Literature Cited

(1) Brady, G. W., *J. Chem. Phys.*, **33**, 1079 (1960).
(2) Choppin, G. R., Henrie, D. E., Buijs, K., *Inorg. Chem.*, **5**, 1743 (1966).
(3) Gurney, R. W., "Ionic Processes in Solution," McGraw-Hill, New York, N.Y., 1953.
(4) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.
(5) Hertz, H. G., in "Water A Comprehensive Treatise," F. Franks, Ed., Vol 3, Chap. 7, Plenum Press, New York, N.Y., 1973.
(6) Kaminsky, M., *Z. Phys. Chem., NF*, **8**, 173 (1956).
(7) Kaminsky, M., *Discuss. Faraday Soc.*, **24**, 171 (1957).
(8) Martin, L. L., Spedding, F. H., *J. Chem. Phys.*, submitted for pubication (1974).
(9) Nightingale, Jr., E. R., *J. Phys. Chem.*, **63**, 742 (1959).
(10) Spedding, F. H., Cullen, P. F., Habenschuss, A., *ibid.*, **78**, 1106 (1974).
(11) Spedding, F. H., Nelson, R. A., Rard, J. A., *J. Chem. Eng. Data*, **19** (4), 379 (1974).
(12) Spedding, F. H., Pikal, M. J., *J. Phys. Chem.*, **70**, 2430 (1966).
(13) Spedding, F. H., Pikal, M. J., Ayers, B. O., *ibid.*, p 2440.
(14) Spedding, F. H., Rard, J. A., *ibid.*, **78**, 1435 (1974).
(15) Spedding, F. H., Rard, J. A., Saeger, V. W., *J. Chem. Eng. Data*, **19** (4), 373 (1974).
(16) Spedding, F. H., Rard, J. A., Weber, H. O., Shiers, L. E., unpublished data.
(17) Spedding, F. H., Shiers, L. E., Brown, M. A., Derer, J. L., Swanson, D., Habenschuss, A., *J. Chem. Eng. Data*, **20** (1), 81 (1975).
(18) Spedding, F. H., Weber, H. O., Saeger, V. W., Petheram, H. H., Rard, J. A., Habenschuss, A., unpublished data.
(19) Spedding, F. H., Witte, D. L., Shiers, L. E., Rard, J. A., *J. Chem. Eng. Data*, **19** (4), 369 (1974).
(20) Templeton, D. H., Dauben, C. H., *J. Amer. Chem. Soc.*, **76**, 5237 (1954).

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

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

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

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

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

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

Experimental

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

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ture was controlled at 25.000° (or 0.000°) ± 0.005°C and checked with a platinum resistance thermometer calibrated by the National Bureau of Standards. All weighings were made on an Ainsworth-type BB analytical balance using a set of calibrated Ainsworth class S certified weights. All weights were corrected to weights in vacuum. The tare and each pycnometer were wiped with alcohol before weighing to minimize weighing errors owing to surface effects.

The pycnometers were calibrated at 0° and 25°C with conductivity water prepared by distillation from an alkaline potassium permanganate solution. The specific conductivity of this water was less than 1×10^{-6} mho/cm. The density of water was taken from Tilton and Taylor (*46*), (25°C, $d^0 = 0.997075$ g/ml; 0°C, $d^0 = 0.999868$ g/ml). The mean deviation of approximately 10 volume calibrations for each pycnometer was less than ±0.0003 ml in all cases. Two to four determinations of the density of each solution, with different pycnometers, were made.

Solutions. The preparation of the solutions has been described elsewhere (*37, 41*). The oxides were purified by ion-exchange methods by the Rare Earth Separation Group of the Ames Laboratory. To insure that we were considering a two-component solution of water and the stoichiometric salt, the stock solutions were adjusted to the equivalence pH by methods already described (*41*).

Weight dilutions were made from the concentrated stock solutions and conductivity water. The stock solutions and saturated solutions were analyzed by at least two of either oxide, sulfate, chloride, or EDTA methods (*37, 41*). The analyses agreed to at least 0.1% and, in most cases, to 0.05% in terms of molality. In those cases where both cation and anion analyses were made, the concentrations agreed to within 0.1%.

Table I. Densities and Apparent Molal Volumes of Some Aqueous Rare Earth Chloride Solutions

m	d	$\Delta d \times 10^5$	ϕ_V	$\Delta\phi_V$
		$LaCl_3$ (25°C)		
0.020724	1.00177	−4	18.02	−0.50
0.039982	1.00611	−6	18.51	−0.13
0.055827	1.00966	−7	18.99	−0.09
0.11094	1.02191	−5	20.30	−0.13
0.13259	1.02669	−4	20.70	−0.14
0.19753	1.04096	−1	21.56	−0.04
0.29085	1.06125	2	22.59	0.02
0.31955	1.06746	1	22.82	0.09
0.37513	1.07937	4	23.39	0.05
0.39047	1.08260	9	23.64	−0.06
0.48666	1.10305	5	24.36	0.04
0.58636	1.12396	4	25.12	0.05
0.72096	1.15182	−2	26.04	0.08
0.75572	1.15890	0	26.32	0.04
0.90873	1.18989	−7	27.28	0.06
0.97118	1.20228	−1	27.74	−0.02
1.1411	1.23570	−2	28.76	−0.06
1.2679	1.26021	−4	29.46	−0.07
1.4763	1.29975	−11	30.50	−0.04
1.6396	1.32988	2	31.35	−0.10
1.8548	1.36890	1	32.30	−0.06
2.0788	1.40837	12	33.25	−0.06
2.2818	1.44340	7	34.01	−0.01
2.5285	1.48478	11	34.90	0.03
3.0512	1.56890	−15	36.53	0.11
3.0819	1.57363	−12	36.63	0.10
3.4562	1.63018	−2	37.76	0.01
3.5966	1.65062	12	38.18	−0.07
3.8959	1.69433	(−95)	38.82	−0.03
		$PrCl_3$ (25°C)		
0.017303	1.00110	−1	13.96	−0.20
0.029693	1.00396	−1	14.66	−0.28
0.063399	1.01172	−2	15.41	0.06
0.080103	1.01554	−2	15.83	0.05
0.11366	1.02318	−1	16.53	0.02
0.18685	1.03972	0	17.66	0.02
0.21562	1.04618	1	18.03	0.02
0.24945	1.05374	2	18.45	0.00
0.29655	1.06424	1	18.90	0.06
0.38231	1.08319	−0	19.72	0.08
0.47876	1.10426	1	20.58	0.05
0.64613	1.14030	0	21.88	0.03
0.82568	1.17820	0	23.14	−0.00
1.0564	1.22580	−2	24.57	−0.02
1.3936	1.29315	−4	26.44	−0.02
		$PrCl_3$ (25°C)		
1.5286	1.31932	1	27.16	−0.05
1.8164	1.37385	4	28.55	−0.05
2.0825	1.42269	2	29.73	−0.02
2.6858	1.52786	−3	32.11	0.04
3.0289	1.58429	−1	33.34	0.04
3.2711	1.62273	2	34.16	0.02
3.8910	1.71626	(−6)	36.06	−0.03
		$NdCl_3$ (25°C)		
0.025985	1.00322	−1	13.40	−0.03
0.037182	1.00585	−1	13.72	0.12
0.048954	1.00861	−1	14.11	0.12
0.073320	1.01428	1	15.00	−0.11
0.11599	1.02421	−0	15.60	0.13
0.18668	1.04048	1	16.72	0.07
0.22257	1.04870	1	17.14	0.10
0.28528	1.06298	−0	17.78	0.15
0.33423	1.07402	2	18.34	0.07
0.40038	1.08892	−1	18.86	0.14
0.50921	1.11313	−1	19.79	0.09
0.62558	1.13872	−3	20.65	0.09
0.82591	1.18203	−7	22.00	0.08
1.0224	1.22345	4	23.33	−0.06
1.2393	1.26821	7	24.58	−0.09
1.5409	1.32880	−3	26.10	−0.03
1.6938	1.35860	4	26.89	−0.07
2.1610	1.44674	−7	28.96	0.01
2.5811	1.52157	−1	30.71	0.02
3.1132	1.61142	6	32.69	0.03
3.6138	1.69079	−2	34.35	0.04
3.9292	1.73794	(36)	35.38	−0.05
		$SmCl_3$ (25°C)		
0.022158	1.00242	−1	14.52	−0.44
0.030016	1.00431	−1	14.82	−0.38
0.044960	1.00790	−2	15.07	−0.10
0.10180	1.02143	−1	16.44	−0.12
0.11417	1.02435	−1	16.67	−0.13
0.22693	1.05085	1	18.12	−0.02
0.35101	1.07961	2	19.33	0.01
0.45735	1.10397	2	20.20	0.02
0.64245	1.14572	1	21.53	0.01
0.82308	1.18572	−3	22.64	0.03
0.96565	1.21672	−1	23.49	−0.01
1.1384	1.25369	−1	24.43	−0.02
1.4265	1.31386	−0	25.87	−0.03
1.7136	1.37196	1	27.18	−0.03

