55230	−3	111.25	0.00
2.4116	1.61213	−6	112.56	0.03
2.7250	1.66899	−1	113.82	0.03
2.9492	1.70727	6	114.65	0.03
3.2705	1.75837	(79)^a	115.90	−0.12
3.5404	1.79960	(49)	116.65	−0.02
4.1892	1.89007	−1	118.23	0.11
4.7601 sat.	1.96009	(82)	119.56	−0.04
		$Pr(ClO_4)_3$		
0.0016049			90.70*^{b}	0.13
0.0064225			91.43*	0.03
0.014461			92.02*	−0.03
0.025736			92.53*	−0.05
0.040267			92.98*	−0.06
0.058081			93.40*	−0.05
0.051174	1.01467	−5	93.11	0.09
0.080146	1.02450	−5	93.80	−0.03
0.096110	1.02989	−5	94.04	−0.00
0.24998	1.08075	−1	95.82	0.06
0.49752	1.15869	5	97.92	0.04
0.76397	1.23760	4	99.79	0.06
0.99984	1.30340	−2	101.27	0.07
1.3046	1.38299	−1	103.10	0.02
1.6078	1.45664	−1	104.75	−0.01
1.9037	1.52362	−2	106.23	−0.01
2.2111	1.58811	(32)	107.78	−0.13
2.8063	1.70173	0	110.14	0.00
3.0862	1.74999	3	111.19	0.01
3.4088	1.80214	3	112.31	0.02
3.7042	1.84690	−1	113.25	0.03
4.0161	1.89131	−5	114.18	0.03
4.3083	1.93039	−1	115.00	0.00
4.5068	1.95567	3	115.53	−0.02
4.6956 sat.	1.97910	(−19)	115.97	−0.01
		$Nd(ClO_4)_3$		
0.082089	1.02547	−4	93.32	−0.51
0.098806	1.03121	−7	93.22	−0.11
0.25182	1.08231	−0	95.28	−0.22
0.50247	1.16211	3	97.39	−0.07
1.0255	1.31398	4	100.96	−0.02
1.3289	1.39382	−2	102.72	0.01
1.6237	1.46611	−7	104.27	0.03
1.9186	1.53347	2	105.77	−0.00
2.2394	1.60182	2	107.22	0.01
2.4626	1.64650	3	108.17	0.01
2.8122	1.71222	−2	109.53	0.02
3.0833	1.75972	0	110.54	−0.00
3.4675	1.82245	−1	111.86	−0.05
3.7084	1.85918	1	112.65	−0.10
4.1152	1.91923	(−211)	113.51	0.16
4.6849 sat.	1.99327	(−302)	115.05	−0.04
		$Sm(ClO_4)_3$		
0.0016049			91.01*	0.17
0.0064225			91.73*	0.03
0.014461			92.31*	−0.05
0.025736			92.79*	−0.09
0.040267			93.21*	−0.10
0.058082			93.57*	−0.07
0.049127	1.01445	−8	92.75	0.56
0.077369	1.02426	−3	94.10	−0.27
0.094875	1.03037	−7	93.96	0.14
0.24058	1.07993	−1	95.70	−0.02
0.48974	1.16097	−1	97.43	0.11
0.73861	1.23735	2	98.99	0.07
0.96752	1.30384	6	100.29	0.02
1.2520	1.38176	7	101.75	−0.02
1.5269	1.45257	−9	102.96	0.04
1.8269	1.52477	−3	104.32	−0.02
2.1037	1.58734	−9	105.42	−0.01
2.3863	1.64718	6	106.56	−0.06
2.6548	1.70081	12	107.53	−0.07
2.9406	1.75483	−7	108.45	−0.00
3.2201	1.80431	3	109.37	−0.01
3.4966	1.85069	−6	110.18	0.03
3.7525	1.89115	2	110.93	0.03
3.9761	1.92491	0	111.54	0.05
4.6400 sat.	2.01587	(70)	113.37	−0.04
		$Eu(ClO_4)_3$		
0.0016049			91.99*	0.12
0.0064226			92.72*	0.01
0.014462			93.32*	−0.04
0.025737			93.81*	−0.05
0.040269			94.24*	−0.03
0.058086			94.61*	0.01
0.045347	1.01312	−6	94.27	0.06
0.077863	1.02449	−7	94.89	0.09
0.10206	1.03286	−4	95.54	−0.17
0.24892	1.08277	0	97.01	−0.06
0.50198	1.16495	−0	98.63	0.13
0.75204	1.24151	5	100.14	0.06
1.0047	1.31463	1	101.41	0.06
1.3117	1.39796	−1	102.86	0.01
1.6123	1.47417	−2	104.15	−0.02
1.9151	1.54594	0	105.35	−0.04
2.2112	1.61173	−2	106.42	−0.03
2.5018	1.67218	(13)	107.45	−0.06
2.8265	1.73572	2	108.44	−0.01
3.1150	1.78859	1	109.29	0.02
3.4097	1.83943	1	110.11	0.03
3.7345	1.89204	−3	110.97	0.04
4.1724	1.95754	1	112.10	−0.00
4.6334 sat.	2.02096	(−59)	113.16	−0.02
		$Gd(ClO_4)_3$		
0.049515	1.01481	−5	95.02	0.07
0.077568	1.02475	−7	95.44	0.17
0.097904	1.03200	−16	94.82	1.11
0.25314	1.08520	14	98.10	−0.54
0.50305	1.16751	2	99.19	0.14
0.74893	1.24384	5	100.61	0.09
1.0027	1.31836	−2	101.83	0.10
1.3167	1.40478	−2	103.26	0.03
1.6527	1.49087	−7	104.60	0.00
1.9075	1.55196	1	105.58	−0.06
2.2097	1.62042	−10	106.56	−0.02
2.5422	1.69061	5	107.65	−0.06
2.8149	1.74465	17	108.47	−0.07
3.1182	1.80159	1	109.26	0.00
3.3880	1.84922	2	109.96	0.02

