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Isopiestic Determination of the Activity Coefficients of Some Aqueous Rare-Earth Electrolyte Solutions at 25 °C. 5. $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$

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The osmotic coefficients of aqueous $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$ have been measured from 0.18 to 6.5–7.2 mol kg^{-1} at 25 °C with the isopiestic method. The resulting osmotic coefficients were fitted to least-squares equations, which were used to calculate water activities and mean molal activity coefficients. These data are compared to activity data for other rare-earth nitrate solutions. The lower concentration results were also fitted to Pitzer's equation.

Introduction

Activity data have been published for 14 rare-earth chlorides, 12 rare-earth perchlorates, and 9 rare-earth nitrates at 25 °C (*1–4*). The water activities of the rare-earth chlorides and perchlorates have been correlated with trends in cation hydration resulting from the lanthanide contraction (*2*). However, inner and outer sphere complexes form in rare-earth nitrate solutions, and these complexes extensively modify the hydration trends of the rare-earth cations (*5*).

In this paper isopiestic data are reported for aqueous $Dy(NO_3)_3$, $Ho(NO_3)_3$, and $Lu(NO_3)_3$ solutions. These data provide additional information about the modification of cation hydration by complex formation, and about changes in the amount of complex formation with changes in the ionic radii of the rare earths.

Experimental Section

The experimental details are nearly identical with those of the previous study (*4*). The measurements were made at 25.00 ± 0.005 °C (IPTS-68). Isopiestic equilibration times were 5–36 days, with the longer times used for lower concentrations. The isopiestic standards were $CaCl_2$ stock no. 1 and KCl; their analyses are described elsewhere (*6*). All weights were converted to mass. The molecular masses used were 348.515 g mol^{-1} for $Dy(NO_3)_3$, 350.945 g mol^{-1} for $Ho(NO_3)_3$, 360.985 g mol^{-1} for $Lu(NO_3)_3$, 110.986 g mol^{-1} for $CaCl_2$, and 74.551 g mol^{-1} for KCl.

The rare-earth nitrate solutions were prepared from pure rare-earth oxides and nitric acid and were adjusted to their equivalence concentrations. The stock solutions were analyzed by EDTA and the gravimetric sulfate method, and the concentrations were measured to at least 0.1%.

Table I. Isopiestic Molalities of Some Rare-Earth Nitrate Solutions from Measurements with KCl Reference Solutions

$[Dy(NO_3)_3]$, m	$[Ho(NO_3)_3]$, m	$[Lu(NO_3)_3]$, m	[KCl], m	Φ(KCl)
0.185 30	0.183 87	0.181 52	0.31905	0.9047
0.192 47	0.191 02	0.188 51	0.33217	0.9041
0.301 76	0.298 55	0.293 08	0.53764	0.8986
0.315 18	0.311 75	0.305 90	0.56410	0.8982
0.413 71	0.408 73	0.399 34	0.76297	0.8968
0.517 95	0.510 46	0.498 03	0.98476	0.8972
0.527 21	0.519 43	0.506 10	1.0054	0.8974
0.597 09	0.588 11	0.571 70	1.1613	0.8985
0.677 69	0.666 63	0.646 44	1.3459	0.9005
0.755 73	0.742 80	0.718 42	1.5324	0.9031
0.841 50	0.826 77	0.796 55	1.7424	0.9065
0.936 24	0.918 68	0.882 53	1.9811	0.9110
1.045 7	1.025 4	0.981 31	2.2650	0.9169
1.068 9	1.049 2	1.003 4	2.3282	0.9183

Duplicate samples were used in the equilibrations. The average molalities are known to at least ±0.1% above 0.3 mol kg^{-1} and better than 0.15% at lower concentrations. However, most equilibrations were to ±0.05% or better. The molalities at isopiestic equilibrium are reported in Tables I and II.

The higher rare-earth nitrate concentrations are for supersaturated solutions (*5*). $Dy(NO_3)_3$ was the only salt that had crystallization problems at the highest concentrations; consequently two of its points are based on single samples. After each high-concentration equilibration, the isopiestic cups were carefully examined to verify the absence of crystals.