(Continued on page 74)

Table I. Continued

m	d	$\Delta d \times 10^5$	ϕ_V	$\Delta\phi_V$
		$SmCl_3$ (25°C)		
1.9466	1.41777	4	28.18	−0.02
2.3841	1.50059	−2	29.92	0.02
2.6945	1.55670	−1	31.10	0.03
3.0587	1.61976	−0	32.43	0.02
3.4090	1.67757	1	33.68	−0.01
3.6401	1.71441	(−23)	34.45	−0.01
		$EuCl_3$ (25°C)[a]		
0.019377	1.00176	−1	15.81	−0.79
0.024975*	1.00309	0	16.72	−1.42
0.040631*	1.00685	−0	16.92	−0.98
0.040986	1.00697	−3	16.08	−0.13
0.059696*	1.01141	0	17.29	−0.77
0.060091	1.01154	−2	16.70	−0.17
0.078526	1.01593	−1	17.23	−0.25
0.10009	1.02105	0	17.71	−0.28
0.15054*	1.03300	−0	18.37	−0.11
0.16167	1.03562	1	18.54	−0.12
0.25148	1.05667	2	19.54	−0.04
0.27408*	1.06197	0	19.63	0.10
0.35584	1.08086	2	20.51	−0.02
0.44417*	1.10121	2	21.05	0.15
0.49611	1.11297	1	21.59	−0.00
0.62364*	1.14192	−3	22.23	0.22
0.64078	1.14559	−1	22.58	−0.03
0.81323	1.18382	−1	23.66	−0.08
0.85499*	1.19320	−0	23.68	0.13
1.0130	1.22727	−2	24.78	−0.12
1.1059*	1.24746	2	25.05	0.08
1.2067	1.26853	−1	25.78	−0.15
1.3885*	1.30694	1	26.40	0.08
1.4576	1.32075	1	26.96	−0.17
1.6970	1.36931	0	27.99	−0.15
1.9931	1.42763	2	29.18	−0.12
2.0544*	1.44018	−2	29.16	0.14
2.2513	1.47694	1	30.16	−0.09
2.4815*	1.52049	−1	30.76	0.17
2.5873	1.53892	−0	31.37	−0.05
2.8892	1.59248	−2	32.42	−0.03
2.9190*	1.59854	2	32.32	0.18
3.2634	1.65600	−1	33.70	−0.05
3.3533*	1.67179	−1	33.81	0.14
3.5225	1.69811	1	34.58	−0.09
3.5839*	1.70856	(34)	34.66	0.02
3.5889	1.70875	(−8)	34.78	−0.09
		$GdCl_3$ (25°C)		
0.023050	1.00276	−2	16.27	−0.20
0.036376	1.00602	−3	16.76	−0.14
0.051437	1.00970	−3	17.27	−0.17
0.12354	1.02717	−1	18.76	−0.13
0.20505	1.04671	2	19.88	−0.12
0.32080	1.07419	2	20.98	0.01
0.42474	1.09856	2	21.83	0.05
0.64112	1.14843	−0	23.37	0.06
0.82366	1.18962	−1	24.51	0.02
1.0011	1.22892	−3	25.50	0.00
1.0793	1.24598	−1	25.94	−0.03
1.3078	1.29511	−1	27.06	−0.04
1.6221	1.36075	2	28.48	−0.05
1.9623	1.42938	2	29.84	−0.03
2.2958	1.49421	2	31.07	0.00
2.6051	1.55221	−2	32.14	0.03
2.9683	1.61763	−3	33.34	0.04
3.3564	1.68427	2	34.59	0.01
3.5906	1.72291	(2)	35.33	−0.03

m	d	$\Delta d \times 10^5$	ϕ_V	$\Delta\phi_V$
		$TbCl_3$ (25°C)		
0.021266	1.00235	−1	16.47	−0.33
0.043191	1.00776	−2	17.04	−0.04
0.057714	1.01132	−1	17.54	−0.13
0.077749	1.01623	−1	17.90	−0.01
0.11505	1.02533	−2	18.51	0.09
0.15144	1.03415	−1	19.10	0.07
0.21925	1.05047	1	20.03	0.01
0.23691	1.05470	1	20.23	0.01
0.30935	1.07195	4	21.02	−0.04
0.39856	1.09309	−3	21.66	0.13
0.51093	1.11929	2	22.68	0.00
0.60705	1.14150	1	23.37	0.00
0.80258	1.18597	0	24.65	−0.01
0.98552	1.22678	−5	25.69	0.01
1.1954	1.27255	−3	26.85	−0.02
1.5098	1.33917	4	28.40	−0.05
1.6939	1.37720	2	29.20	−0.03
2.0233	1.44336	−1	30.53	0.01
2.5095	1.53661	1	32.32	0.03
2.9319	1.61360	−3	33.70	0.04
3.3803	1.69117	2	35.09	−0.04
3.5713	1.72349	(−49)	35.56	0.01
		$DyCl_3$ (25°C)		
0.025036	1.00339	−2	15.69	0.06
0.037732	1.00657	−2	16.29	−0.04
0.049460	1.00950	−1	16.78	−0.15
0.12118	1.02730	−0	18.20	−0.02
0.23862	1.05609	1	19.70	0.06
0.34630	1.08217	1	20.72	0.12
0.48745	1.11585	1	21.94	0.09
0.64737	1.15340	1	23.13	0.05
0.81840	1.19285	−0	24.26	0.01
1.0551	1.24627	−1	25.67	−0.03
1.1240	1.26158	−3	26.03	−0.02
1.4089	1.32359	1	27.52	−0.07
1.7002	1.38508	2	28.87	−0.07
2.2307	1.49214	3	31.01	−0.02
2.5897	1.56110	−2	32.30	0.03
2.9606	1.62941	−2	33.54	0.05
3.3344	1.69526	2	34.72	0.04
3.3610	1.74509	(41)	35.67	−0.05
		$HoCl_3$ (25°C)		
0.020900	1.00241	−1	15.25	−0.56
0.041136	1.00755	−2	15.78	−0.27
0.056431	1.01142	−1	16.16	−0.19
0.076016	1.01636	−1	16.58	−0.14
0.11311	1.02571	−3	16.95	0.21
0.15312	1.03573	−4	17.48	0.31
0.21500	1.05106	2	18.51	0.07
0.25472	1.06088	2	18.91	0.12
0.29856	1.07168	0	19.29	0.19
0.37640	1.09064	5	20.15	0.04
0.51825	1.12489	3	21.28	0.06
0.60231	1.14495	0	21.88	0.06
0.81946	1.19593	−6	23.34	0.03
1.1536	1.27204	−7	25.34	−0.05
1.3494	1.31536	−3	26.40	−0.08
1.4766	1.34295	6	27.08	−0.12
1.6853	1.38756	7	28.04	−0.10
2.0073	1.45452	1	29.38	−0.01
2.3651	1.52613	−3	30.76	0.07
2.6690	1.58466	−2	31.86	0.10
3.3231	1.70354	1	34.09	0.03
3.6942	1.76694	(−24)	35.25	−0.05