Table I. Continued

m	d, g/ml	$\Delta d \times 10^5$	ϕ_V, ml/mol	$\Delta\phi_V$
$Gd(ClO_4)_3$				
3.7602	1.91088	−8	110.87	0.07
4.0613	1.95737	−11	111.61	0.07
4.4321	2.01049	9	112.55	−0.01
4.6088 sat.	2.03444	(7)	112.98	−0.05
$Tb(ClO_4)_3$				
0.0016049			92.79*	0.12
0.0064226			93.56*	0.03
0.014462			94.20*	−0.01
0.025738			94.75*	−0.03
0.040271			95.24*	−0.03
0.058089			95.69*	−0.02
0.051878	1.01572	−7	95.37	0.14
0.077438	1.02474	−2	96.62	−0.55
0.099820	1.03269	−7	96.31	0.14
0.25549	1.08638	−0	98.23	0.03
0.50897	1.16980	1	99.95	0.18
0.76231	1.24837	2	101.46	0.11
1.0177	1.32314	−2	102.75	0.07
1.3354	1.41022	2	104.23	−0.03
1.6294	1.48555	1	105.42	−0.07
1.9443	1.56104	4	106.57	−0.09
2.2591	1.63173	−5	107.57	−0.04
2.5551	1.69400	−2	108.45	−0.02
2.8957	1.76120	−5	109.37	0.02
3.2061	1.81845	4	110.17	0.03
3.5399	1.87625	5	110.96	0.04
3.8425	1.92548	0	111.64	0.03
4.0952	1.96433	−3	112.20	−0.02
4.6072 sat.	2.03846	(−153)	113.12	−0.02
$Dy(ClO_4)_3$				
0.0016049			92.26*	0.16
0.0064226			93.03*	0.05
0.014462			93.67*	−0.02
0.025737			94.23*	−0.05
0.040270			94.73*	−0.05
0.058087			95.19*	−0.05
0.049765	1.01515	−5	95.19	−0.25
0.082070	1.02676	−7	95.56	0.08
0.10734	1.03574	−5	96.17	−0.09
0.24872	1.08507	−3	97.71	0.09
0.49659	1.16763	2	99.68	0.14
0.74606	1.24605	1	101.24	0.14
0.97757	1.31493	−5	102.48	0.12
1.2990	1.40453	7	104.14	−0.05
1.5991	1.48260	17	105.45	−0.15
1.8991	1.55623	−25	106.38	0.01
2.2027	1.62551	−1	107.48	−0.08
2.4931	1.68792	15	108.38	−0.11
2.7969	1.75025	(−51)	109.00	0.11
3.0816	1.80438	−9	109.79	0.03
3.4054	1.86293	−11	110.50	0.07
3.7055	1.91345	(48)	111.23	−0.03
4.0038	1.96168	25	111.75	0.01
4.3576	2.01551	−12	112.35	0.01
4.6016 sat.	2.05060	(−47)	112.76	−0.02
$Ho(ClO_4)_3$				
0.0016049			91.21*	0.15
0.0064226			91.97*	0.05
0.014462			92.61*	−0.01
0.025736			93.15*	−0.04
0.040268			93.64*	−0.05
0.058084			94.09*	−0.04
0.077322	1.02531	−4	94.68	−0.24
0.10230	1.03431	−4	95.00	−0.12
0.23906	1.08261	−1	96.47	0.04
0.49425	1.16873	0	98.36	0.17
0.74173	1.24751	−0	99.92	0.13
0.98891	1.32206	(−22)	101.13	0.23
1.2766	1.40322	3	102.77	−0.05
1.5741	1.48209	2	104.08	−0.08
1.8725	1.55618	3	105.27	−0.10
2.1613	1.62359	−4	106.28	−0.07
2.4568	1.68842	−7	107.24	−0.04
2.7295	1.74471	4	108.08	−0.03
3.0385	1.80499	1	108.93	0.01
3.2906	1.85145	2	109.58	0.04
3.5405	1.89535	−3	110.18	0.06
3.8251	1.94265	4	110.86	0.05
4.2744	2.01228	−2	111.85	−0.01
4.6241 sat.	2.06281	(−60)	112.53	−0.04
$Er(ClO_4)_3$				
0.0016049			90.45*	0.15
0.0064225			91.17*	0.01
0.014461			91.74*	−0.06
0.025736			92.20*	−0.07
0.040266			92.59*	−0.04
0.058080			92.93*	0.03
0.047792	1.01479	−6	92.54	0.19
0.081976	1.02729	−5	93.43	−0.04
0.10297	1.03492	−5	93.75	−0.03
0.25203	1.08797	1	95.50	−0.07
0.50804	1.17495	3	97.42	0.06
0.74731	1.25177	−2	98.89	0.12
1.0113	1.33166	6	100.48	0.01
1.2959	1.41278	−4	101.85	0.03
1.5896	1.49118	−3	103.18	−0.01
1.8986	1.56840	−0	104.44	−0.04
2.1906	1.63680	5	105.52	−0.06
2.4923	1.70340	−7	106.48	−0.01
2.7869	1.76432	7	107.41	−0.03
3.0731	1.82035	−2	108.18	0.01
3.3924	1.87912	−1	109.01	0.03
3.6740	1.92796	1	109.70	0.03
3.9791	1.97796	−0	110.41	0.03
4.4216	2.04532	−0	111.40	−0.03
4.6185 sat.	2.07393	(−52)	111.75	−0.00
$Tm(ClO_4)_3$				
0.0016049			89.24*	0.10
0.0064225			89.95*	−0.01
0.014461			90.52*	−0.05
0.025735			90.98*	−0.05
0.040265			91.38*	−0.01
0.058076			91.72*	0.07
0.040490	1.01222	−5	91.10	0.28
0.077060	1.02570	−3	92.39	−0.24
0.097533	1.03321	−3	92.65	−0.17
0.25008	1.08800	3	94.34	−0.07
0.49390	1.17172	3	96.13	0.09
0.74549	1.25334	1	97.75	0.10
0.99006	1.32837	−4	99.14	0.09
1.2886	1.41444	−1	100.71	0.00
1.5883	1.49535	−3	102.08	−0.02
1.8931	1.57232	5	103.37	−0.07
2.1754	1.63938	2	104.40	−0.05
2.4702	1.70530	2	105.40	−0.04