The presence of a small amount of nitrite ions in the rare-earth nitrate solutions was indicated by a positive "brown ring" test. The rare-earth nitrate solutions were heated during their preparation from rare-earth oxides and nitric acid. Thus, any nitrite or nitrogen oxides in the nitric acid should have been decomposed or expelled. Consequently, any nitrite in the final solution was formed after preparation.

A 4.4551 mol kg^{-1} $La(NO_3)_3$ solution, prepared several years ago, was studied further. Each nitrate ion decomposing to nitrite consumes two hydrogen ions, so pH changes will result. The

Table II. Isopiestic Molalities of Some Rare-Earth Nitrate Solutions from Measurements with $CaCl_2$ Reference Solutions

$[Dy(NO_3)_3]$, *m*	$[Ho(NO_3)_3]$, *m*	$[Lu(NO_3)_3]$, *m*	$[CaCl_2]$, *m*	$\Phi(CaCl_2)$
0.96099	0.94397	0.90558	1.1472	1.0860
0.97429	0.95678	0.91739	1.1628	1.0907
1.0519	1.0326	0.98759	1.2517	1.1181
1.1373	1.1166	1.0641	1.3469	1.1484
1.2373	1.2141	1.1540	1.4599	1.1853
1.3426	1.3174	1.2483	1.5759	1.2244
1.4137	1.3870	1.3113	1.6544	1.2515
1.5235	1.4947	1.4105	1.7725	1.2930
1.6212	1.5913	1.4969	1.8776	1.3308
1.7340	1.7021	1.5973	1.9967	1.3744
1.8217	1.7890	1.6769	2.0889	1.4088
1.9212	1.8878	1.7643	2.1913	1.4474
2.0134	1.9786	1.8469	2.2881	1.4845
2.1125	2.0767	1.9357	2.3863	1.5225
2.2217	2.1854	2.0344	2.4935	1.5644
2.2367	2.2009	2.0479	2.5144	1.5726
2.2442	2.2068	2.0536	2.5152	1.5730
2.3325	2.2948	2.1326	2.6074	1.6095
2.3964	2.3595	2.1918	2.6678	1.6335
2.4250	2.3877	2.2164	2.6934	1.6438
2.4344	2.3967	2.2236	2.7078	1.6495
2.5192	2.4817	2.3020	2.7860	1.6809
2.6467	2.6098	2.4189	2.9124	1.7321
2.7631	2.7252	2.5235	3.0215	1.7765
2.8646	2.8272	2.6178	3.1181	1.8161
2.9744	2.9369	2.7193	3.2213	1.8586
3.1044	3.0656	2.8396	3.3427	1.9087
3.1724	3.1364	2.9017	3.4053	1.9346
3.2467	3.2098	2.9700	3.4741	1.9631
3.3377	3.3009	3.0562	3.5561	1.9971
3.4482	3.4115	3.1600	3.6577	2.0392
3.5569	3.5210	3.2623	3.7565	2.0801
3.6402	3.6043	3.3435	3.8301	2.1106
3.7403	3.7048	3.4362	3.9208	2.1481
3.8419	3.8080	3.5336	4.0099	2.1847
3.9672	3.9341	3.6550	4.1218	2.2306
4.0613	4.0289	3.7450	4.2066	2.2652
4.1723	4.1397	3.8539	4.3021	2.3038
4.2584	4.2275	3.9404	4.3790	2.3348
4.3693	4.3361	4.0447	4.4734	2.3724
4.4796	4.4490	4.1552	4.5715	2.4111
4.5813	4.5496	4.2533	4.6606	2.4459
4.6644	4.6348	4.3372	4.7303	2.4728
4.7550	4.7256	4.4308	4.8122	2.5040
4.8421	4.8117	4.5204	4.8857	2.5317
4.9472	4.9171	4.6227	4.9784	2.5660
5.0479	5.0201	4.7219	5.0674	2.5984
5.1596	5.1288	4.8349	5.1614	2.6318
5.2316	5.2045	4.9073	5.2237	2.6536
5.3352	5.3055	5.0124	5.3161	2.6853
5.4711	5.4423	5.1491	5.4353	2.7249
5.5914	5.5623	5.2823	5.5421	2.7591
5.6729	5.6440	5.3688	5.6146	2.7816
5.7649	5.7340	5.4566	5.6963	2.8062
5.8780	5.8541	5.5806	5.8063	2.8382
5.9734	5.9519	5.6780	5.8896	2.8614
6.0775	6.0541	5.7890	5.9887	2.8878
6.2033	6.1783	5.9172	6.1062	2.9175
6.3151[a]	6.2875	6.0315	6.2120	2.9426
6.4849	6.4590	6.2141	6.3739	2.9781
6.4905[a]	6.4611	6.2179	6.3799	2.9793
		6.2665	6.4254	2.9886
6.5677	6.5471	6.3061	6.4599	2.9955
		6.3350	6.4900	3.0013
		6.4503	6.6033	3.0221
		6.4869	6.6419	3.0288
		6.5154	6.6710	3.0338
		6.5635	6.7120	3.0405
		6.7168	6.8626	3.0633
		6.8023	6.9525	3.0755
		6.8996	7.0453	3.0870
		6.9549	7.1056	3.0940
		6.9729	7.1231	3.0959
		7.0132	7.1683	3.1008
		7.1461	7.3092	3.1145
		7.1806	7.3392	3.1171