Table I. Continued

m	d	$\Delta d \times 10^5$	ϕ_V	$\Delta\phi_V$
		$ErCl_3$ (25°C)		
0.023577	1.00318	−2	13.97	−0.20
0.035107	1.00614	−1	14.62	−0.34
0.046163	1.00898	−2	14.80	−0.13
0.073922	1.01607	−1	15.71	−0.26
0.11280	1.02596	−0	16.41	−0.16
0.17522	1.04174	−1	17.24	−0.00
0.22260	1.05361	2	17.93	−0.09
0.31230	1.07600	−1	18.74	0.08
0.39786	1.09708	2	19.61	−0.00
0.50427	1.12309	2	20.47	0.01
0.60324	1.14703	0	21.19	0.03
0.79641	1.19305	−2	22.49	0.02
0.97087	1.23379	−2	23.57	−0.01
1.1963	1.28535	−2	24.85	−0.04
1.6192	1.37873	3	26.99	−0.06
1.9888	1.45696	4	28.62	−0.03
2.4989	1.55991	−5	30.59	0.04
2.9875	1.65300	2	32.32	0.04
3.7821	1.79389	(−1)	34.74	−0.02
		$TmCl_3$ (25°C)		
0.020380	1.00242	−3	12.23	0.06
0.041670	1.00794	−1	13.68	−0.44
0.061800	1.01316	−2	14.07	−0.20
0.081560	1.01826	−2	14.52	−0.16
0.10263	1.02368	−1	14.95	−0.14
0.15507	1.03712	−1	15.71	−0.00
0.20688	1.05030	2	16.44	−0.01
0.28835	1.07089	3	17.32	0.03
0.40482	1.10004	3	18.36	0.09
0.59181	1.14613	−0	19.80	0.10
0.80069	1.19656	−1	21.25	0.04
1.0036	1.24454	−3	22.49	0.00
1.1968	1.28928	−2	23.60	−0.04
1.5148	1.36097	3	25.25	−0.09
1.6843	1.39826	1	26.03	−0.07
2.0054	1.46704	2	27.44	−0.04
2.4182	1.55202	−1	29.08	0.01
2.8062	1.62838	−3	30.50	0.06
3.2949	1.71971	1	32.17	0.07
3.8773	1.82148	(28)	34.06	−0.05
		$YbCl_3$ (25°C)		
0.025889	1.00398	−1	12.01	0.25
0.036177	1.00669	−0	12.65	0.02
0.046279	1.00937	−1	12.73	0.27
0.077930	1.01770	0	13.75	0.05
0.11559	1.02758	−0	14.33	0.18
0.17393	1.04278	−0	15.22	0.16
0.23913	1.05964	1	16.04	0.12
0.34445	1.08664	0	17.12	0.10
0.44549	1.11229	−1	17.99	0.10
0.55485	1.13971	3	18.93	−0.00
0.67737	1.17016	−1	19.77	0.03
0.87558	1.21857	−1	21.08	−0.01
1.0857	1.26886	−1	22.33	−0.04
1.7397	1.41860	2	25.65	−0.05
2.2400	1.52637	−1	27.79	−0.01
2.7681	1.63385	−1	29.80	0.02
3.2336	1.72341	0	31.40	0.03
4.0028	1.86137	(−4)	33.76	−0.02
		$LuCl_3$ (25°C)		
0.021500	1.00286	−0	11.44	−0.64
0.045520	1.00930	−2	11.87	−0.11
0.061010	1.01343	−2	12.31	−0.09
0.082070	1.01902	−1	12.91	−0.18
0.10334	1.02466	−1	13.28	−0.12
0.15347	1.03788	1	14.13	−0.12
0.20494	1.05140	1	14.72	0.00
0.30486	1.07741	2	15.82	0.03
0.39520	1.10071	1	16.65	0.05
0.60071	1.15295	0	18.29	0.05
0.79944	1.20250	−4	19.64	0.04
1.2032	1.30015	−1	22.07	−0.04
1.5062	1.37090	1	23.64	−0.06
1.7154	1.41848	2	24.64	−0.05
2.0094	1.48363	3	25.94	−0.03
2.4095	1.56913	−3	27.54	0.02
2.7701	1.64297	−4	28.90	0.05
3.3326	1.75209	4	30.88	0.03
3.9179	1.85813	−1	32.78	−0.03
4.1165	1.89291	(−58)	33.32	0.00
		YCl_3 (25°C)		
0.0016047			(13.98)[b]	0.25
0.0064194			(14.78)	0.17
0.014445			(15.47)	0.12
0.025686			(16.08)	0.09
0.040144			(16.64)	0.06
0.057826			(17.17)	0.03
0.019698	1.00059	−1	16.29	−0.41
0.031249	1.00263	−0	16.94	−0.54
0.039568	1.00410	−0	17.13	−0.45
0.050454	1.00603	−1	17.15	−0.15
0.069446	1.00937	−1	17.54	−0.06
0.11449	1.01724	−1	18.30	0.03
0.19090	1.03046	−0	19.28	0.12
0.28842	1.04709	2	20.39	0.06
0.38492	1.06335	1	21.24	0.08
0.47921	1.07904	−0	21.98	0.08
0.65210	1.10727	1	23.29	0.00
0.80387	1.13156	−1	24.28	−0.02
0.98630	1.16016	−4	25.37	−0.03
1.2813	1.20498	−1	26.99	−0.06
1.5005	1.23722	3	28.09	−0.07
1.8240	1.28329	2	29.52	−0.02
2.5070	1.37464	−2	32.17	0.08
3.1067	1.44845	0	34.21	0.05
3.5976	1.50462	0	35.74	−0.07
3.9478	1.54379	(−138)	36.52	0.02
		YCl_3 (0°C)		
0.019698	1.00349	−2	11.30	0.25
0.031249	1.00559	−1	12.05	−0.14
0.039568	1.00711	−2	12.12	0.02
0.050454	1.00909	−2	12.34	0.05
0.069446	1.01253	−2	12.75	0.04
0.11449	1.02062	0	13.70	−0.12
0.19090	1.03423	1	14.73	−0.04
0.28842	1.05136	2	15.89	0.00
0.38492	1.06807	1	16.90	0.04
0.47921	1.08416	1	17.84	0.04
0.65210	1.11310	1	19.40	0.02
0.80387	1.13795	−1	20.62	0.02
0.98630	1.16716	−5	21.96	0.03
1.2813	1.21283	−2	23.94	−0.02
1.5005	1.24560	4	25.27	−0.05
1.8240	1.29236	3	26.99	−0.03
2.5070	1.38485	−3	30.10	0.03
3.1067	1.45920	1	32.48	0.02
3.5976	1.51551	0	34.26	−0.02

[a] Starred values are Set 1; all others are Set 2. [b] ϕ_V values in parentheses are estimated from Equation 4.