(Continued on page 84)

Table I. Continued

m	d, g/ml	$\Delta d \times 10^5$	ϕ_V, ml/mol	$\Delta\phi_V$
$Tm(ClO_4)_3$				
2.7825	1.77099	−4	106.34	0.01
3.0881	1.83135	−5	107.21	0.03
3.3772	1.88517	−3	107.97	0.04
3.6636	1.93545	13	108.71	0.01
3.9643	1.98567	−7	109.37	0.03
4.1899	2.02125	1	109.90	−0.02
4.6172 sat.	2.08550	(−87)	110.70	−0.01
$Yb(ClO_4)_3$				
0.0016049			88.82*	0.23
0.0064225			89.51*	0.06
0.014461			90.06*	−0.05
0.025735			90.50*	−0.10
0.040264			90.87*	−0.09
0.058074			91.18*	−0.05
0.039757	1.01212	−2	90.83	−0.06
0.083360	1.02844	−2	91.46	0.09
0.086986	1.02978	−1	91.61	−0.00
0.22545	1.08039	6	93.26	−0.07
0.49177	1.17351	−4	95.07	0.28
0.73704	1.25420	4	96.88	0.08
0.98584	1.33176	−4	98.30	0.09
1.3047	1.42488	1	100.03	−0.03
1.5713	1.49820	(−27)	101.14	0.07
1.8635	1.57321	8	102.54	−0.12
2.1455	1.64183	−10	103.54	−0.05
2.4221	1.70504	3	104.54	−0.08
2.7148	1.76831	1	105.45	−0.04
3.0205	1.83054	−2	106.33	−0.00
3.2962	1.88348	1	107.08	0.02
3.5914	1.93713	−0	107.83	0.05
3.8786	1.98641	2	108.52	0.06
4.2377	2.04431	−1	109.35	0.06
4.6044 sat.	2.09877	(48)	110.27	−0.08
$Lu(ClO_4)_3$				
0.074066	1.02517	−2	90.64	−0.56
0.094990	1.03302	−2	90.83	−0.38
0.24664	1.08870	4	92.53	−0.19
0.48972	1.17407	6	94.40	0.01
0.72797	1.25337	−0	95.91	0.11
0.96943	1.32952	−6	97.32	0.11
1.5464	1.49565	−4	100.27	−0.01
1.8363	1.57158	−1	101.52	−0.05
2.1296	1.64378	4	102.66	−0.07
2.4016	1.70695	7	103.62	−0.07
2.6957	1.77150	1	104.54	−0.03
2.9611	1.82656	−2	105.32	0.00
3.2514	1.88360	−7	106.11	0.04
3.5368	1.93653	−2	106.85	0.05
3.8075	1.98410	4	107.52	0.05
4.6334 sat.	2.11488	(8)	109.40	−0.04

[a] Values in parentheses were not used in the density fits.
[b] Values with an asterisk were estimated from Equation 4.

within ±5 × 10^{-5} g/ml in most cases. d° was fixed at 0.997075 g/ml. The saturated solutions, which were analyzed independently, were not internally consistent with the rest of the solutions and were not used in obtaining these fits. The parameters in Equation 1 are listed in Table II, together with the standard deviations of the fits. The deviations of the experimental densities from Equation 1, Δd, are listed in Table I. The deviation of the saturated density from the density extrapolated from Equation 1 is listed in parentheses in Table I. In most cases, the differences at saturation fall within our expected absolute errors due to the 0.1% analysis errors in the stock and saturated solutions.

Apparent and partial molal volumes. The apparent molal volumes were calculated from

