Acknowledgment

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Apparent and Partial Molal Heat Capacities of Aqueous Rare Earth Nitrate Solutions at 25 °C

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Specific heats of aqueous solutions of the trinitrates of La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were measured from 0.1 m to saturation at 25 °C. Apparent molal heat capacities, ϕ_{cp}, were calculated for these solutions, and empirical polynomial equations were obtained which expressed ϕ_{cp} as a function of $m^{1/2}$ for each salt. The partial molal heat capacities of the solvent, $\bar{C}_{p1}$, and solute, $\bar{C}_{p2}$, were calculated from these equations. Unlike chloride and perchlorate data reported earlier, values of $\bar{C}_{p1}$ for nitrate solutions across the rare earth series did not show a two series effect. Instead, $\bar{C}_{p1}$ values at lower concentrations (0.5 and 1.0 m) appear correlated with reported first formation constants for rare earth–nitrate complexes.

Introduction

Heat capacity data for rare earth chlorides (*23*, *30*) and perchlorates (*18*) up to saturation have previously been reported. Trends across the rare earth series for heat capacity and other properties (*19*, *20*, *24–26*, *28*) for chloride and perchlorate solutions indicate a difference in the inner-sphere hydration with the lighter rare earths having a coordination number one greater than for the smaller, heavier rare earths. Any complexation in these solutions is believed to occur at higher concentrations and involve only outer-sphere interactions between cation and anion.

For rare earth nitrate solutions, the two series effect is evident (*15*, *21*, *27*, *29*) only at very low concentrations, if at all. In these solutions electrical conductance data (*7*, *22*) indicate that complex formation between the rare earth and nitrate ions is beginning to be important even at very low concentrations, with a mixture of inner- and outer-sphere complexation occurring (*1*, *2*). At low concentrations, a maximum in complex formation was found around Eu (*3*, *4*, *12*). At higher concentrations, the predominant complex is believed to be inner sphere with coordination occurring through oxygen (*1*, *8–10*, *16*). For the hydrated crystals of $Nd(NO_3)_3$ and $Pr(NO_3)_3$, three doubly bonded nitrate ions and four water molecules were found adjacent to the rare earth ion (*17*). Also at higher concentrations, electrical conductance data were interpreted to imply that the various complexing constants decrease from La to Lu (*15*).

The study reported here investigates the effect on heat capacity properties of increased cation–anion interactions for rare earth nitrate solutions relative to chloride and perchlorate solutions. The data presented are the specific heats and the apparent and partial molal heat capacities of aqueous solutions of 12 rare earth nitrates from 0.1 m to saturation at 25 °C.

Experimental Section

Apparatus and Procedure. An adiabatic single-can solution calorimeter was used to measure specific heats of solutions; a detailed description of the apparatus and procedure is given elsewhere (*18*, *23*). Basically, the value for the heat capacity of the calorimeter, plus appendages, was determined by subtraction of the heat capacity of a weighed amount of air-saturated water from the total heat capacity of the water plus calorimeter. This was done several times during the course of this work, with checks on the accuracy of the system made by using NaCl solutions at different concentrations. Average specific heats obtained in this study agreed to within 0.05% of those measured by Randall and Rossini (*13*).

Materials. Rare earth nitrate solutions at 0.1 intervals in $m^{1/2}$ ranging from 0.3 $m^{1/2}$ to near saturation were prepared from weighed portions of concentrated stock solutions and water (all weights were corrected to vacuum). The stock solutions, at concentrations near saturation, were prepared by adding an excess of rare earth oxide to reagent grade nitric acid and boiling. After filtration of the solution, the pH of the solution was lowered to the previously determined equivalence point (three anions to one cation) by adding nitric acid (see ref 19 for a more complete description). The oxides used, prepared by the Rare Earth Separation Group of Ames Laboratory, USDOE, were at least 99.85% pure by weight. The principal impurities were the adjacent rare earths, iron, and calcium, with less than 0.05% being iron and calcium. The water used was distilled from a solution of $KMnO_4$ and KOH and had a specific conductance $<1.0 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$.

The stock solutions were analyzed by EDTA titration and an oxide and/or sulfate gravimetric method, with the resulting absolute concentrations reliable to at least ±0.1% in terms of molality. Relative concentrations of a series of dilutions were at least an order of magnitude more accurate.

Saturated solutions were prepared from portions of stock solutions concentrated in a desiccator with $Mg(ClO_4)_2$. The saturated solutions were stored in contact with the rare earth nitrate crystals, formed during concentration, for at least 2 weeks at 25 ± 0.01 °C. The concentrations of the saturated solutions were determined by one or more of the previously named methods.

Results

The apparent molal heat capacity, ϕ_{cp}, for each solution was calculated from measured specific heat by using the equation

$$\phi_{cp} = \left(\frac{1000}{m} + M_2\right)s - \left(\frac{1000}{m}\right)s^{\circ} \qquad (1)$$

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Table I. Least-Squares Constants for the Concentration Dependence of ϕ_{cp} Given by Equation 2

salt	$A(0)$	$A(1)$	$A(2)$	$A(3)$	$A(4)$	$A(5)$	$A(6)$
lanthanum nitrate	−68.42	60.243	33.354	−25.3437	4.2338		
praseodymium nitrate	−71.68	77.955	6.655	−10.4382	1.5400		
neodymium nitrate	−66.38	71.732	4.636	−6.2434	0.3744		
samarium nitrate	−60.27	59.154	12.078	−8.4303	0.7162		
gadolinium nitrate	−58.12	57.846	7.834	−4.2713	−0.3112		
terbium nitrate	−63.29	63.854	10.157	−8.8183	0.9809		
dysprosium nitrate	−57.16	40.049	41.056	−23.9737	3.4402		
holmium nitrate	−56.84	32.222	54.113	−30.7738	4.5837		
erbium nitrate	−46.21	−11.561	113.073	−60.4480	9.5703		
thulium nitrate	−82.35	179.476	−269.233	319.1635	−187.5645	51.57866	−5.40410
ytterbium nitrate	−84.52	202.504	−332.090	386.6587	−219.8222	58.32165	−5.87257
lutetium nitrate	−107.02	319.037	−567.428	614.1603	−331.3332	85.06211	−8.36628