Results

Densities. The experimental densities in g/ml and the molal concentrations of the solutions are listed in Table I. The highest experimental concentration for each salt in Table I is the saturated value, except for YCl_3 at 0°C, for which the saturated value was not measured.

The error in the density measurement is approximately $\pm 1 \times 10^{-5}$ g/ml over the whole concentration range. The uncertainty in the density owing to the ±0.1% absolute error in the analysis of the stock and saturated solutions ranges from $\pm 0.5 \times 10^{-5}$ g/ml at 0.02*m* to $\pm 100 \times 10^{-5}$ g/ml at saturation. If at high concentrations, the errors in the density owing to the uncertainty in the concentration were to be of the same order as the error in the density measurement itself, the concentrations of the stock solutions would have to be determined to 0.001%. Nevertheless, since the solutions were made up by weighing out required amounts of water and stock solutions, the relative errors in the concentrations are much less than the absolute error in the stock solution analysis. Therefore, the densities of those dilutions made by weight are internally consistent to $\pm 2 \times 10^{-5}$ g/ml, even at high concentrations, which is of the same order of magnitude as the error in the density measurement itself. Except for $LaCl_3$, this includes all the concentrations below the saturated value.

Empirical equations representing the densities within $\pm 2 \times 10^{-5}$ g/ml in most cases were obtained.

$$d - d^{\circ} = A_1 m + A_2 m^{3/2} + A_3 m^2 + A_4 m^{5/2} + A_5 m^3 \quad (1)$$

d° was fixed at the density of water in these equations. The parameters in Equation 1 are listed in Table II, together with the standard deviations of the fits. The deviations, Δd, of the experimental densities from the densities calculated from these equations are given in Table I. Since the concentrations of the saturated solutions were determined by separate analyses, the densities at saturation are not related to those at lower concentrations through weight dilution and were not used in obtaining Equation 1. The difference between the experimental density at saturation and the saturated density extrapolated from Equation 1 are also given in Table I in parentheses. These differences are all within the absolute error expected.

As indicated in Table I, the density data of $EuCl_3$ consist of measurements on two complete sets of dilutions from stock solutions prepared and analyzed separately. There are also two determinations of the density at saturation. These two sets were fitted to separate equations in the same way as with the other salts. The deviations, Δd, listed in Table I for $EuCl_3$ refer to the two respective fits. The difference between the densities calculated from these two equations rises to 100×10^{-5} g/ml at high concentrations which is within the absolute analysis error.

The data for $LaCl_3$ consist of measurements on dilutions prepared from several stock solutions. In addition, some of the concentrations of the dilutions for this salt were determined analytically instead of by weight. Therefore, although the $LaCl_3$ data were treated in the same way as the other salts, they do not show the internal consistency of the other density data.

It should be emphasized that the absolute errors in the experimental densities are $\pm 1 \times 10^{-5}$ g/ml at low concentrations, rising to $\pm 100 \times 10^{-5}$ g/ml at high concentrations, while the internal consistency of these densities is better than $\pm 2 \times 10^{-5}$ g/ml over the whole concentration range. If a concentrated solution could be made up by weight from the stoichiometric salt and water to a greater accuracy than by analysis and the density determined, then our densities could be adjusted to give values to this accuracy over the whole concentration range. Once this is done, an excellent means of determining the concentration of a solution of unknown composition would be to determine the density and obtain the concentration from our adjusted densities.

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

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

where m is the molal concentration, d is the experimental density of the solution, d° is the density of water, and M_2 is the molecular weight of the salt (1969 IUPAC atomic weights). The apparent molal volumes, in ml/mol, are given in Table I.

The apparent molal volumes were fitted to a Redlich-Meyer type equation

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

where $S_V = 27.45$ (21.23 at 0°C) for 3:1 salts (22), and $\phi_V{}^0$, B_2, B_3, . . . are empirical constants determined by least squares. Since we want to compare the ϕ_V's of the

Table II. Density Parameters for Equation 1

Salt	A_1	A_2	A_3	A_4	A_5	SD × 10^5
$LaCl_3$	0.224751	0.002423	−0.021341	0.005968	−0.000893	7
$PrCl_3$	0.233521	−0.010274	−0.002719	−0.004376	0.001039	2
$NdCl_3$	0.238275	−0.012536	0.001171	−0.006628	0.001440	4
$SmCl_3$	0.242300	−0.007779	−0.006516	−0.000962	−0.000005	2
$EuCl_3$[a]	0.241825	−0.004160	−0.011170	0.001704	−0.000534	2
$EuCl_3$[b]	0.242397	−0.006135	−0.009472	0.000993	−0.000408	2
$GdCl_3$	0.246545	−0.004738	−0.011443	0.001628	−0.000419	2
$TbCl_3$	0.249022	−0.008117	−0.006771	−0.001698	0.000409	3
$DyCl_3$	0.252882	−0.007005	−0.008178	−0.001154	0.000324	2
$HoCl_3$	0.255492	−0.003264	−0.014093	0.002695	−0.000583	4
$ErCl_3$	0.259748	−0.009487	−0.003585	−0.004234	0.000984	2
$TmCl_3$	0.262170	−0.006955	−0.007359	−0.001589	0.000325	2
$YbCl_3$	0.268177	−0.012089	0.000125	−0.006067	0.001249	1
$LuCl_3$	0.270202	−0.008345	−0.005401	−0.002486	0.000425	2
YCl_3	0.178986	−0.005717	−0.008864	0.000827	−0.000063	2
YCl_3[c]	0.183603	−0.001839	−0.016216	0.004644	−0.000783	2

[a] Set 1. [b] Set 2. [c] At 0°C, all other parameters refer to 25°C.

various rare earth chlorides, the absolute errors in the concentrations enter into the determination of the error in ϕ_V. For this reason, we have combined the $EuCl_3$ data and included all the saturated values in obtaining the ϕ_V equations. The differences between the experimental and calculated ϕ_V's are listed in Table I.

There is a pronounced downturn in ϕ_V at concentrations lower than those studied in this work (Figure 1). Therefore, to force Equation 3 to agree with the known concentration dependence of ϕ_V below 0.02*m*, the magnetic float ϕ_V data of Spedding et al. (*37, 41*) were included in the determination of Equation 3. These dilute data are not listed in Table I, since they have already been published (*37, 41*). Since the rate earth chlorides conform to the Debye-Hückel theory in very dilute solutions (*37, 41*), the theoretical limiting slope was included in Equation 3. The $d^{\circ 1/2}$ term converts S_V from the molar to the molal scale at infinite dilution. Of course, S_V has theoretical significance only at infinite dilution. The ϕ_V points were weighted with the reciprocal of the square of the probable error in ϕ_V. The ¼ power series in m gave a significantly better fit than a similar series in $m^{1/2}$.