$$\phi_V = \frac{1000\,(d^\circ - d)}{m d^\circ d} + \frac{M_2}{d} \qquad (2)$$

where the symbols have their usual meanings (*20*). In Figure 1 the apparent molal volumes of La, Nd, Tb, and Lu perchlorates are shown. The dilute data (*17*) for La, Nd, and Lu perchlorate, determined by a magnetic float method, are also shown together with the Debye-Hückel limiting slope. The Debye-Hückel limiting slope is adequately approached for La, Nd, and Lu at infinite dilution. Furthermore, there is a pronounced downturn in ϕ_V below 0.05m where the errors in the pycnometric ϕ_V's become large. To force the semiempirical ϕ_V equations to conform to similar behavior in the chlorides below the experimental range of the pycnometric measurements, the dilute magnetic float data (*17, 18*) for the rare earth chlorides and the Debye-Hückel limiting slope were included in obtaining the least-squares equations in the previous paper on the chlorides (*20*). The dilute ϕ_V's have only been reported for La, Nd, Gd, and Lu perchlorate (*17*); therefore, a similar treatment of the remaining perchlorates is not possible. However, the $\phi_V{}^0$'s at infinite dilution of the 13 chlorides, 13 nitrates, and the four perchlorates obey the additivity principle (*3, 15, 17, 18*). From these data the $\phi_V{}^0(=\bar V_2{}^0)$ for the remaining rare earth perchlorates can be estimated. From the $\bar V_2{}^0$'s of La, Nd, Gd, and Lu chlorides, nitrates, and perchlorates (*17, 18*), we obtain the average differences $3\bar V^0(ClO_4{}^-) - 3\bar V^0(Cl^-)$ = 78.5 ± 0.4 ml/mol and $3\bar V^0(ClO_4{}^-) - 3\bar V^0(NO_3{}^-)$ = 44.6 ± 0.4 ml/mol. These can be compared to 78.9 and 45.3 ml/mol obtained by Millero (*12*) from monovalent salts. The $\bar V_2{}^0$'s of the remaining perchlorates are given by

$$\bar V^0{}_{RE(ClO_4)_3} = \tfrac{1}{2}\,(\bar V^0{}_{RECl_3} + 78.5 + \bar V^0{}_{RE(NO_3)_3} + 44.6) \qquad (3)$$

The $\bar V_2{}^0$'s for the perchlorates so obtained are listed in Table III. The errors in these estimated $\bar V_2{}^0$'s are about ±0.3 ml/mol.

Taking advantage of the fact that the dilute rare earth perchlorates conform to the Owen-Brinkley equation (*6, 17*),

$$\phi_V = \phi_V{}^0 + S_V\Omega(\kappa \mathring{a})c^{1/2} + \tfrac{1}{2}K_V c \qquad (4)$$

six ϕ_V points were calculated on the interval from c = 0.0016 to 0.0576M, for those perchlorates where the magnetic float data are not available. These six ϕ_V points were calculated from Equation 4 by taking $\phi_V{}^0$ from Table III, $\mathring{a}$ from refs. *17* and *18*, and choosing $\tfrac{1}{2}K_V$ such that the ϕ_V's calculated at 0.0576M joined smoothly with the pycnometric ϕ_V's. These six ϕ_V points for each salt were then included with the pycnometric ϕ_V's of those perchlorates where experimental dilute data were not available. These estimated points are listed in Table I for each salt. The success of the above treatment is apparent in Figure 1 where the results for $Tb(ClO_4)_3$ are shown, including the estimated values in the dilute interval. The results for the other salts were similar.

The apparent molal volumes of this research, together with the dilute data (experimental or estimated), were then fitted to the Redlich-Meyer type equation (*16*) over the whole concentration range

$$\phi_V = \phi_V{}^0 + S_V\sqrt{d^\circ}\,m^{1/2} + B_2 m^{3/4} + B_3 m + B_4 m^{5/4} + B_5 m^{3/2} \qquad (5)$$

where $\phi_V{}^0$, B_2, B_3, ... are empirical constants, S_V = 27.45, and d^0 = 0.997075 g/ml. The saturated points were included in these fits. The points were weighted statistically. As with the chlorides, the $m^{1/4}$ power series gave a better fit than a similar series in $m^{1/2}$. The apparent molal volumes in ml/mol and the differences between experimental and calculated ϕ_V's are given in Table I. The parameters in Equation 5, together with the standard deviations of the fits, are given in Table IV. $\phi_V{}^0$'s should, of course, be taken from Table III instead of Table IV, since those in Table III are based directly on the dilute measurements.

The errors in the ϕ_V's are substantially the same as reported in the previous paper (*20*), ranging from ±0.2 ml/mol at 0.05*m* to ±0.1 ml/mol at saturation. The agreement between the dilute measurements and this research for La, Nd, and Lu perchlorates is satisfactory in the overlapping region, as shown in Figure 1. The agreement for $Gd(ClO_4)_3$ is comparable.

Table II. Density Parameters for Equation 1

Salt	A_1	A_2	A_3	A_4	SD × 10^5
$La(ClO_4)_3$	0.338875	−0.042560	0.003544	−0.000131	5
$Pr(ClO_4)_3$	0.344904	−0.041747	0.003311	−0.000123	4
$Nd(ClO_4)_3$	0.348895	−0.042272	0.003495	−0.000151	4
$Sm(ClO_4)_3$	0.354058	−0.041206	0.003253	−0.000132	7
$Eu(ClO_4)_3$	0.354397	−0.041492	0.003495	−0.000164	4
$Gd(ClO_4)_3$	0.359128	−0.042151	0.003708	−0.000189	10
$Tb(ClO_4)_3$	0.360279	−0.043042	0.003981	−0.000213	4
$Dy(ClO_4)_3$	0.364381	−0.044091	0.004211	−0.000224	12
$Ho(ClO_4)_3$	0.367987	−0.043727	0.003934	−0.000198	4
$Er(ClO_4)_3$	0.371510	−0.043913	0.003915	−0.000195	5
$Tm(ClO_4)_3$	0.374421	−0.043868	0.003844	−0.000186	5
$Yb(ClO_4)_3$	0.379622	−0.044459	0.003950	−0.000198	5
$Lu(ClO_4)_3$	0.382319	−0.044240	0.003828	−0.000184	5

Table III. Apparent Molal Volumes at Infinite Dilution of Some Aqueous Rare Earth Perchlorate Solutions at 25°C