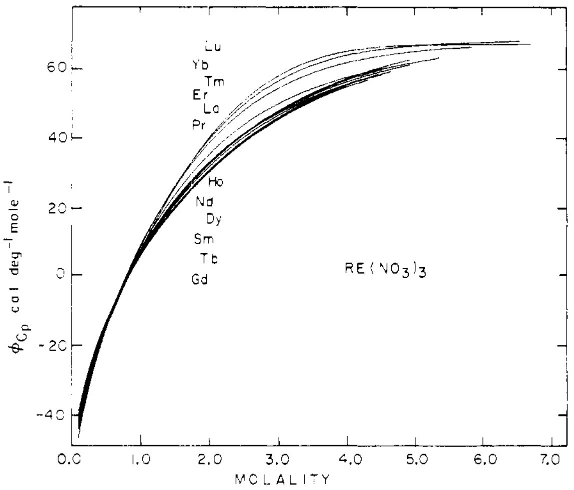

Figure 1. Apparent molal heat capacities of RE(NO$_3$)$_3$ solutions vs. molality at 25 °C.

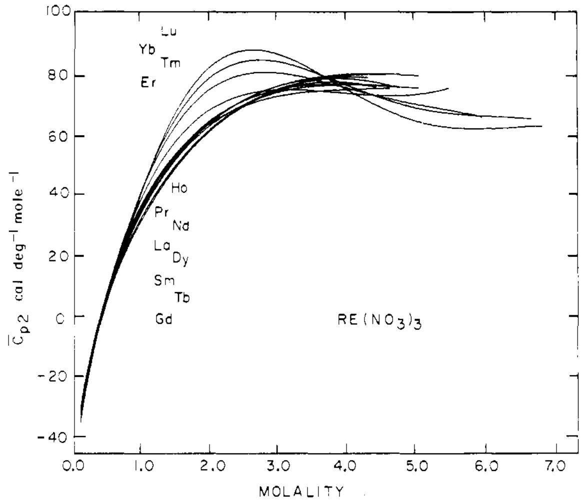

Figure 2. Partial molal heat capacities of solute for RE(NO$_3$)$_3$ solutions vs. molality at 25 °C.

where m is molality, M_2 is the molecular weight of the rare earth nitrate (1969 IUPAC atomic weights), S is the solution specific heat, and S° is the specific heat of pure liquid water at 25 °C (0.9989 cal deg^{-1}, from ref 11). For each rare earth nitrate, an empirical polynomial equation of the form

$$\phi_{cp} = \sum_{k=0}^{n} A_k m^{k/2} \qquad (2)$$

was obtained by using the least-squares method. Fourth-order equations ($n = 4$) were adequate for all but Tm, Yb, and Lu. For these heavier rare earth nitrates, which were much more soluble, sixth-order equations ($n = 6$) were necessary. In obtaining the A_k's, data points were weighted proportionately to the square of the inverse of the probable error in ϕ_{cp} at each concentration. The probable error in ϕ_{cp} was calculated by assuming a probable error of 0.05% in specific heat and a probable error in concentration resulting from a probable error of 0.1% in the molality of the stock solution.

$\bar{C}_{p1}$ and $\bar{C}_{p2}$ were calculated from eq 3 and 4 where M_1

$$\bar{C}_{p1} = \bar{C}_{p1}^{\circ} - \frac{M_1}{2000} m^{3/2} \left(\frac{d\phi_{cp}}{dm^{1/2}} \right)_{T,P,n_1} \qquad (3)$$

$$\bar{C}_{p2} = \phi_{cp} + \tfrac{1}{2} m^{1/2} \left(\frac{d\phi_{cp}}{dm^{1/2}} \right)_{T,P,n_1} \qquad (4)$$

(18.015 g mol^{-1}) is the molecular weight of water and $\bar{C}_{p1}^{\circ}$ (17.996 cal deg^{-1} mol^{-1}) is the molal heat capacity of pure water at 25 °C (11). The derivatives were computed from eq 2 by using the A_k's in Table I.

The square root of molality, ratio of moles of water to moles of RE(NO$_3$)$_3$ (RE = rare earth), specific heat, experimental (eq 1) and calculated (eq 2) apparent molal heat capacities, and partial molal heat capacity of the solute (eq 4) and solvent (eq 3) are listed in Table II for each solution run. Figures 1–3 illustrate ϕ_{cp}, $\bar{C}_{p2}$, and $\bar{C}_{p1}$ for the rare earth nitrates as a function of molality. Figures 4–6 illustrate the trends in heat capacity properties across the rare earth series, at even molalities, as a function of rare earth ionic radius (31). Figures 7–9 compare the heat capacity properties of the nitrate solutions of the representative rare earths, Pr, Gd, and Tm, with chloride and perchlorate solutions, reported earlier (18, 23, 30).

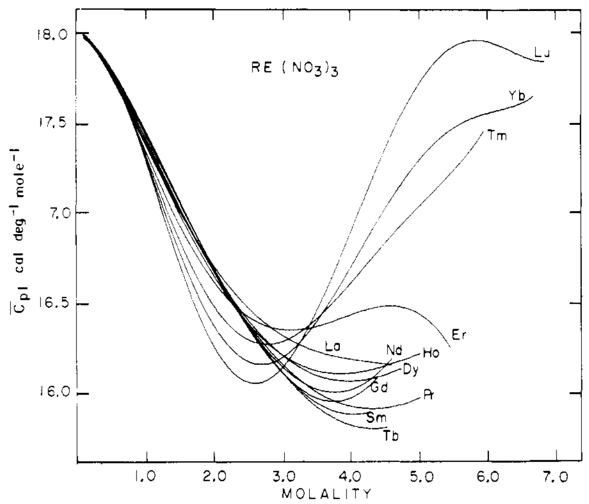

Figure 3. Partial molal heat capacities of water for RE(NO$_3$)$_3$ solutions vs. molality at 25 °C.