The empirical constants in Equation 3 are given in Table III, together with the standard deviations of the fits. The inclusion of the magnetic float data and the limiting slope is only intended to anchor the dilute end of the pycnometric measurements where the errors become large for such measurements. Equation 3 does not represent the magnetic float data within their experimental error and should be used only in the experimental range of the pycnometric measurements. Below this range the equations of Spedding et al. (*37, 41*) should be used. Likewise, if accurate $\phi_V{}^0$'s are desired, they should be taken from the earlier magnetic float measurements on dilute solutions (*37, 41*), where the more appropriate Owen-Brinkley extrapolation function was used.

Unfortunately, the dilute data are not available for YCl_3. Nevertheless, the yttrium ion in many respects acts like a rare earth ion (*23, 38*) (Figures 1 and 2). Taking advantage of this fact, the low-concentration behavior of YCl_3 at 25°C was estimated in the following way. $\phi_V{}^0$ and å, the mean distance of closest approach, for YCl_3 were estimated from the $\phi_V{}^0$'s and å's of the rare earth chlorides (*37, 41*), assuming that YCl_3 falls between Tb and Dy. The Owen-Brinkley equation (*13*)

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

was then used to estimate six ϕ_V points below 0.06*m*. This was done by letting K_V vary until these points joined smoothly with the pycnometric ϕ_V's at 0.06*m*. These six points were then included in the determination of Equation 3. The estimated points are listed in Table I for YCl_3 at 25°C. The success of this procedure can be judged from Figures 1 and 2. Equation 3 for YCl_3 at 0°C is based only on the pycnometric measurements.

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

$$\bar{V}_2 = \phi_V + m\left(\frac{\partial \phi_V}{\partial m}\right)_{T,P,n_1} \qquad (5)$$

and

$$\bar{V}_1 = \bar{V}_1{}^0 - \frac{M_1m^2}{1000}\left(\frac{\partial \phi_V}{\partial m}\right)_{T,P,n_1} \qquad (6)$$

where M_1 = 18.0154 g/mol, is the molecular weight of water, and $\bar{V}_1{}^0 = M_1/d^{\circ}$, is the molal volume of pure water.

An experimental error of 1×10^{-5} g/ml in the density measurement contributes to the error in ϕ_V ranging from ±0.5 ml/mol at 0.02*m* to ±0.002 ml/mol at saturation. An absolute concentration error of 0.1% contributes an error of ±0.2 ml/mol at 0.02*m* to ±0.1 ml/mol at saturation. The total error in ϕ_V therefore ranges from about ±0.5 ml/mol at 0.02*m* to ±0.1 ml/mol at saturation. The inclusion of the more accurate magnetic float data lowers the errors in Equation 3 to approximately ±0.2 ml/mol at low concentrations. From Figure 1, the ϕ_V's of this research agree satisfactorily with those of the magnetic float measurements (*37, 41*) in the overlapping regions. The agreement for the other salts is similar. Our results for $LaCl_3$ are in excellent agreement with the measurements of Dunn (*9*).

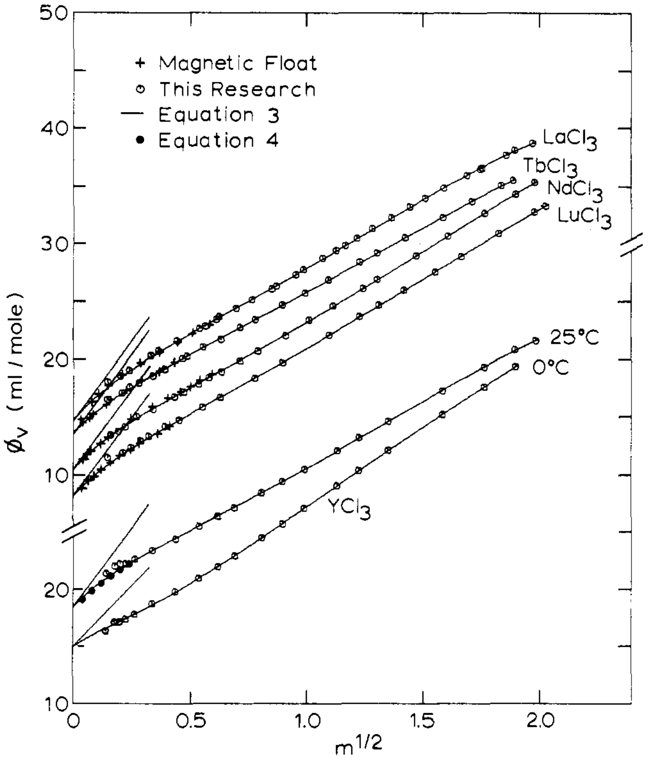

Figure 1. Apparent molal volumes of some aqueous rare earth chloride solutions. Straight lines represent Debye-Hückel limiting slope

Table III. ϕ_V **Parameters for Equation 3**

Salt	$\phi_V{}^0$	B_2	B_3	B_4	B_5	SD
$LaCl_3$	14.688	−19.407	−10.901	25.934	−9.841	0.11
$PrCl_3$	11.237	−25.617	3.867	13.352	−6.035	0.07
$NdCl_3$	10.367	−23.051	−3.401	19.336	−7.529	0.09
$SmCl_3$	11.374	−29.818	15.392	0.993	−1.681	0.08
$EuCl_3$	12.343	−24.301	2.733	10.524	−4.120	0.23
$GdCl_3$	13.319	−30.402	17.026	−0.437	−1.416	0.07
$TbCl_3$	13.520	−30.677	14.561	4.664	−3.699	0.07
$DyCl_3$	12.903	−29.136	12.018	5.924	−3.790	0.07
$HoCl_3$	12.027	−27.269	5.570	12.647	−5.945	0.12
$ErCl_3$	10.827	−21.848	−4.539	19.385	−7.511	0.10
$TmCl_3$	9.479	−20.321	−6.437	19.394	−7.054	0.11
$YbCl_3$	9.433	−30.718	14.121	5.353	−3.801	0.16
$LuCl_3$	8.063	−27.507	10.187	6.313	−3.570	0.09
YCl_3	13.354	−29.465	8.250	11.995	−6.130	0.13
YCl_3[a]	9.929	−47.736	74.306	−45.314	9.662	0.05

[a] At 0°C, all other parameters refer to 25°C.

Discussion

Typical concentration dependences of the ϕ_V's of the rare earth chlorides are shown in Figure 1, together with the Debye-Hückel limiting slope. Except for slight differences in slope, the ϕ_V curves of the other rare earth chlorides are very similar to those shown in Figure 1. The results for YCl_3 at 0° and 25°C are also shown in Figure 1. These data on YCl_3 will be discussed in a paper in preparation on the expansibilities of the rare earth chloride solutions.

In Figure 2 the partial molal volumes of the rare earth chlorides, as calculated from Equation 3 at equal molalities, are given as a function of the ionic radii (*45*) of the rare earth cations. The lowest curve in this figure represents the partial molal volumes of the rare earth chlorides at *infinite dilution*, $\bar{V}_2{}^0$ $(=\phi_V{}^0)$, taken from Spedding et al. (*37, 41*).

The partial molal volume of the salt, $\bar{V}_2$, represents the volume change in a solution that occurs as a mole of rare earth salt is added to an infinite amount of this solution at some fixed concentration. For electrolytes containing ions of high-surface charge density, this volume increase in the aqueous solution is much less than simply that owing to the volume of the cations and anions added and that owing to possible void space packing effects. The interaction of the ions with the environment present at this fixed concentration can result in further appreciable volume changes. In the case of a highly charged cation, this can result in a relatively large negative contribution to the volume change.