Salt	$\phi_V{}^0$, ml/mol	Salt	$\phi_V{}^0$, ml/mol
$La(ClO_4)_3$	93.36[a]	$Dy(ClO_4)_3$	91.30[b]
$Pr(ClO_4)_3$	89.76[b]	$Ho(ClO_4)_3$	90.25[b]
$Nd(ClO_4)_3$	88.55[a]	$Er(ClO_4)_3$	89.51[b]
$Sm(ClO_4)_3$	90.06[b]	$Tm(ClO_4)_3$	88.30[b]
$Eu(ClO_4)_3$	91.04[b]	$Yb(ClO_4)_3$	87.88[b]
$Gd(ClO_4)_3$	91.77[a]	$Lu(ClO_4)_3$	86.18[a]
$Tb(ClO_4)_3$	91.83[b]		

[a] Spedding et al. (*17*). [b] Estimated from Equation 3.

Table IV. ϕ_V Parameters for Equation 5

Salt	$\phi_V{}^0$	B_2	B_3	B_4	B_5	SD
$La(ClO_4)_3$	93.535	−36.059	18.652	7.655	−5.799	0.10
$Pr(ClO_4)_3$	90.028	−42.538	32.265	−3.074	−2.756	0.05
$Nd(ClO_4)_3$	88.855	−41.172	32.556	−4.641	−2.229	0.11
$Sm(ClO_4)_3$	90.393	−48.188	45.205	−15.645	1.303	0.09
$Eu(ClO_4)_3$	91.293	−41.658	31.748	−6.485	−0.865	0.05
$Gd(ClO_4)_3$	92.144	−49.023	49.823	−21.944	3.507	0.15
$Tb(ClO_4)_3$	92.063	−35.338	20.644	0.494	−2.540	0.09
$Dy(ClO_4)_3$	91.593	−40.132	34.337	−10.878	0.379	0.08
$Ho(ClO_4)_3$	90.526	−38.252	27.070	−3.673	−1.673	0.08
$Er(ClO_4)_3$	89.832	−51.727	57.461	−26.769	4.215	0.05
$Tm(ClO_4)_3$	88.558	−47.376	46.537	−17.413	1.556	0.06
$Yb(ClO_4)_3$	88.325	−59.990	73.755	−37.860	6.818	0.09
$Lu(ClO_4)_3$	86.418	−47.055	49.042	−21.093	2.877	0.11

The partial molal volumes of the salt and water were calculated from

$$\bar{V}_2 = \phi_V + m\left(\frac{\partial \phi_V}{\partial m}\right)_{T,P,n_1} \qquad (6)$$

and

$$\bar{V}_1 = \bar{V}_1{}^0 - \frac{M_1 m^2}{1000}\left(\frac{\partial \phi_V}{\partial m}\right)_{T,P,n_1} \qquad (7)$$

where M_1 = 18.0154 g/mol, is the molecular weight of water and $V_1{}^0 = M_1/d^0$, is the molar volume of pure water.

The concentration dependence of the apparent molal volume, ϕ_V, the partial molal volume of the solute, $\bar{V}_2$, and the partial molal volume of the water, $\bar{V}_1$, of La, Nd, Tb, and Lu perchlorate are shown in Figures 1, 2, and 3, respectively. The order of the other rare earths will be shown in Figures 4-6. Except for an anion shift, the order

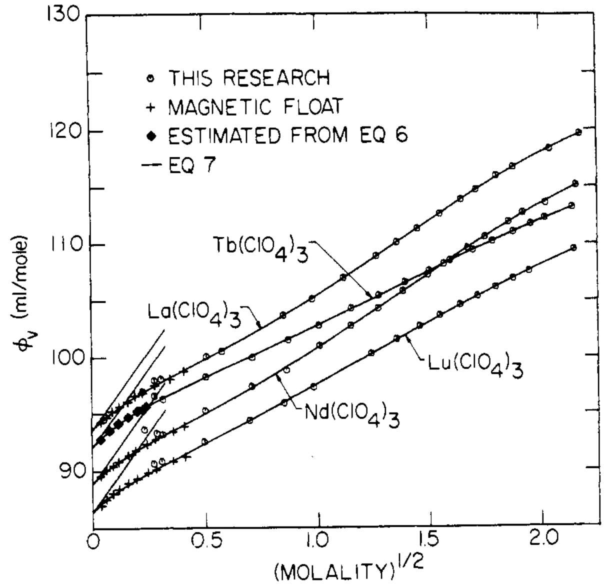

Figure 1. Apparent molal volumes of some aqueous rare earth perchlorate solutions at 25°C

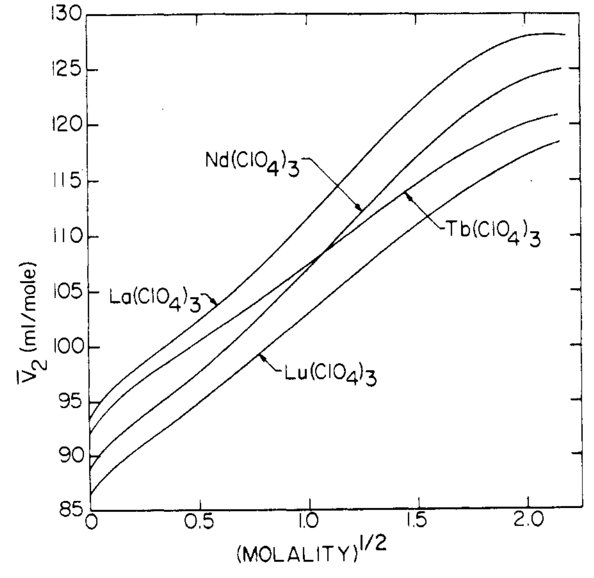

Figure 2. Partial molal volumes of solute of some aqueous rare earth perchlorate solutions at 25°C

is the same as in the chlorides (*20*) at low concentrations but changes with increasing concentration to a greater extent for the perchlorates than in the chlorides. As with the chlorides, the ϕ_V's and $\bar{V}_2$'s are not linear in $m^{1/2}$ or $c^{1/2}$ and conform only qualitatively to Masson's rule (*11*).