Discussion

As shown in Figures 1 and 2, ϕ_{cp} and $\bar{C}_{p2}$ values are negative for dilute rare earth nitrate solutions. This is also true for chloride

Table II. Specific Heats and Apparent Molal and Partial Molal Heat Capacities of $RE(NO_3)_3$ Solutions at 25 °C

			ϕ_{cp}			
$m^{1/2}$	mole ratio[a]	specific heat	exptl	calcd[b]	$\bar{C}_{p_2}$	$\bar{C}_{p_1}$
			Lanthanum Nitrate			
0.3146	560.8	0.9634	−45.7	−46.9	−35.2	17.97
0.3999	347.1	0.9434	−40.5	−40.5	−25.3	17.95
0.4998	222.2	0.9162	−33.3	−32.9	−13.7	17.91
0.5998	154.3	0.8863	−25.0	−25.2	−2.2	17.85
0.6994	113.5	0.8544	−17.8	−17.6	8.8	17.76
0.7998	86.8	0.8216	−10.2	−10.1	19.3	17.66
0.9000	68.5	0.7889	−2.9	−2.9	29.1	17.53
1.0001	55.5	0.7571	4.3	4.1	38.0	17.38
1.0989	46.0	0.7265	10.5	10.6	45.9	17.23
1.1578	41.4	0.7092	14.3	14.3	50.1	17.13
1.3017	32.8	0.6692	22.8	22.8	59.0	16.89
1.3999	28.3	0.6439	28.1	28.0	63.8	16.73
1.4462	26.5	0.6324	30.2	30.3	65.7	16.66
1.5992	21.7	0.5975	37.2	37.3	70.6	16.46
1.7007	19.2	0.5766	41.4	41.3	72.8	16.35
1.7998	17.1	0.5572	44.7	44.7	74.2	16.28
1.8988	15.4	0.5393	47.8	47.8	75.0	16.22
1.9999	13.9	0.5222	50.5	50.5	75.5	16.19
2.1109	12.5	0.5047	53.1	53.1	75.8	16.17
2.1467[c]	12.0	0.4992	53.8	53.8	75.9	16.16
			Praseodymium Nitrate			
0.3073	587.6	0.9645	−48.8	−47.4	−35.2	17.97
0.4094	331.2	0.9408	−39.1	−39.3	−23.2	17.95
0.5089	214.3	0.9136	−30.7	−31.6	−11.9	17.90
0.6123	148.0	0.8818	−24.0	−23.6	−0.4	17.84
0.7167	108.1	0.8484	−15.6	−15.8	10.6	17.75
0.8187	82.8	0.8147	−8.4	−8.4	20.7	17.64
0.9207	65.5	0.7812	−1.4	−1.3	30.2	17.51
1.0232	53.0	0.7484	5.4	5.6	39.0	17.36
1.1300	43.5	0.7158	12.3	12.4	47.3	17.19
1.2327	36.5	0.6863	18.6	18.5	54.5	17.01
1.3372	31.0	0.6580	24.5	24.4	60.9	16.82
1.4431	26.7	0.6316	30.1	30.0	66.4	16.63
1.5483	23.2	0.6071	35.0	35.1	71.0	16.45
1.6568	20.2	0.5841	39.8	39.9	74.7	16.27
1.7623	17.9	0.5636	44.1	44.1	77.5	16.13
1.8707	15.9	0.5441	47.9	48.0	79.4	16.01
1.9793	14.2	0.5261	51.3	51.4	80.5	15.94
2.0878	12.7	0.5099	54.5	54.4	80.8	15.92
2.1986	11.5	0.4938	56.9	56.9	80.4	15.96
2.2401[c]	11.1	0.4880	57.7	57.8	80.1	15.98
			Neodymium Nitrate			
0.3199	542.3	0.9618	−44.8	−43.2	−31.5	17.97
0.4048	338.8	0.9420	−36.2	−37.0	−22.3	17.95
0.5061	216.7	0.9138	−30.4	−29.7	−11.5	17.91
0.6080	150.2	0.8830	−21.9	−22.4	−0.9	17.85
0.7093	110.3	0.8498	−15.7	−15.3	9.3	17.77
0.8121	84.2	0.8162	−7.5	−8.3	19.2	17.67
0.9134	66.5	0.7820	−1.7	−1.5	28.5	17.54
1.0158	53.8	0.7490	5.2	5.1	37.3	17.40
1.1182	44.4	0.7170	11.3	11.5	45.5	17.23
1.2211	37.2	0.6868	17.5	17.6	52.9	17.05
1.3248	31.6	0.6585	23.5	23.4	59.6	16.85
1.4258	27.3	0.6326	28.7	28.8	65.3	16.66
1.5314	23.7	0.6078	34.0	34.0	70.3	16.46
1.6316	20.9	0.5862	38.6	38.5	74.0	16.29
1.7424	18.3	0.5642	43.2	43.1	77.0	16.14
1.8423	16.4	0.5460	46.9	46.8	78.7	16.05
1.9475	14.6	0.5277	50.0	50.2	79.2	16.01
2.0357	13.4	0.5137	52.6	52.6	78.7	16.05
2.1445[c]	12.1	0.4973	55.2	55.1	76.8	16.20
			Samarium Nitrate			
0.3016	610.2	0.9652	−45.8	−41.6	−31.9	17.98
0.4008	345.6	0.9424	−34.8	−35.1	−22.1	17.96
0.4992	222.8	0.9153	−27.6	−28.7	−12.4	17.92
0.5981	155.2	0.8846	−22.0	−22.3	−2.8	17.87
0.6983	113.8	0.8516	−15.7	−15.8	6.8	17.80
0.8008	86.6	0.8169	−9.0	−9.2	16.3	17.70
0.8958	69.2	0.7844	−3.5	−3.2	24.8	17.59
0.9901	56.6	0.7529	2.3	2.6	32.9	17.46
1.0986	46.0	0.7185	9.4	9.2	41.6	17.29
1.2042	38.3	0.6863	15.3	15.3	49.3	17.11
1.3043	32.6	0.6578	20.8	20.8	56.0	16.92