At infinite dilution the interaction of the ions with their molecular environment reduces to an interaction with the surrounding water; furthermore, the cationic and anionic contributions can be separated. Making reasonable assumptions as to the ionic partial molal volume of the hydrogen ion (−5.4 ml/mol), the ionic partial molal volume of the chloride ion is 23.3 ml/mol (*22*). Subtracting the ionic partial molal volume of three chloride ions from $\bar{V}_2{}^0$ across the rare earth series, the ionic partial molal volumes of the rare earth ions have been calculated as −54.5 (La^{+3}) to −61.2 (Lu^{+3}) ml/mol at infinite dilution (*37*). Ignoring the volume of the rare earth ion itself (1.5–3 ml/mol) and possible void space packing effects, this reflects the decrease in the volume of the water which comes under the influence of the intense electric field of the trivalent ion.

The strong ion–water dipole interactions cause a distortion or disruption of the highly open,, hydrogen-bonded "structure" of water, contracting the water molecules around the rare earth ions. These water molecules, particularly those near the ion in the first hydration sphere, will occupy a smaller effective volume per molecule than the molal volume of the hydrogen-bonded pure water. The water molecules in the second hydration sphere and beyond will also have a reduced effective volume per molecule, the reductions becoming less the farther they are from the ion. Of course, the number of water molecules at a given distance increases approximately as the square of the distance from the central ion, and the summation of the volume decrease for all the affected waters contributes to the large negative ionic partial molal volumes of the rare earth ions.

As expected, it has been shown from semiempirical considerations that this contraction in the water near the ion is dependent on the surface charge density of the ion (*8, 14, 26, 29*). Since the radii of the rare earth ions decrease regularly across the series (*45*), the increasing charge density at the surface of the ion causes this contraction in the volume of the interacting waters to increase from La to Lu. The size of the region of water affected by the rare earth ion also increases across the rare earth series. In other words, both the strength and the extent of the rare earth ion–water interaction increases across the series. This increase in "total hydration" is reflected in the conductivities (*42, 43*) and viscosities (*40, 44*) of the rare earth chlorides and accounts for the decrease in $\bar{V}_2{}^0$ of the rare earth chlorides from La to Nd and Tb to Lu.

The displacement of this trend in $\bar{V}_2{}^0$ to higher values for the heavy rare earths has been attributed to a structural change in the inner hydration sphere, where the coordination number is thought to decrease from 9 (La to Nd) to 8 (Tb to Lu) (*41*). Between Nd and Tb an equilibrium between the two coordinated forms is displaced from the higher to the lower coordination. Since the volume decrease in the water that ends up in the first hydration sphere will, to a first approximation, be proportional to the number of water molecules in this sphere, the decrease in inner sphere hydration will result in the loss of the electrostriction of this water molecule, and $\bar{V}_2{}^0$ will increase between Nd and Tb. This effect will depend to a minor extent on the difference in geometry of the 9- and 8-coordinated hydrated ions. Since the electrostriction of the waters beyond the first sphere depends on the molecular configuration of the triply charged ion and its first sphere, and since this configuration would be expected to differ according to the number of water dipoles in the first sphere, the change in electrostriction for these outer waters, owing to the inner sphere hydration change, will also contribute to the displacement of the $\bar{V}_2{}^0$'s between the light and heavy rare earths. The summation of these changes in the electrostriction, owing to a change in inner sphere water coordination, results in the shift in $\bar{V}_2{}^0$ between Nd and Tb. The fact that the variation of $\bar{V}_2{}^0$ across three different rare earth anion series is the same at infinite dilution (*37, 41*) confirms that it is a cation effect.

From Figure 2, this general trend in $\bar{V}_2$ across the series persists to high concentrations, suggesting that the cation–water interaction dominant at infinite dilution plays an important role over the whole concentration range. The increase in $\bar{V}_2$ between Nd and Tb becomes smaller with increasing concentration, and the slope of the trends in $\bar{V}_2$ from La to Nd and Tb to Lu becomes less. The position of the shift in $\bar{V}_2$ in the rare earth series remains essentially the same with increasing concentration, with possibly a slight shift toward smaller radii. The more erratic behavior of $\bar{V}_2$ across the series at the highest concentrations is possibly due to the least-squares treatment of the ϕ_V's, since the slopes of empirical polynomials (which appear in Equation 5) characteristically give larger deviations at the endpoints of data sets.

As the concentration increases, the cation–anion interactions have to be considered in addition to the ion–water interactions. In very dilute solutions, the variation of this ion–ion interaction with concentration is given by the Debye-Hückel theory. Unfortunately, at the concentrations considered here, the Debye-Hückel theory is inadequate in dealing with these interactions. Nevertheless, we can try to make some reasonable inferences from the data presented here. The interaction of the rare earth ions with the chloride ions will range from being negligible at infinite dilution, to short-range interactions at saturation. Since the two-series effect, attributed to a cation–water interaction at infinite dilution, persists to high concentrations, we shall assume that the rare earth–chloride interactions are similar for all the rare earths, and that the trend of this interaction across the series changes little with increasing concentration. Therefore, we will try to show that the two-series effect is due to the change in inner sphere water coordination over the whole concentration range, possibly modified at high concentrations by the presence of outer sphere rare earth chloride complexes.

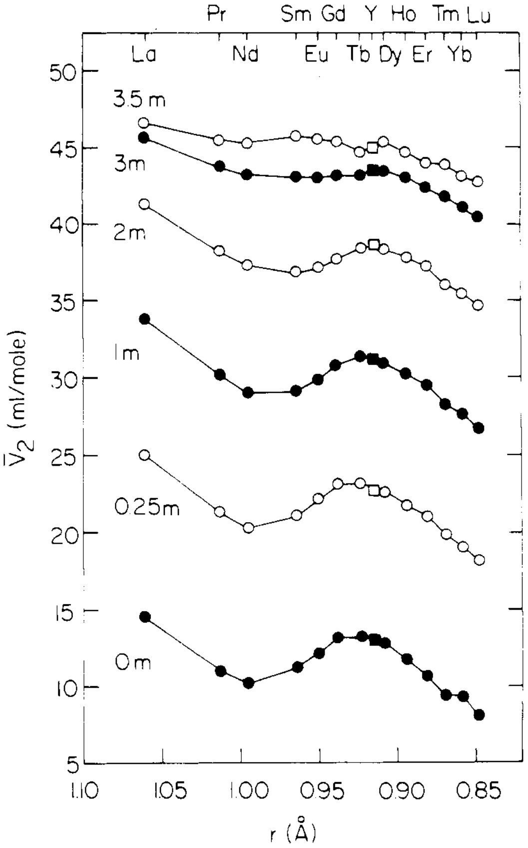

Figure 2. Partial molal volumes of solute, $\bar{V}_2$, of some aqueous rare earth chloride solutions