[a] These two $Dy(NO_3)_3$ molalities are for single samples. All other concentrations in Tables I and II are the average of duplicate samples.

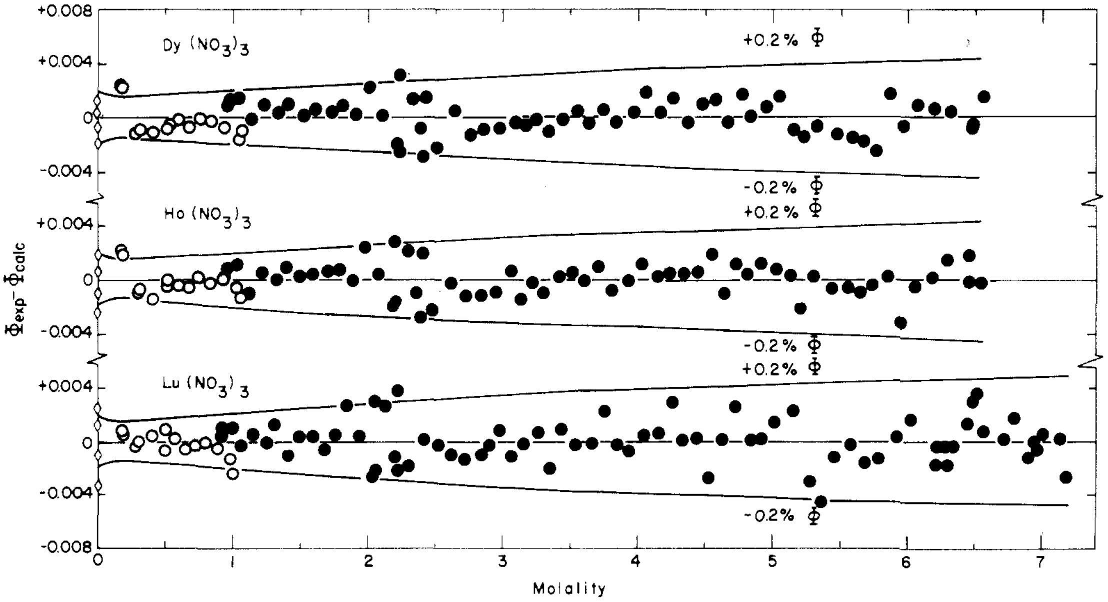

Figure 1. Differences between experimental and calculated osmotic coefficients of rare-earth nitrate solutions at 25 °C: (●) isopiestic vs. $CaCl_2$; (○) isopiestic vs. KCl; (◇) estimated from electrical conductances.

solution pH was found to be 3.30; titration with dilute HNO_3 indicates that the correct equivalence pH should be 3.0. If slow cation hydrolysis is negligible, and the hydrogen ion activity equated to its concentration, then there is 0.002% $La(NO_2)_3$ and 99.998% $La(NO_3)_3$ in the solution.