Table II (*Continued*)

$m^{1/2}$	mole ratio^a	specific heat	ϕ_{cp} exptl	ϕ_{cp} calcd^b	$\bar{C}_{p2}$	$\bar{C}_{p1}$
1.4026	28.2	0.6319	26.0	26.0	61.9	16.72
1.5026	24.6	0.6077	31.1	30.9	67.1	16.53
1.6029	21.6	0.5847	35.5	35.6	71.4	16.34
1.7029	19.1	0.5641	39.8	39.9	74.9	16.17
1.8043	17.1	0.5450	43.9	43.9	77.4	16.03
1.9000	15.4	0.5282	47.3	47.2	79.0	15.93
1.9563	14.5	0.5187	49.0	49.1	79.4	15.90
2.0688^c	13.0	0.5012	52.3	52.3	79.4	15.90
Gadolinium Nitrate						
0.3162	555.2	0.9618	−40.9	−39.2	−29.5	17.98
0.3958	354.4	0.9427	−35.2	−34.3	−22.0	17.96
0.5000	222.0	0.9136	−27.6	−27.8	−12.2	17.93
0.5997	154.3	0.8824	−21.0	−21.6	−2.9	17.87
0.7006	113.1	0.8485	−15.2	−15.3	6.5	17.80
0.8011	86.5	0.8139	−8.9	−9.1	15.6	17.71
0.9008	68.4	0.7794	−3.0	−3.0	24.3	17.60
1.0022	55.3	0.7450	2.9	3.1	32.9	17.46
1.1003	45.9	0.7130	8.6	8.9	40.7	17.30
1.1998	38.6	0.6827	14.7	14.5	48.2	17.12
1.3007	32.8	0.6533	20.0	20.1	55.1	16.93
1.4024	28.2	0.6263	25.5	25.4	61.3	16.72
1.5015	24.6	0.6016	30.3	30.4	66.6	16.52
1.6018	21.6	0.5791	35.2	35.0	71.0	16.33
1.7018	19.2	0.5581	39.4	39.3	74.5	16.16
1.7995	17.1	0.5393	43.2	43.2	76.7	16.04
1.9033	15.3	0.5208	46.8	46.8	77.9	15.97
1.9878	14.0	0.5066	49.3	49.4	77.8	15.97
2.0975^c	12.6	0.4896	52.3	52.2	76.2	16.10
Terbium Nitrate						
0.2961	633.0	0.9659	−43.1	−43.7	−33.7	17.98
0.3995	347.9	0.9409	−38.9	−36.7	−23.1	17.96
0.4958	225.9	0.9141	−29.7	−30.2	−13.3	17.92
0.5946	157.0	0.8830	−23.3	−23.5	−3.4	17.87
0.6946	115.0	0.8496	−16.4	−16.8	6.3	17.79
0.7946	87.9	0.8151	−10.0	−10.2	15.8	17.70
0.8945	69.4	0.7804	−3.9	−3.7	24.7	17.59
0.9890	56.8	0.7485	2.2	2.2	32.8	17.46
1.0896	46.8	0.7155	8.1	8.3	40.8	17.30
1.1874	39.4	0.6854	14.1	14.0	48.0	17.13
1.2883	33.4	0.6560	19.7	19.7	54.8	16.95
1.3844	29.0	0.6300	24.8	24.8	60.6	16.76
1.4800	25.3	0.6059	29.6	29.6	65.6	16.57
1.5805	22.2	0.5827	34.4	34.3	70.2	16.38
1.6768	19.7	0.5621	38.5	38.5	73.8	16.21
1.7734	17.7	0.5431	42.4	42.4	76.6	16.06
1.8713	15.9	0.5254	46.0	46.0	78.7	15.93
1.9372	14.8	0.5141	48.2	48.2	79.7	15.87
2.0337	13.4	0.4989	51.2	51.2	80.4	15.82
2.1306^c	12.2	0.4845	53.8	53.8	80.4	15.82
Dysprosium Nitrate						
0.3017	609.6	0.9644	−42.8	−42.0	−33.1	17.98
0.4058	337.0	0.9391	−35.8	−35.7	−23.0	17.96
0.5062	216.6	0.9101	−29.3	−29.3	−12.8	17.92
0.6080	150.2	0.8776	−22.3	−22.6	−2.3	17.86
0.7106	109.9	0.8428	−15.4	−15.7	8.1	17.78
0.8125	84.1	0.8073	−8.9	−8.9	18.2	17.67
0.9153	66.3	0.7716	−2.4	−2.1	27.9	17.54
1.0153	53.8	0.7382	4.4	4.4	36.7	17.40
1.1184	44.4	0.7051	10.8	10.8	45.0	17.22
1.2201	37.3	0.6743	17.0	16.9	52.4	17.04
1.3250	31.6	0.6446	22.9	22.8	59.0	16.85
1.4286	27.2	0.6174	28.2	28.3	64.5	16.66
1.5323	23.6	0.5923	33.3	33.3	68.9	16.49
1.6360	20.7	0.5694	38.0	37.9	72.4	16.33
1.7416	18.3	0.5476	42.1	42.1	74.9	16.21
1.8449	16.3	0.5283	45.9	45.8	76.4	16.12
1.9581	14.5	0.5083	49.2	49.3	77.1	16.08
2.0656	13.0	0.4910	52.1	52.1	76.9	16.08
2.1767^c	11.7	0.4742	54.5	54.5	76.2	16.14
Holmium Nitrate						
0.3149	559.6	0.9611	−43.8	−42.2	−33.2	17.98
0.4101	330.1	0.9372	−38.0	−36.5	−23.7	17.96
0.5007	221.4	0.9112	−30.0	−30.7	−14.3	17.92
0.5998	154.3	0.8793	−23.8	−24.1	−3.7	17.86