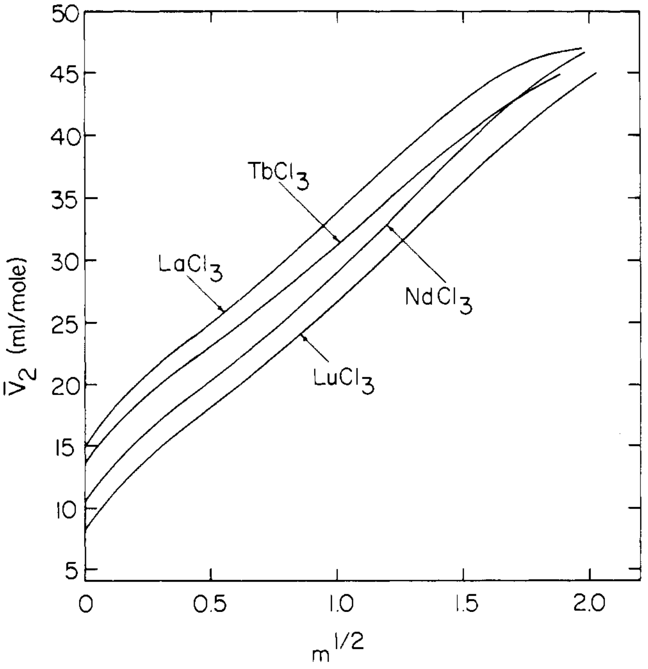

Figure 3. Partial molal volumes of solute, $\bar{V}_2$, of some aqueous rare earth chloride solutions

At concentrations greater than infinite dilution, the environment consists of a distribution of ions, the electrostricted water near these ions, and regions of unaffected water (if present). Recalling the definition of $\bar{V}_2$, the overall increase in $\bar{V}_2$ of the rare earth chlorides with increasing concentration (Figure 3) is due to the decreasing possibility for electrostriction of this molecular environment as a mole of ions is introduced into the solution. This environment is, on the average, already under electrostrictive pressure appropriate for that concentration. The additional electrostrictive volume decrease in this environment as a mole of rare earth salt is added is consequently less than at lower concentrations, and the effective volume, $\bar{V}_2$, increases with concentration. Excluding the curvature in the dilute region ($<0.1m$) accounted for by the extended Debye-Hückel theory, this increase in $\bar{V}_2$ (and ϕv, see Figure 1) is approximately linear in $m^{1/2}$, although the departure from linearity is greater than our experimental error. As is the case for many other electrolytes, the $\bar{V}_2$ (and ϕv) are also approximately linear in $c^{1/2}$ [Masson's rule (*20*)], although the departure from linearity is greater than in the case of $m^{1/2}$.

The flattening out of the curves across the series and the decrease in displacement between the trends in $\bar{V}_2$ for the light and heavy rare earths with increasing concentration can also be attributed to this decrease in the possibility for electrostriction of the environment of the ions with increasing concentration. Namely, the volume effects considered thus far must become smaller as the solution becomes more and more electrostricted with increasing concentration.

If the rare earth ions do not retain the 9- and 8-water coordination with increasing concentration, significant changes in $\bar{V}_2$ across the rare earth series should occur. This could occur by either a change in these inner sphere water coordination numbers with concentration, or a displacement of water molecules in the inner sphere by chloride ions. At saturation there are only 14–16 water molecules for each rare earth ion and three chloride ions. Therefore, at least outer sphere chloride complexation (ions separated by one layer of water molecules) must be present at high concentration. Most of the rare earth chloride complexation studies (*1, 5–7, 10, 11, 16, 28, 30, 33, 34*) seem to indicate that outer sphere chloride complexes are formed by an ionic strength of 1*M*. Furthermore, the amount of inner sphere chloride complexation, if present at all, is very small (*4–7, 10, 16, 33*).

Unfortunately, the stability constants have not been determined at high concentrations. The possibility of forming inner sphere chloride complexes at the highest concentrations is suggested by the crystal structures of the rare earth chloride hydrates (*3, 12, 18, 47*), which form two isomorphous series, where the rare earth ions have two chlorides and seven (La to Pr) or six (Nd to Lu) waters as nearest neighbors. However, Raman studies (*27*) of aqueous $LaCl_3$, $GdCl_3$, and $LuCl_3$ indicate that the complexes are mostly outer sphere at high concentration. X-ray diffraction data obtained by Martin and Spedding (*19*) show that there is a layer of water between cation and anions; furthermore, they found inner sphere water coordination numbers of 9 for nearly saturated $PrCl_3$ and an inner sphere water coordination number of 8 for nearly saturated $TbCl_3$ and $ErCl_3$ solutions. Thus, it appears that the rare earth chlorides form predominantly outer sphere chloride complexes with little inner sphere chloride complexes, if any, at high concentrations.

The partial molal heat capacities (*39, 48*), $\bar{C}p_2$, and the relative partial molal heats of dilution (*24, 36*), $\bar{L}_2$, of the rare earth chlorides at high concentrations show a distinct two-series effect in the vicinity of Nd and Tb.

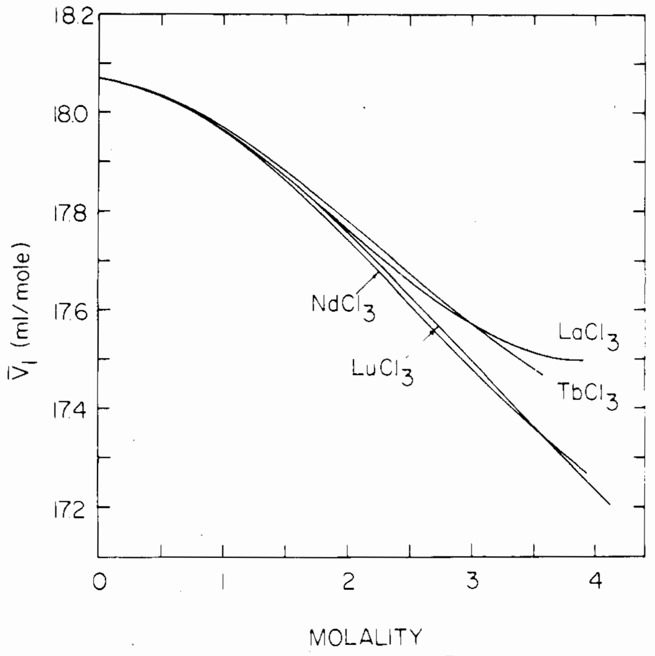

Figure 4. Partial molal volumes of solvent, $\bar{V}_1$, of some aqueous rare earth chloride solutions

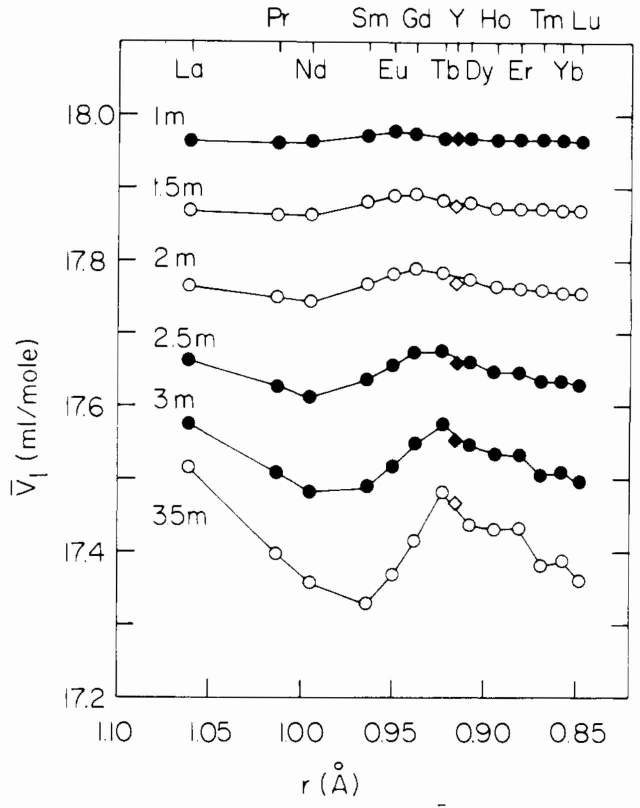

Figure 5. Partial molal volumes of solvent, $\bar{V}_1$, of some aqueous rare earth chloride solutions

These properties have been interpreted in terms of the inner sphere water coordination change.