As a further check, a sample of this $La(NO_3)_3$ was acidified with $HClO_4$ and then oxidized with $KMnO_4$ in the absence of light. This method indicated a maximum of 0.0017% $La(NO_2)_3$, which is in reasonable agreement with the pH-based estimate. Nitrate decomposition is therefore too small to have a detect-

Table III. Coefficients and Powers for Osmotic Coefficient Polynomials

i	r_i	$A_i(Dy(NO_3)_3)$	$A_i(Ho(NO_3)_3)$	$A_i(Lu(NO_3)_3)$
1	0.75	−2.009 692	−2.542 587	−3.680 921
2	1.00	38.255 39	42.055 77	49.527 78
3	1.25	−91.965 41	−102.376 6	−120.368 8
4	1.50	106.176 6	120.762 67	141.655 7
5	1.75	−66.265 18	−77.267 93	−89.401 56
6	2.00	21.544 98	25.782 85	29.032 41
7	2.25	−2.873 645	−3.527 294	−3.817 119
SD		0.001 3	0.001 3	0.001 6

able effect on the properties of rare-earth nitrate solutions.

Calculations and Errors

The osmotic coefficients, Φ, of the rare-earth nitrate solutions were calculated from eq 1

$$\Phi = \nu^* m^* \Phi^* / \nu m \qquad (1)$$

where m is the rare-earth nitrate solution molality and $\nu = 4$ is the number of ions formed by the complete dissociation of one molecule of rare-earth nitrate. The equivalent quantities for the KCl or $CaCl_2$ isopiestic standards are indicated with asterisks. The osmotic coefficients of the reference solutions were calculated from available equations (*7*, *8*). These Φ^* values are reported in Tables I and II along with the isopiestic molalities.

The osmotic coefficients of the rare-earth nitrates were represented by eq 2

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

where $A = 8.6430$ is the Debye–Hückel limiting slope for 3–1 electrolytes. The mean molal activity coefficients are then given by eq 3

$$\ln \gamma_\pm = -Am^{1/2} + \sum_i A_i[(r_i + 1)/r_i] m^{r_i} \qquad (3)$$

which is the Debye–Hückel limiting law plus a series in the molal concentration. Series in $m^{1/4}$ worked best for these salts. Water activities can be calculated from eq 4

$$\ln a_1 = -\nu m M_1 \Phi / 1000 \qquad (4)$$

where $M_1 = 18.0154$ g mol^{-1} is the molecular mass of water.

All of the isopiestic data in Tables I and II were given unit weights for the least-squares fits to eq 2. Dilute solution osmotic coefficients were estimated from ion-size parameters derived from electrical-conductance data (*3*), and these Φ values were used to constrain eq 2 and 3 at concentrations below the isopiestic measurements. These estimated osmotic coefficients, which are probably uncertain by 0.005 units, were also given unit weights. The least-squares parameters to eq 2 and 3 are given in Table III, along with the standard deviations for the best fits. Values of Φ, a_1, and $\gamma_\pm$, for various round concentrations are reported in Table IV.

The osmotic coefficients up to 2.0 mol kg^{-1} were also fitted to Pitzer's equation (*9*), and the parameters are listed in Table V. Parameters for other rare-earth electrolytes are given elsewhere (*4*, *9*). Pitzer's equation does not represent the data as well as eq 2 since it involves fewer parameters.

The maximum uncertainties in the experimental Φ values are 0.3%, with the probable error being 0.2%. The differences between the experimental Φ values and eq 2 are shown in Figure 1.

Isopiestic data for rare-earth nitrates seem to be fairly reproducible. Libuš et al. (*10*) have reported data for three rare-earth nitrates at 25 °C. Their results for $Nd(NO_3)_3$ and $Sm(NO_3)_3$ at all concentrations, and for $Gd(NO_3)_3$ up to 2.0 mol kg^{-1}, agree with previous data from our laboratories to within experimental error (*3*, *4*). However, differences for $Gd(NO_3)_3$ at higher concentrations are significant.