Table II (*Continued*)

			ϕ_{cp}			
$m^{1/2}$	mole ratio[a]	specific heat	exptl	calcd[b]	$\bar{C}_{p_2}$	$\bar{C}_{p_1}$
0.7010	112.9	0.8450	−16.6	−17.2	7.0	17.78
0.7350	102.8	0.8330	−14.8	−14.8	10.6	17.75
0.8955	69.2	0.7771	−3.9	−3.7	26.8	17.55
0.9964	55.9	0.7429	2.9	3.1	36.2	17.40
1.0999	45.9	0.7094	9.7	9.8	45.0	17.23
1.1944	38.9	0.6807	15.8	15.7	52.2	17.06
1.2978	33.0	0.6510	21.9	21.9	59.0	16.87
1.3990	28.4	0.6238	27.3	27.4	64.6	16.68
1.4950	24.8	0.6005	32.5	32.3	68.9	16.52
1.5966	21.8	0.5772	37.1	37.1	72.4	16.37
1.6820	19.6	0.5589	40.6	40.7	74.6	16.27
1.8257	16.7	0.5312	46.1	46.0	76.7	16.15
1.9283	14.9	0.5126	49.1	49.2	77.3	16.12
2.0308	13.5	0.4955	51.8	52.0	77.2	16.12
2.1347	12.2	0.4800	54.6	54.4	76.7	16.16
2.2402[c]	11.1	0.4641	56.3	56.4	76.0	16.23
			Erbium Nitrate			
0.3180	549.0	0.9600	−45.6	−40.3	−33.4	17.98
0.5046	218.0	0.9093	−30.6	−30.4	−14.9	17.92
0.6016	153.4	0.8782	−23.2	−24.1	−3.9	17.86
0.7006	113.1	0.8444	−16.4	−17.3	7.6	17.78
0.8018	86.4	0.8090	−9.6	−10.0	19.2	17.66
0.9021	68.2	0.7742	−2.6	−2.7	30.3	17.51
1.0022	55.3	0.7408	4.8	4.6	40.4	17.35
1.0973	46.1	0.7100	10.9	11.3	49.0	17.18
1.2272	36.9	0.6714	19.7	19.9	58.9	16.94
1.3084	32.4	0.6488	24.7	24.9	63.9	16.79
1.4059	28.1	0.6237	30.5	30.4	68.6	16.64
1.5042	24.5	0.5998	35.5	35.5	72.0	16.51
1.6084	21.5	0.5763	40.2	40.2	74.3	16.41
1.7079	19.0	0.5556	44.3	44.2	75.3	16.36
1.8005	17.1	0.5372	47.4	47.3	75.4	16.36
1.9124	15.2	0.5166	50.6	50.4	74.8	16.39
2.0002	13.9	0.5008	52.4	52.5	74.1	16.44
2.1095	12.5	0.4827	54.5	54.7	73.5	16.48
2.2099	11.4	0.4674	56.3	56.3	73.7	16.47
2.2758	10.7	0.4577	57.2	57.3	74.5	16.39
2.3358[c]	10.2	0.4501	58.4	58.2	75.9	16.26
			Thulium Nitrate			
0.3022	607.9	0.9636	−44.5	−45.3	−32.4	17.97
0.4022	343.2	0.9386	−39.7	−37.3	−22.2	17.95
0.4630	258.9	0.9219	−31.9	−32.9	−16.2	17.93
0.6002	154.1	0.8783	−23.1	−23.2	−2.2	17.86
0.6928	115.7	0.8467	−16.6	−16.7	7.8	17.78
0.7851	90.0	0.8145	−10.0	−10.1	18.2	17.68
0.9052	67.7	0.7730	−1.3	−1.3	32.0	17.50
0.9989	55.6	0.7416	5.4	5.6	42.4	17.33
1.1002	45.9	0.7097	13.0	13.0	52.9	17.13
1.2022	38.4	0.6795	20.2	20.3	62.1	16.91
1.3025	32.7	0.6523	27.2	27.0	69.6	16.69
1.4004	28.3	0.6272	33.1	33.2	75.1	16.51
1.4996	24.7	0.6042	39.0	38.8	78.9	16.37
1.5994	21.7	0.5823	43.8	43.8	80.8	16.29
1.7048	19.1	0.5607	48.3	48.3	81.0	16.28
1.8018	17.1	0.5418	51.5	51.6	80.0	16.34
1.9403	14.7	0.5164	55.1	55.4	77.2	16.52
1.9993	13.9	0.5068	56.8	56.6	75.8	16.61
2.1004	12.6	0.4897	58.4	58.3	73.3	16.80
2.2396	11.1	0.4675	60.0	59.9	70.4	17.05
2.3361	10.2	0.4524	60.4	60.7	68.6	17.22
2.4389[c]	9.3	0.4383	61.3	61.2	66.3	17.45
			Ytterbium Nitrate			
0.3074	587.3	0.9620	−45.0	−44.2	−31.2	17.97
0.3990	348.6	0.9394	−36.4	−37.0	−22.4	17.95
0.4968	224.9	0.9107	−30.4	−30.2	−13.4	17.92
0.5957	156.4	0.8786	−23.6	−23.6	−3.7	17.87
0.6947	115.0	0.8446	−16.5	−16.9	6.8	17.79
0.7957	87.7	0.8085	−10.5	−9.9	18.4	17.67
0.8934	69.5	0.7748	−2.6	−2.8	30.1	17.52
0.9935	56.2	0.7409	4.6	4.7	42.1	17.33
1.0927	46.5	0.7095	12.4	12.2	53.4	17.11
1.1901	39.2	0.6804	19.4	19.5	63.3	16.88
1.2898	33.4	0.6529	26.4	26.6	71.9	16.64
1.3876	28.8	0.6285	33.3	33.3	78.3	16.43