In Figures 4-6 the ϕ_V's, $\bar{V}_2$'s, and $\bar{V}_1$'s are shown as a function of the ionic radii (*24*) of the rare earth cation at various constant concentrations calculated from Equations 5-7. The curves at 0*m* represent the $\phi_V{}^0 (= \bar{V}_2{}^0)$ at infinite dilution, listed in Table III. Note that the trends in the estimated $\bar{V}_2{}^0$'s at infinite dilution are consistent with those based on experimental pycnometric data at 0.1*m*.

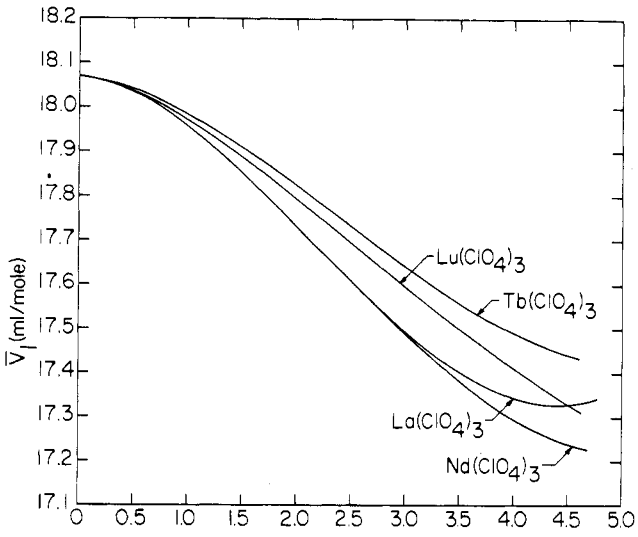

Figure 3. Partial molal volumes of water of some rare earth perchlorate solutions at 25°C

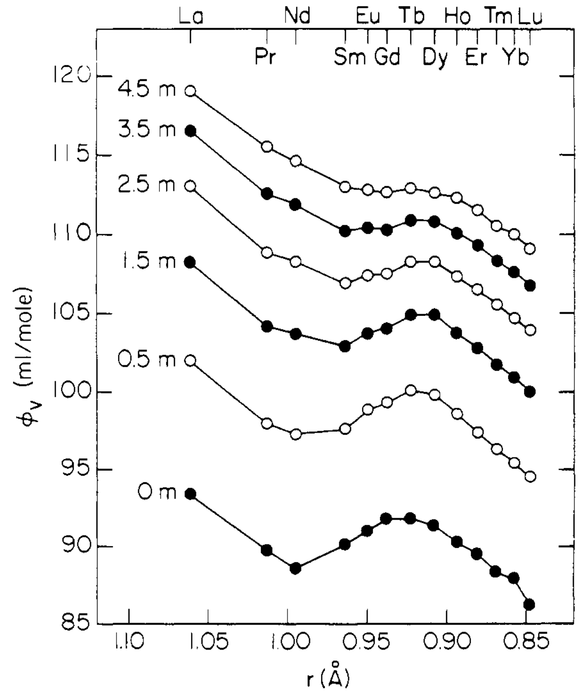

Figure 4. Apparent molal volumes of some aqueous rare earth perchlorate solutions at 25°C. Values at 0*m* are taken from Table III

As was the case in the rare earth chlorides, the ϕ_V's, $\bar{V}_2$'s, and $\bar{V}_1$'s go through a pronounced two-series trend across the rare earth series at all concentrations, where these properties decrease for the light and heavy rare earths but increase in the middle of the series.

In dilute solutions it is usually immaterial whether ϕ_V or $\bar{V}_2$ is considered since these quantities converge to the same limit. At high concentrations, however, the different operational definitions of these two properties must be considered. Whereas ϕ_V is the cumulative (integral) volume change upon the addition of salt from pure water to the concentration of interest, $\bar{V}_2$ is the (differential) volume change at the concentration of interest. Comparison of Figures 4 and 5 shows that these two properties show the two-series effect at different positions in the rare earth series at high concentrations (at 3.5*m*, for example). Also, the curves for $Nd(ClO_4)_3$ and $Tb(ClO_4)_3$ cross at a different concentration in ϕ_V (Figure 1) than in $\bar{V}_2$ (Figure 2). The $\bar{V}_2$ values are the quantities of interest at high concentrations, since these represent volume changes at the concentration under consideration. Note that although there is little scatter in ϕ_V across the series at high concentrations, the $\partial \phi_V / \partial m$ term in Equation 6 for $\bar{V}_2$ exaggerates this scatter owing to the errors in curve fitting necessary in obtaining the derivative. This problem is most severe at the ends of the data sets. Similar considerations apply to the scatter in $\bar{V}_1$ at high concentrations (Figure 6).