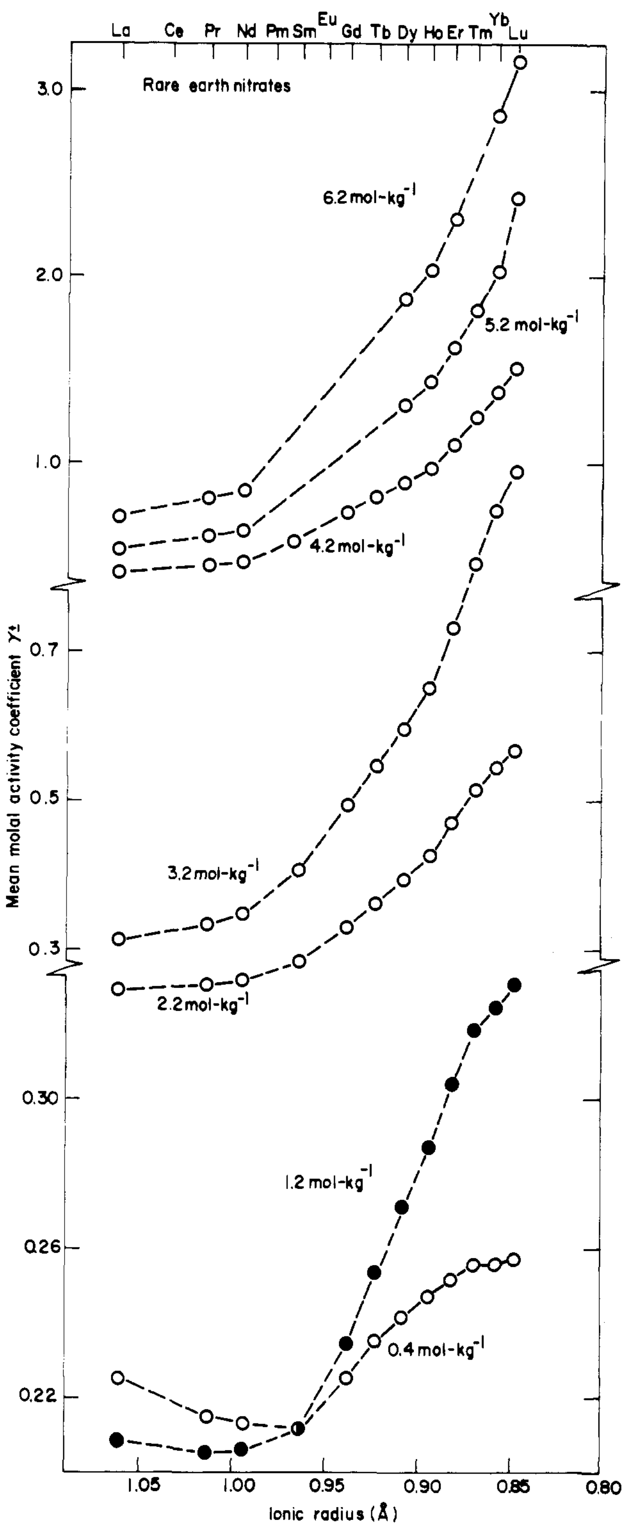

Figure 2. Mean molal activity coefficients of rare-earth nitrate solutions at constant molalities.

Results and Discussion

Figures 2 and 3 show the mean molal activity coefficients and water activities of the rare-earth nitrates, at various molalities, as a function of the cation radius (*11*). The activity coefficients at low concentrations decrease from $La(NO_3)_3$ to $Sm(NO_3)_3$ ($Eu(NO_3)_3$ was not studied) and then increase to $Lu(NO_3)_3$. By 1.0–1.2 mol kg^{-1}, $\gamma_\pm$ is nearly constant for $La(NO_3)_3$ to $Nd(NO_3)_3$ and then increases to $Lu(NO_3)_3$. The water activities