Table II (*Continued*)

$m^{1/2}$	mole ratio[a]	specific heat	ϕ_{cp} exptl	ϕ_{cp} calcd[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
1.4855	25.2	0.6058	39.4	39.3	82.6	16.27
1.5833	22.1	0.5848	44.8	44.6	84.8	16.18
1.6827	19.6	0.5645	49.3	49.3	85.0	16.17
1.7788	17.5	0.5460	52.9	53.0	83.6	16.25
1.8756	15.8	0.5283	55.9	55.9	81.0	16.41
1.9754	14.2	0.5104	58.1	58.2	77.5	16.64
2.0718	12.9	0.4946	60.1	59.8	74.1	16.89
2.1686	11.8	0.4780	60.9	60.9	71.0	17.14
2.2650	10.8	0.4628	61.7	61.7	68.7	17.35
2.3616	10.0	0.4480	62.1	62.2	67.3	17.48
2.4579	9.2	0.4344	62.5	62.5	66.6	17.55
2.5540	8.5	0.4217	62.9	62.8	66.1	17.61
2.5788[c]	8.3	0.4181	62.8	62.9	65.8	17.64
Lutetium Nitrate						
0.3157	556.9	0.9597	−46.9	−46.6	−29.7	17.97
0.4004	346.2	0.9386	−37.2	−38.5	−21.4	17.95
0.5002	221.8	0.9092	−30.3	−30.7	−12.9	17.91
0.5999	154.2	0.8761	−24.9	−23.9	−4.0	17.87
0.7078	110.8	0.8386	−17.3	−16.8	6.8	17.78
0.8002	86.7	0.8059	−10.5	−10.5	17.3	17.67
0.8998	68.6	0.7711	−3.0	−3.4	29.6	17.51
0.9958	56.0	0.7385	4.0	3.8	41.8	17.32
1.0979	46.1	0.7058	11.6	11.7	54.5	17.07
1.2001	38.5	0.6759	19.7	19.6	66.0	16.79
1.3003	32.8	0.6488	27.1	27.2	75.4	16.53
1.4058	28.1	0.6231	34.8	34.8	82.8	16.29
1.5037	24.6	0.6009	40.9	41.1	87.0	16.13
1.6063	21.5	0.5797	46.8	46.9	88.5	16.06
1.6986	19.2	0.5620	51.4	51.3	87.7	16.10
1.8017	17.1	0.5427	55.4	55.2	84.6	16.28
1.9012	15.4	0.5242	57.9	57.9	80.1	16.55
2.0142	13.7	0.5043	60.1	60.1	74.3	16.95
2.1337	12.2	0.4832	61.1	61.3	68.6	17.40
2.2273	11.2	0.4674	61.6	61.7	65.1	17.69
2.3265	10.3	0.4517	62.0	61.9	63.0	17.89
2.4270	9.4	0.4365	62.1	62.0	62.4	17.94
2.5325	8.7	0.4213	62.0	62.0	63.1	17.87
2.6116[c]	8.1	0.4108	62.1	62.1	63.4	17.83

[a] Moles of water per mole of $RE(NO_3)_3$. [b] Calculated from eq 2 by using coefficients given in Table I. [c] Saturated solutions.

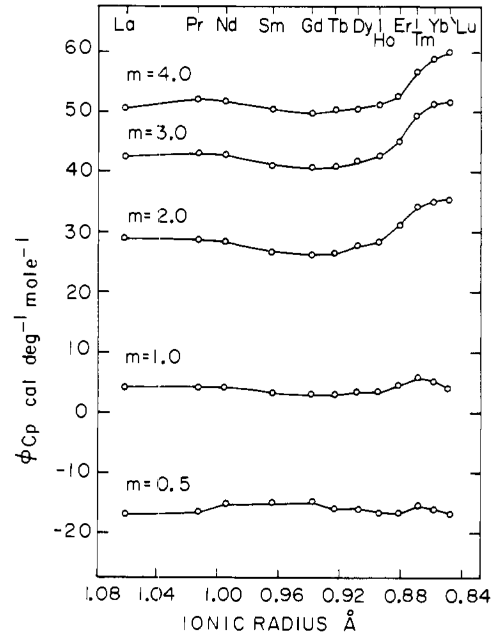

Figure 4. Apparent molal heat capacities of $RE(NO_3)_3$ solutions at given molalities vs. RE ionic radius at 25 °C.