In Figure 4 the partial molal volumes of the water in La, Nd, Tb, and Lu chloride solutions are given as a function of concentration. $\bar{V}_1$, representing the average molal volume of the water in solution, decreases for all the salts with increasing concentration from the molal volume of pure water at infinite dilution. This decrease in $\bar{V}_1$ reflects the increasing strength and extent of electrostriction of the water with increasing salt concentration.

The variation of $\bar{V}_1$ at even molalities across the rare earth series is shown in Figure 5. The decrease in $\bar{V}_1$ for the light and heavy rare earths at fixed concentrations reflects the increasing total hydration across the rare earth series, owing to the increasing surface charge density. The net effect of the inner sphere hydration change is to reverse this trend in $\bar{V}_1$ in the middle of the series. That is, the decrease in the number of inner sphere waters results in a decrease in the total electrostriction of the affected waters. As in the $\bar{V}_2$'s this trend is only slightly altered with increasing concentration.

In summary, the volume data represent an envelope over a large number of molecular level interactions which cannot be separated uniquely by examining the thermodynamic volume data alone. Nevertheless, the persistence of the two-series effect to high concentrations in the partial molal volumes reported here, the relevant complexation, spectroscopic and X-ray scattering evidence, and the results of other thermodynamic studies on these solutions tend to confirm the conclusions that: the rare earth ions retain their first hydration sphere to high concentrations; the inner sphere hydration change is present from infinite dilution to saturation in the vicinity of Nd and Tb; and this inner sphere water coordination is 9 and 8 for the light and heavy rare earth ions, respectively, from infinite dilution to saturation.

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Literature Cited

(1) Bansal, B. M. L., Patil, S. K., Sharma, H. D., *J. Inorg. Nucl. Chem.*, **26**, 993 (1963).
(2) Bauer, N., Lewin, S. Z., in "Physical Methods of Organic Chemistry," A. Weissberger, Ed., 3rd ed., Vol 1, Part 1, pp 131–75, Interscience, New York, N.Y., 1959.
(3) Bel'skii, N. K., Struchkov, Yu. T., *Sov. Phys. Cryst.*, **10**, 15 (1965).
(4) Choppin, G. R., Bertha, S. L., *J. Inorg. Nucl. Chem.*, **35**, 1309 (1973).
(5) Choppin, G. R., Henrie, D. E., Buijs, K., *Inorg. Chem.*, **5**, 1743 (1966).
(6) Choppin, G. R., Strazik, W. F., *J. Inorg. Chem.*, **4**, 1250 (1965).
(7) Choppin, G. R., Unrein, P. I., *J. Inorg. Nucl. Chem.*, **25**, 387 (1963).
(8) Couture, A. M., Laidler, K. J., *Can. J. Chem.*, **34**, 1209 (1956).
(9) Dunn, L. A., *Trans. Faraday Soc.*, **62**, 2348 (1966).
(10) Garnsey, R., Ebdon, D. W., *J. Amer. Chem. Soc.*, **91**, 50 (1969).
(11) Goto, T., Smutz, M., *J. Inorg. Nucl. Chem.*, **27**, 663 (1965).
(12) Graeber, E. J., Conrad, G. H., Duliere, S. F., *Acta Cryst.*, **21**, 1012 (1966).
(13) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.
(14) Hepler, L. G., *J. Phys. Chem.*, **61**, 1426 (1957).
(15) Karraker, D. G., *Inorg. Chem.*, **7**, 473 (1968).
(16) Kozachenko, N. N., Batyaev, I. M., *Russ. J. Inorg. Chem.*, **16** (1), 66 (1971).
(17) Lewis, W. B., Jackson, J. A., Lemons, J. E., Taube, H., *J. Chem. Phys.*, **36**, 694 (1962).
(18) Marezio, M., Plettinger, H. A., Zachariasen, W. H., *Cryst.*, **14**, 234 (1961).
(19) Martin, L. L., Spedding, F. H., *J. Chem. Phys.*, submitted for publication (1974).
(20) Masson, D. O., *Phil. Mag., Ser. 7*, **8**, 218 (1929).
(21) Millero, F. J., *Chem. Rev.*, **71**, 147 (1971).
(22) Millero, F. J., in "Water and Aqueous Solutions," R. A. Horne, Ed., Chap. 13, 14, Wiley-Interscience, New York, N.Y., 1972.
(23) Moeller, T., Martin, D. F., Thompson, L. C., Ferrus, R., Feistel, G. R., Randall, W. J., *Chem. Rev.*, **65**, 1 (1965).
(24) Mohs, M. A., unpublished PhD thesis, Iowa State University, Ames, Iowa, 1970.
(25) Morgan, L. O., *J. Chem. Phys.*, **38**, 2788 (1963).
(26) Mukerjee, P., *J. Phys. Chem.*, **65**, 740 (1961).
(27) Mundy, W. C., Spedding, F. H., *J. Chem. Phys.*, **59**, 2183 (1973).
(28) Nakamura, K., Kawamura, K., *Bull. Chem. Soc. Jap.*, **44**, 330 (1971).
(29) Padova, J., *J. Chem. Phys.*, **39**, 1552 (1963).
(30) Peppard, D. F., Mason, G. W., Hucher, I., *J. Inorg. Nucl. Chem.*, **24**, 881 (1962).
(31) Redlich, O., *J. Phys. Chem.*, **44**, 619 (1940).

(32) Redlich, O., Meyer, D., *Chem. Rev.*, **64**, 221 (1964).
(33) Reuben, J., Fiat, D., *J. Chem. Phys.*, **51**, 4909 (1969).
(34) Sayre, E. V., Miller, D. G., Freed, S., *ibid.*, **26**, 109 (1957).
(35) Spedding, F. H., Atkinson, G., in "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., Chap. 22, Wiley, New York, N.Y., 1959.
(36) Spedding, F. H., Csejka, D. A., DeKock, C. W., *J. Phys. Chem.*, **70**, 2423 (1966).
(37) Spedding, F. H., Cullen, P. F., Habenschuss, A., *ibid.*, **78**, 1106 (1974).
(38) Spedding, F. H., Flynn, J. P., *J. Amer. Chem. Soc.*, **76**, 1474 (1954).
(39) Spedding, F. H., Jones, K. C., *J. Phys. Chem.*, **70**, 2450 (1966).
(40) Spedding, F. H., Pikal, M. J., *ibid.*, p 2430.
(41) Spedding, F. H., Pikal, M. J., Ayers, B. O., *ibid.*, p 2440.
(42) Spedding, F. H., Rard, J. A., *ibid.*, **78**, 1435 (1974).
(43) Spedding, F. H., Rard, J. A., Saeger, V. W., *J. Chem. Eng. Data*, **19** (4), 373 (1974).
(44) Spedding, F. H., Witte, D., Shiers, L. E., Rard, J. A., *ibid.*, p 369.
(45) Templeton, D. H., Dauben, C. H., *J. Amer. Chem. Soc.*, **76**, 5237 (1954).
(46) Tilton, L. W., Taylor, J. K., *J. Res. Nat. Bur. Stand.*, **18**, 205 (1937).
(47) Ugro, J. V., unpublished PhD thesis, Iowa State University, Ames, Iowa, 1967.
(48) Walters, J. P., Spedding, F. H., U.S. At. Energy Comm., Rept. IS-1988, 1968.

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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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