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

m	Φ	a_1	$\gamma_\pm$	m	Φ	a_1	$\gamma_\pm$
			$Dy(NO_3)_3$				
0.1	0.7640	0.994509	0.3071	3.0	1.5166	0.7205	0.5486
0.2	0.7795	0.98883	0.2658	3.2	1.5645	0.6971	0.5960
0.3	0.8012	0.98283	0.2495	3.4	1.6113	0.6738	0.6472
0.4	0.8248	0.97651	0.2420	3.6	1.6569	0.6506	0.7024
0.5	0.8493	0.96986	0.2391	3.8	1.7014	0.6276	0.7618
0.6	0.8747	0.96289	0.2391	4.0	1.7448	0.6048	0.8256
0.7	0.9008	0.95558	0.2412	4.2	1.7870	0.5822	0.8941
0.8	0.9275	0.94794	0.2449	4.4	1.8283	0.5601	0.9674
0.9	0.9546	0.93997	0.2499	4.6	1.8685	0.5383	1.0458
1.0	0.9820	0.93168	0.2560	4.8	1.9076	0.5169	1.1294
1.2	1.0376	0.91418	0.2711	5.0	1.9457	0.4961	1.2185
1.4	1.0936	0.8955	0.2896	5.2	1.9828	0.4757	1.3133
1.6	1.1494	0.8759	0.3112	5.4	2.0189	0.4558	1.4140
1.8	1.2048	0.8553	0.3358	5.6	2.0540	0.4365	1.5207
2.0	1.2594	0.8340	0.3634	5.8	2.0880	0.4178	1.6335
2.2	1.3130	0.8121	0.3940	6.0	2.1209	0.3997	1.7526
2.4	1.3656	0.7896	0.4277	6.2	2.1527	0.3822	1.8779
2.6	1.4171	0.7668	0.4647	6.4	2.1833	0.3653	2.0095
2.8	1.4675	0.7437	0.5049	6.5677	2.2081	0.3517	2.1247
			$Ho(NO_3)_3$				
0.1	0.7681	0.994480	0.3085	3.0	1.5448	0.7161	0.5982
0.2	0.7863	0.98873	0.2688	3.2	1.5915	0.6928	0.6502
0.3	0.8104	0.98263	0.2536	3.4	1.6370	0.6696	0.7062
0.4	0.8363	0.97618	0.2473	3.6	1.6813	0.6465	0.7666
0.5	0.8632	0.96938	0.2457	3.8	1.7245	0.6236	0.8314
0.6	0.8908	0.96222	0.2469	4.0	1.7666	0.6010	0.9010
0.7	0.9191	0.95470	0.2503	4.2	1.8077	0.5786	0.9756
0.8	0.9478	0.94683	0.2553	4.4	1.8479	0.5566	1.0554
0.9	0.9767	0.93862	0.2616	4.6	1.8870	0.5350	1.1407
1.0	1.0059	0.93008	0.2691	4.8	1.9253	0.5138	1.2317
1.2	1.0643	0.91207	0.2871	5.0	1.9626	0.4931	1.3288
1.4	1.1224	0.8929	0.3086	5.2	1.9989	0.4728	1.4320
1.6	1.1797	0.8728	0.3335	5.4	2.0343	0.4531	1.5416
1.8	1.2359	0.8519	0.3615	5.6	2.0687	0.4340	1.6578
2.0	1.2909	0.8302	0.3926	5.8	2.1021	0.4154	1.7806
2.2	1.3445	0.8080	0.4270	6.0	2.1344	0.3974	1.9102
2.4	1.3967	0.7854	0.4646	6.2	2.1656	0.3800	2.0465
2.6	1.4474	0.7625	0.5055	6.4	2.1956	0.3633	2.1893
2.8	1.4968	0.7393	0.5500	6.5471	2.2169	0.3514	2.2985
			$Lu(NO_3)_3$				
0.1	0.7769	0.994417	0.3114	3.4	1.8287	0.6389	1.0534
0.2	0.7990	0.98855	0.2744	3.6	1.8745	0.6149	1.1577
0.3	0.8265	0.98229	0.2613	3.8	1.9177	0.5915	1.2688
0.4	0.8565	0.97561	0.2572	4.0	1.9586	0.5686	1.3869
0.5	0.8884	0.96850	0.2581	4.2	1.9972	0.5464	1.5120
0.6	0.9220	0.96092	0.2623	4.4	2.0338	0.5247	1.6443
0.7	0.9569	0.95288	0.2690	4.6	2.0685	0.5038	1.7837
0.8	0.9928	0.94438	0.2779	4.8	2.1013	0.4834	1.9304
0.9	1.0294	0.93542	0.2886	5.0	2.1326	0.4638	2.0845
1.0	1.0665	0.92603	0.3011	5.2	2.1622	0.4448	2.2461
1.2	1.1413	0.90602	0.3306	5.4	2.1905	0.4264	2.4153
1.4	1.2158	0.8846	0.3661	5.6	2.2174	0.4087	2.5923
1.6	1.2891	0.8619	0.4073	5.8	2.2430	0.3916	2.7770
1.8	1.3603	0.8382	0.4544	6.0	2.2676	0.3751	2.9697
2.0	1.4291	0.8139	0.5074	6.2	2.2910	0.3593	3.1704
2.2	1.4951	0.7890	0.5665	6.4	2.3135	0.3441	3.3792
2.4	1.5581	0.7638	0.6316	6.6	2.3349	0.3294	3.5961
2.6	1.6182	0.7385	0.7030	6.8	2.3554	0.3153	3.8211
2.8	1.6752	0.7132	0.7808	7.0	2.3751	0.3018	4.0541
3.0	1.7292	0.6881	0.8650	7.1806	2.3920	0.2900	4.2714
3.2	1.7804	0.6633	0.9559				