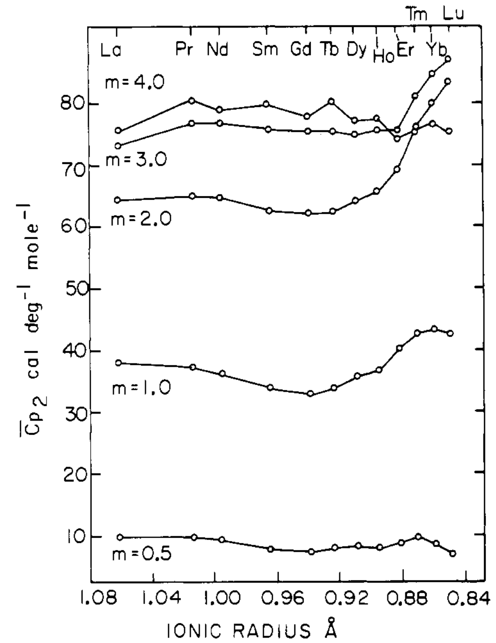

Figure 5. Partial molal heat capacities of solute for $RE(NO_3)_3$ solutions at given molalities vs. RE ionic radius at 25 °C.

and perchlorate solutions (*18*, *23*, *30*) and is thought to be the result of disruption of the hydrogen bonding of water by the presence of ions. The effect is greatest for the most dilute solutions, with less solvent structure remaining to be disrupted with each incremental addition of salt. Eventually, as concentration is increased, the additional intrinsic heat capacity of the ions plus that of their hydrates exceeds that lost due to

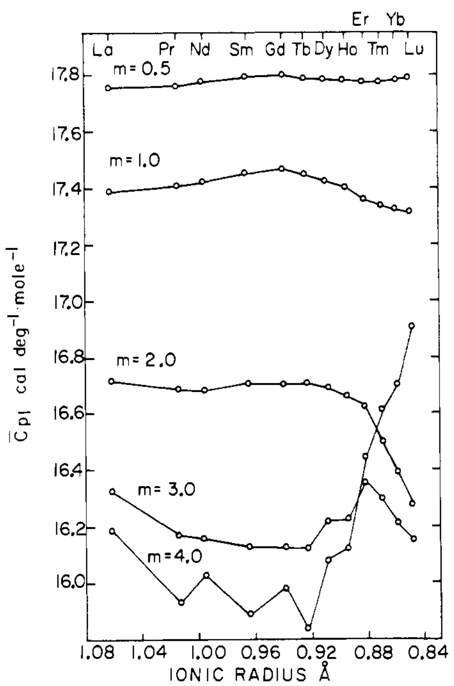

Figure 6. Partial molal heat capacities of water for RE(NO_3)$_3$ solutions at given molalities vs. RE ionic radius at 25 °C.

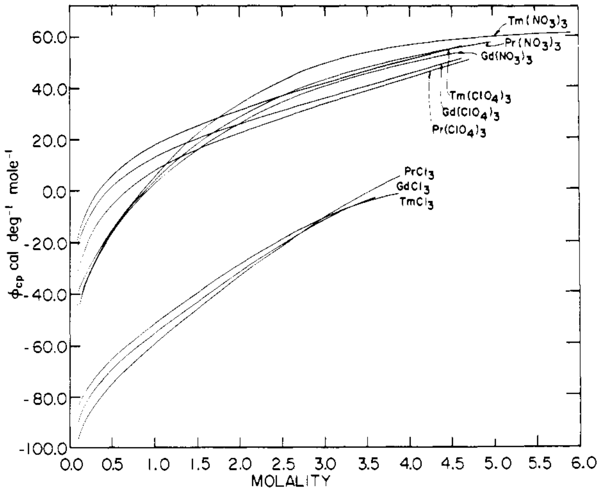

Figure 7. Comparison of concentration dependence of apparent molal heat capacities for solutions of typical rare earth nitrates, chlorides, and perchlorates.

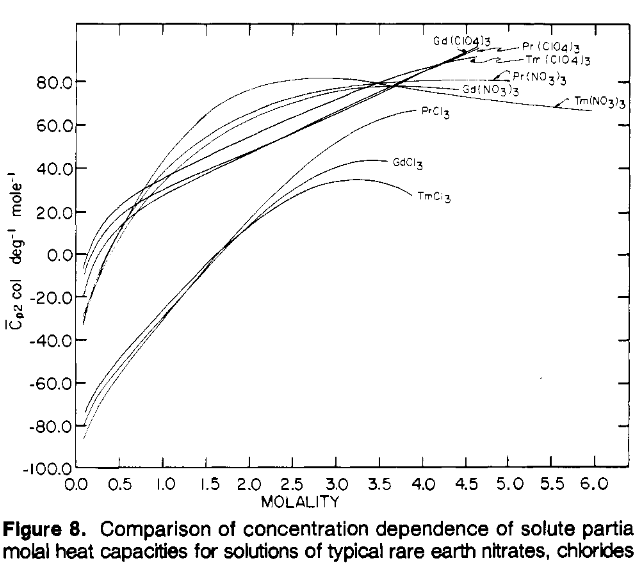

Figure 8. Comparison of concentration dependence of solute partial molal heat capacities for solutions of typical rare earth nitrates, chlorides, and perchlorates.

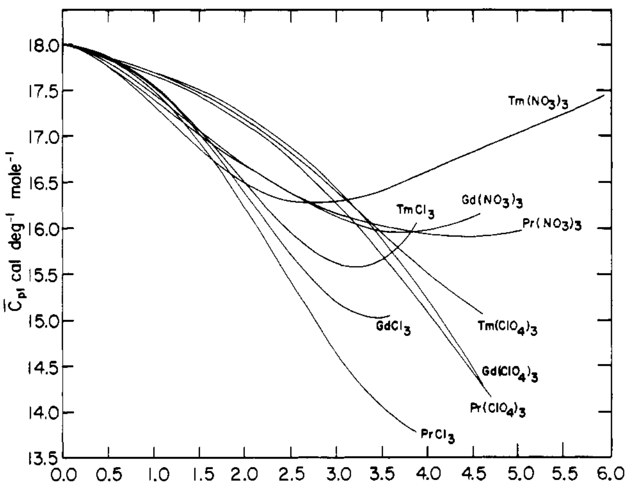

Figure 9. Comparison of concentration dependence of solvent partial molal heat capacities for solutions of typical rare earth nitrates, chlorides, and perchlorates.

decreased solvent structure, and $\bar{C}_{p2}$ becomes positive (by 0.5 *m*).