Discussion

The two-series effect has been interpreted (*18*) as reflecting a change in inner sphere water coordination of the rare earth cation in the vicinity of Nd to Tb. Because of the decreasing size of the trivalent rare earth cation, the inner sphere water coordination decreases from nine in the rare earths from La to Nd to eight in those from Tb to Lu. Between Nd and Tb mixtures of nine and eight coordinated ions were postulated (*18*). The inner sphere hydration change and consequent changes in the molecular configuration of the environment beyond the inner sphere give rise to the reversal in these volume properties between Nd and Tb in the rare earth chlorides (*20*).

Despite a slight change in the position of this two-series effect in the $\bar{V}_2$'s of the rare earth chloride series with increasing concentration, it was concluded that the chlorides do not penetrate the inner hydration sphere of the cation with increasing concentration, and the inner sphere water coordination change from nine to eight remains in the vicinity of Nd to Tb from infinite dilution to saturation (*20*).

At infinite dilution, where there are no cation-anion interactions, and the two-series effect is purely a cation-water interaction, the interpretation of the $\bar{V}_2{}^0$'s of the perchlorates must be identical to the chlorides. However, as the concentration increases, there is a large shift in this two-series effect in the $\bar{V}_2$'s of the perchlorates from the vicinity of Nd to Tb at infinite dilution to the region of Tb-Dy-Ho at 3.5*m*. At higher concentration the scatter of the $\bar{V}_2$ data becomes too large to see the two-series effect clearly, if it is still present. On the other hand, the two-series effect in the $\bar{V}_1$'s of the perchlorates, ignoring the considerable scatter, seems to be centered between Nd and Dy, even at high concentrations.

Although the perchlorate-cation interaction is thought to be very small, there is some evidence for outer sphere complex formation (*1, 2, 7-9, 14, 22, 23*). Raman studies (*5*) of La, Gd, and Lu perchlorate solutions and an X-ray diffraction study (*10*) of a nearly saturated $Dy(ClO_4)_3$ solution are also consistent with this interpretation. Both of

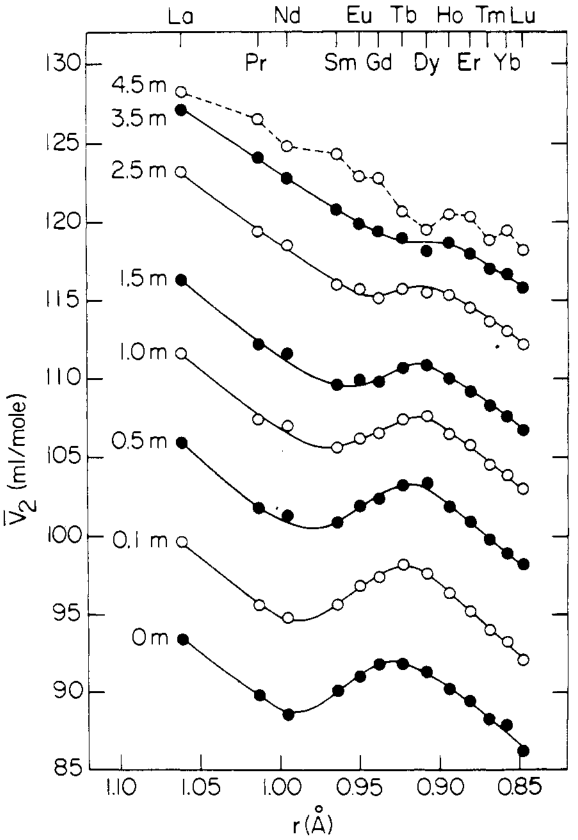

Figure 5. Partial molal volumes of solute of some aqueous rare earth perchlorate solutions at 25°C. Values at 0*m* are taken from Table III

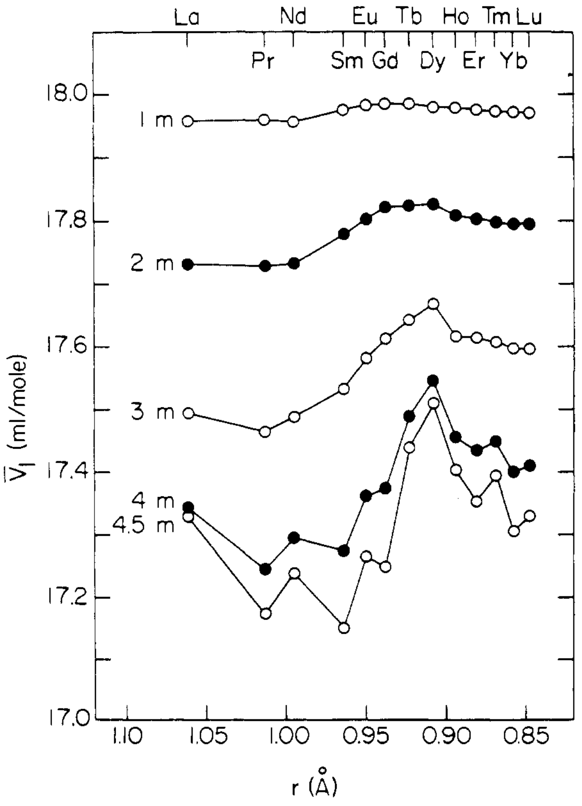

Figure 6. Partial molal volumes of water of some rare earth perchlorate solutions at 25°C

these studies indicate that the cation retains its inner hydration sphere up to saturation. The X-ray study (*10*) of the nearly saturated $Dy(ClO_4)_3$ solution also indicates that the inner sphere water coordination is eight for the Dy ion at high concentrations. The two-series effect in the relative partial molal heats of dilution, $\bar{L}_2$, of eight rare earth perchlorates (*4, 13*) remains near Nd–Dy up to saturation ($Tb(ClO_4)_3$ was not studied).