Table V. Parameters for Pitzer's Equation

parameter	$Dy(NO_3)_3$	$Ho(NO_3)_3$	$Lu(NO_3)_3$
$3\beta^{(0)}/2$	0.8484	0.8769	0.9264
$3\beta^{(1)}/2$	7.700	7.700	7.700
$(3^{3/2}/2)C^{\Phi}$	−0.1809	−0.1852	−0.1749
SD	0.0085	0.0086	0.0080

exhibit similar trends but in the opposite direction.

In contrast, the activity data for rare-earth chlorides and perchlorates (*1*, *2*) are S-shaped as a function of the cation radius. Complex formation is fairly weak for these two systems, so activity trends mainly reflect cation hydration. An increase in total hydration occurs from La^{3+} to Lu^{3+}, due to the increase in the surface charge density of the bare ion as the lanthanide contraction occurs. Superimposed on this is an inner sphere hydration number decrease between Nd^{3+} and Tb^{3+}. This inner sphere hydration decrease causes the inner sphere (hydrated) radius to decrease more rapidly (*12*), and total hydration to increase more rapidly, with ionic radius in the middle of the rare-earth series. The same model was used to explain the

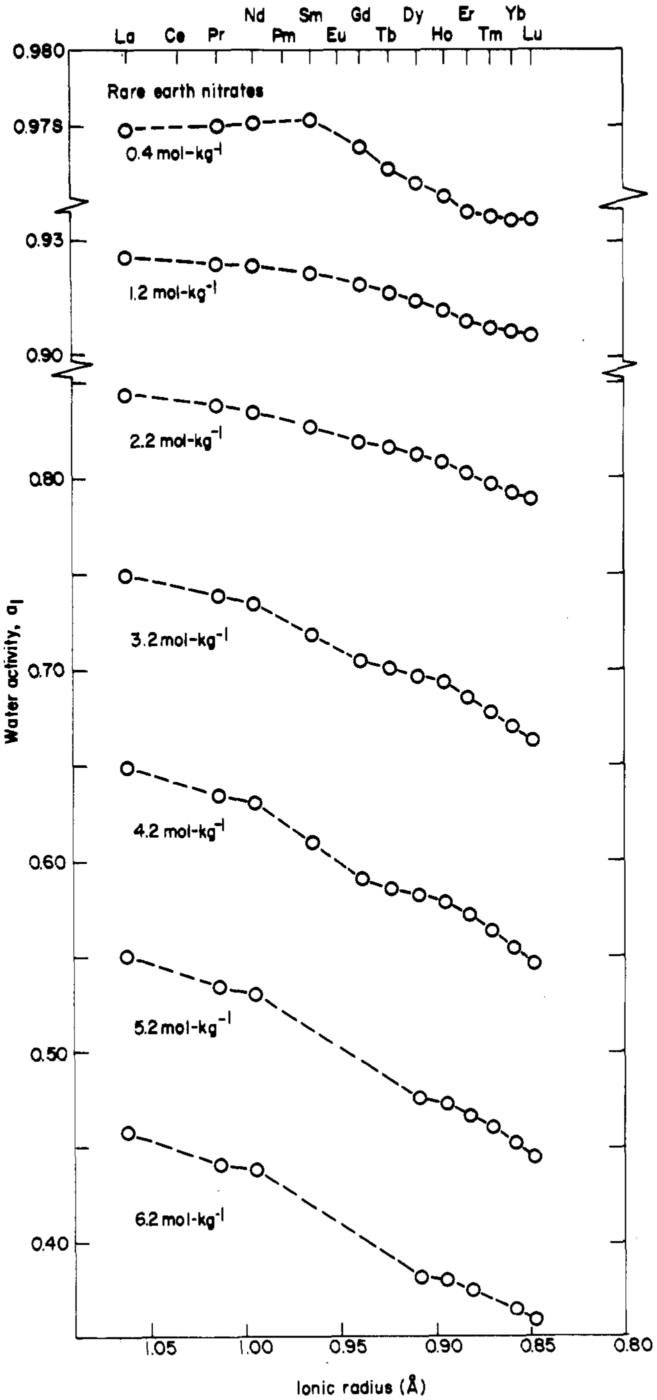

Figure 3. Water activities of rare-earth nitrate solutions at constant molalities.

variation of the standard state ionic entropies (*13*).

Libuš et al. (*10*) suggested that an inner sphere increase, rather than a decrease, occurs with decreasing ionic radius. This conflicts with X-ray diffraction results (*12*) which show the inner sphere hydration number decreases by one between Nd^{3+} and Tb^{3+}. Also, hydration numbers obtained by fitting thermodynamic models to volumetric and heat-capacity data (*14*) indicate a unit decrease in the cation hydration number. Glass transition temperatures for the rare-earth chlorides and perchlorates likewise correlate with hydration trends (*15*).