The two series effect evident in the $\bar{C}_{p1}$ data across the rare earth series for the chlorides and perchlorates (*18*, *30*) is not evident at any concentration shown in Figure 6 for the rare earth nitrates. Even at the lowest concentration measured, the two series effect is obscured by cation–nitrate ion interactions. Values of $\bar{C}_{p1}$ at 0.5 and 1.0 *m* peak in the middle of the series at Gd. The first formation constants for rare earth nitrate complexes, measured at low ionic strength, increase to a maximum in the vicinity of Eu and then decrease for the heavy rare earths (*3*, *4*, *12*). Complex formation could reduce the disruption of hydrogen bonds and increase $\bar{C}_{p1}$. The fact that the activity of water in rare earth nitrate solutions at 0.4 *m* peaks at Sm (*14*) may enforce this hypothesis. However, extrapolation to concentration solutions ($\geq$4.0 *m*) where $\bar{C}_{p1}$'s are much greater, and increase with atomic number for the heavy rare earths, may not be valid as it implies the heavy rare earths are complexing more. This contradicts previous conclusions (*15*) and the fact that the activity of water decreases with atomic number for concentrated nitrate solutions of the heavy rare earths.

Figures 7 and 8 show that in dilute solution apparent and partial molal heat capacities for a given rare earth are in the order perchlorate > nitrate > chloride. This order is also the same for the heat capacities of dilute solutions of the sodium salts of these anions (*5*, *6*, *13*). Part of the difference is due to the contribution of the intrinsic heat capacities associated with the anions, with the perchlorate ion having the most vibrational degrees of freedom and the chloride ion none. Anion–water and cation–anion interactions are also important. Figure 9 shows that at 1.0 *m* $\bar{C}_{p1}$ values are in the order perchlorate > chloride > nitrate, which is inversely related to the degree of complex formation. If increased complex formation in less concentrated solutions increases $\bar{C}_{p1}$, as hypothesized earlier, then differences in anion–water interactions must dominate differences in heat capacity behavior between salts of the same rare earth.

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Solubility of Carbon Dioxide in Silicone Oil

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The solubility of CO_2 in a Dow Corning FS-1265, 300 cS silicone oil has been determined at 22 °C as a function of CO_2 pressure. Results indicate solubility increases with pressure and thus high-pressure systems containing CO_2 cannot be considered isolated if they are in contact with this or similar oils.

In our work related to *V–L* equilibria of hydrocarbon systems at high pressures we have investigated a sampling arrangement in which a silicone oil was used to compress the system. We believe that a result from this investigation is of general interest but in particular it has a bearing on the decomposition pressures of sodium bicarbonate as recently observed by Templeton.[1]

The use of silicone oil in our and other applications arises out of its generally low vapor pressure and its chemical stability. However, an additional requirement in our application is that components of the hydrocarbon system not be soluble in the silicone oil at high pressures.

We have measured the solubility of Linde, commercial grade (99.5% pure) CO_2 in a freshly degassed sample of Dow Corning FS-1265, 300 cS silicone oil at room temperature (21.8 ± 0.4 °C). (Dow Corning FS-1265 silicone oil is a trade name for trifluoropropylmethylsiloxane. The structure and the physical properties of this material have been described elsewhere.[2–4] Two density determinations (78.019 ± 0.003 lb/ft^3) of the material used in this work at 22.0 °C are in good agreement with the literature value[4] (78.0 lb/ft^3 at 25.0 °C).) Measurements were made through mass balances within a stainless steel apparatus made up of high-pressure bombs, two Heise gages, interconnecting manifold, and associated valves. Volumes within different sections of the apparatus were determined either by gravimetric procedures using water or by the expansion of Linde research grade (99.993% pure) N_2. (Physical properties of N_2 were taken from tables by Jacobsen and Stewart.[5])

Pressures and temperatures for individual measurements are believed to be accurate to within ±1 psi and ±0.1 °C, respectively. Variation in determining section volumes was less than 0.2%.

Incremental CO_2 solubilities were determined by the mass of CO_2 which desorbed under a reduced pressure or by the mass of CO_2 which was adsorbed under an increased pressure. Mass balances were determined by using CO_2 densities calculated by the correlation reported by Bishnoi et al.[6]

Table I. Solubility of CO_2 in Silicone Oil at 22 °C

total pressure, psia	wt of CO_2 dissolved in 0.1495 lb of silicone oil, lb × 10^2	ratio of CO_2 wt to silicone oil wt, lb of CO_2/lb of silicone oil
109.5	0.35	0.023
160.0	0.57	0.038
230.0	0.92	0.061
289.0	1.27[a]	0.085
325.8	1.46	0.098
446.0	2.35	0.157
587.3	3.86	0.258
691.0	5.71	0.382
775.9	8.67	0.580
833.7	13.38	0.895

[a] Determined by an absorption measurement. All others were determined by desorbing CO_2 from the silicone oil.

Initially, the entire apparatus was rocked for 12 h before measurements were made. This interval was later shortened to 8 h when the additional time was shown to have no significant effect on the final pressure above the silicone oil.

The experimental results are reported in Table I. An analysis of random error in these measurements indicates that the precision of the reported solubility is ±3%. The data, also shown in Figure 1, have a limiting slope at 0.0 psia of 2.1 × 10^{-4} lb of CO_2 lb^{-1} of silicone $psia^{-1}$. This value is in good agreement with a value of 2.20 × 10^{-4} lb of CO_2 lb^{-1} of silicone $psia^{-1}$ reported by Dow Corning in a private communication. Since calculations assume ideal mixing of silicone oil and liquid CO_2, nonidealities may introduce a small systematic error at high CO_2 concentrations.

In the reference cited above, Templeton has reported equilibrium pressures associated with the thermal decomposition of sodium bicarbonate. As shown in his Figure 2, the dissociation pressure is characterized by three discontinuities in addition to being a function of the vapor to solid volume ratio, V_g/V_s, inside the bomb.