Both the viscosities (*21*) and conductances (*19*) of 13 and 11 rare earth perchlorates, respectively, go through the two-series trend between Nd and Tb up to saturation. In the latter study (*19*) it was concluded that the shift in coordination at Nd to Tb remains essentially unchanged over the whole concentration range. Thus, it appears that the inner sphere hydration change occurs near Nd to Tb from infinite dilution to saturation, and the change in the position of the reversal in the $\bar{V}_2$'s and $\bar{V}_1$'s in the rare earth perchlorate series with increasing concentration is due to secondary effects.

As detailed in the chloride paper, the trends in the $\bar{V}_2$'s and $\bar{V}_1$'s across the rare earth series reflect changes in the electrostriction of the water in the inner cation hydration sphere, as well as changes in the electrostriction of the environment beyond the first sphere. At infinite dilution this environment beyond the first sphere consists of water only. However, this environment at high concentrations will consist of perchlorate ions sharing the first sphere waters of the cation, since at saturation there are only 12 waters for each rare earth perchlorate unit. Therefore, the contribution to the volume properties by the environment beyond the first hydration sphere would be expected to differ markedly, depending on whether it is mostly water (at infinite dilution) or outer sphere perchlorate complexes (at saturation).

Evidently, the effect of the inner sphere hydration change on the molecular configuration of the rare earth–water-perchorate complex beyond the inner hydration sphere at high concentrations is such that the summation of the volume changes results in a displacement of the two-series effect (but not the position of the inner sphere hydration change) to smaller radii. The reason for this behavior is not clear at this time. Further X-ray diffraction studies on the remaining rare earth perchlorate solutions at high concentrations are needed to determine the position of the hydration change in the rare earth perchlorate series at high concentrations. Such studies are presently contemplated.

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

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The relative viscosities of aqueous solutions of the trivalent nitrates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, and Lu were measured over the concentration range of approximately 0.05*m* to saturation at 25°C. The relative viscosities of the aqueous rare earth chlorides and perchlorates were reported previously. The rare earth nitrate relative viscosities at constant molal concentrations increased regularly from La to Lu. The nitrate viscosity data are briefly compared to the chloride and perchlorate viscosities, and the trends in the nitrate viscosities are briefly discussed in terms of complexation between the rare earth and nitrate ions and in terms of hydration changes across the rare earth series.

In dilute rare earth nitrate solutions it is believed that a mixture of inner and outer sphere complexation occurs between the rare earth and nitrate ions (*2, 3*) with the major species being outer sphere. In more concentrated solutions the predominant form of interaction appears to be inner sphere with binding probably occurring through the oxygens of the nitrates (*1, 4, 5, 8, 10*). In addition, three nitrates are doubly coordinated to the rare earth ion in the hydrated crystals (*11*).

The trends observed in the rare earth chloride and perchlorate transport properties (*13, 15, 16, 18, 19*) are consistent with a change in the inner sphere hydration of the rare earth ion and with changes in overall hydration across the rare earth series. The formation of inner sphere complexes in the rare earth nitrates would result in the displacement of inner sphere water; consequently, the same explanation will not be expected to hold for the rare earth nitrates except in very dilute solutions. This study was undertaken to investigate the effect of inner sphere complexation on rare earth salt solution transport properties.

Experimental

The viscosities were measured at 25°C with the same suspended level Ubbelohde viscometers that were used for the rare earth chloride (*13, 19*) and perchlorate (*18*) viscosity determinations. The experimental techniques and procedures were the same as previously reported (*13*). Stock solutions of the stoichiometric salts were prepared by the method of Spedding et al. (*14*), and dilutions were prepared by weight from conductivity water and stock solution. All stock and saturated solutions were analyzed by EDTA (*12*) and sulfate (*14*) methods; these analyses agreed to ±0.1% or better in terms of the molality. In performing the sulfate analyses, the nitrate ions were decomposed by evaporating the samples with hydrochloric acid before the sulfuric acid additions were made.

Errors and Data Treatment

The kinetic energy corrections are negligible for the viscometers used in this research; therefore, the relative viscosities are given by

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

where d is the solution density, d_0 the water density, t the solution efflux time, and t_0 the water efflux time. The densities of the solutions studied in this research will be reported separately along with the partial molal volumes (*17*). In Table I the experimental relative viscosities and the corresponding molal concentrations of the solutions are listed. Except for $Pr(NO_3)_3$, the highest concentration in each case is the saturated solution. The highest concentration for $Pr(NO_3)_3$ is a supersaturated solution.

The errors in the solution densities are negligible compared to the other experimental errors. The total error in each viscosity is then mainly due to the error in the viscosity measurement and to the solution concentration uncertainty. The solution concentration uncertainties are ±0.1% or less, and the experimental viscosity determinations are reliable to at least ±0.05%. The total maximum probable error in the viscosity, when the concentration uncertainty is included, is 0.13% at 1.0*m*, 0.23% at 2.0*m*, 0.32% at 3.0*m*, 0.40% at 4.0*m*, 0.47% at 5.0*m*, 0.54% at 6.0*m*, and 0.78% at 6.8*m*. The relative concentration uncertainties for each salt are much smaller than the above numbers since the dilutions were prepared by weight from a concentrated stock solution and conductivity water. Since the measured viscosity data for each salt, except for the saturated solution, are self-consistent to within 0.05%, the data in Table I are given to five figures.

The rare earth nitrate viscosity data were fitted to the equation

$$\frac{\eta_R - 1}{\eta_R} = \sum_{i=1}^{6} A_i m^{i/2} \tag{2}$$

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