Both inner and outer sphere complexes form in rare-earth nitrate solutions, and they begin to modify rare-earth hydration at fairly low concentrations by displacing water from the cation hydration sheath. Figure 2 indicates that $\gamma_\pm$ decreases from $La(NO_3)_3$ to $Sm(NO_3)_3$ or $Eu(NO_3)_3$ and then increases to $Lu(NO_3)_3$ at low concentrations. Above ca. 1.0–1.2 mol kg^{-1} the minimum disappears, and $\gamma_\pm$ increased from $La(NO_3)_3$ to $Lu(NO_3)_3$. This suggests that complex formation increases from $La(NO_3)_3$ to $Sm(NO_3)_3$–$Eu(NO_3)_3$ and then decreases to $Lu(NO_3)_3$ at low concentrations. At higher concentrations, complex formation should decrease from $La(NO_3)_3$ to $Lu(NO_3)_3$. This is in complete agreement with changes in the electrical-conductance data (*5*) and with the known association constants (*16*) at low concentrations.

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Glossary

Φ	molal osmotic coefficient
ν	number of ions formed by the dissociation of one molecule of solute
m	molal concentration of the solute, mol kg^{-1}
$\gamma_\pm$	mean molal activity coefficient
a_1	water activity
$\beta^{(0)}$, $\beta^{(1)}$, C^Φ	parameters for Pitzer's equation
*	symbols with asterisks refer to KCl or $CaCl_2$ isopiestic standards
A	Debye–Hückel constant
A_i	least-squares coefficients of eq 2 and 3
r_i	powers of eq 2 and 3

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