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

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Specific heats of aqueous solutions of the stoichiometric trivalent Pr, Sm, Eu, Gd, Tb, Ho, Tm, and Lu chlorides were measured over the concentration range of 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}, within experimental accuracy, as a function of $m^{1/2}$ for each salt. From these equations the partial molal heat capacities of the solvent, $\bar{C}_{p1}$, and the solute, $\bar{C}_{p2}$, were calculated. Together with earlier reported data on five other rare earth chlorides, the $\bar{C}_{p1}$ data at even molalities exhibited a two series effect across the rare earth series over the whole concentration range, similar to the rare earth perchlorate data. The differences in the concentration dependence of the heat capacity properties between rare earth chloride and rare earth perchlorate solutions are discussed in terms of ion-ion and ion-solvent interactions.

Aqueous solutions of the trivalent rare earth salts have been studied in this laboratory to determine the effect of cation size on their thermodynamic and transport properties. These studies have been conducted with the perchlorate, chloride, and nitrate anions to observe the effects of varying strengths of cation-anion interactions. This effort has resulted in the observation that thermodynamic properties of dilute solutions (*2, 5, 11, 12, 15–17*) including heat capacity (*10*), when considered for a common anion and a given concentration, are not monotonic functions of ionic radius across the rare earth series. Instead, thermodynamic properties indicate that the rare earth salt solutions are divided into two series.

It has been proposed (*15*) that one series, consisting of the larger, light rare earth cations, exists in solution with one more water molecule in their first hydration sphere than the other series consisting of the smaller, heavy rare earth cations; and furthermore, that the intermediate rare earths exist in solution with an equilibrium between the two hydration types. It is then believed that the shift in the values of thermodynamic properties of dilute solutions near the middle of the rare earth series is due to a shift in the equilibrium from the higher to lower coordination type with decreasing ionic radius. The difference in the values of thermodynamic properties between the light and heavy rare earth series is believed to be due to the combined effect of the change in the inner sphere coordination and the results of this change on the remaining surrounding water.

It is believed that in concentrated rare earth chloride and perchlorate solutions, outer sphere complexes between cation and anion exist in appreciable quantities (*3, 6, 14*). This is due in part, particularly for the perchlorates, to the forced sharing of water because at increasing concentrations the hydration requirements of the ions begin to exceed the amount of water present. However, data in the literature indicate that outer sphere chloride complexes are formed by an ionic strength of 1*M* (*1, 8*), whereas sharing of water between a perchlorate ion and rare earth ion probably does not occur at an appreciable extent until at least 2*m* (ionic strength of about 12*m*).

The study reported here further explores the rare earth chloride solutions for the two series effect and investigates the effect on heat capacity properties of the apparently different cation-anion interaction for the rare earth chlorides relative to the rare earth perchlorates. The partial molal heat capacities determined in this work can be used to calculate the temperature dependence of heats of dilution and activities for the rare earth chloride solutions. The data presented are the specific heats and the apparent and partial molal heat capacities of aqueous solutions of eight rare earth chlorides from 0.1*m* to saturation at 25°C.

Experimental

Apparatus and procedure. The specific heats were measured with an adiabatic, single-can, solution calorimeter. A detailed description of the apparatus and experimental procedure is provided elsewhere (*10, 13*). In general, before a series of solution runs, the heat capacity of the calorimeter, plus appendages, was determined with a known amount of air saturated water. The accuracy of these determinations was checked by determining the specific heats of NaCl solutions and comparing the data to that of Randall and Rossini (*9*). An average deviation of less than 0.05% for multiple determinations of eight different NaCl solutions during these studies implies an accuracy of at least that amount.

Materials. Solutions at 0.1 intervals in $m^{1/2}$ ranging from roughly 0.09*m* to near saturation were made from stock solutions of the rare earth chlorides. The stock solutions were prepared by adding an excess of the appropriate rare earth oxide to reagent grade hydrochloric acid and boiling. After filtration, the solutions were adjusted to the equivalence pH to dissolve any rare earth colloid present and to assure a three-to-one ratio of anions to cations. A more complete description of this preparation is given elsewhere (*15*).

The rare earth oxides used were prepared by the Rare Earth Separation Group of the Ames Laboratory of the U.S. Atomic Energy Commission. The purity of the oxides was determined by spectroscopic analysis. In all cases, the total impurities of iron, calcium, and adjacent rare earths were 0.15% or less by weight with less than 0.05% being iron and calcium. Concentrations of the stock solution were determined by two or more analytical methods. The methods used were oxide gravimetric, sulfate gravimetric, EDTA titration, and chloride titration. The average deviation of the concentration determined by the various methods from the mean was about 0.05%. Because the solutions studied were prepared from weighed portions of the stock solution and water (specific conductance $<1.0 \times 10^{-6}$ ohm^{-1} cm^{-1}), relative concentrations of a series of solutions for a particular rare earth chloride were at least an order of magnitude more accurate than the absolute concentrations. All weights were corrected to vacuum.

Saturated solutions were prepared by concentrating portions of stock solutions in a desiccator with $Mg(ClO_4)_2$. The saturated solution was stored in contact with the hydrated

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rare earth chloride crystals, formed during preparation, for two weeks or more at 25.00° ± 0.01°C. The concentrations of the saturated solutions at this temperature had previously been determined by coworkers.

Results

The apparent molal heat capacity for each solution was calculated from the equation:

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

where m is the molality, M_2 is the molecular weight of the salt (1969 IUPAC atomic weights), S is the measured specific heat of the solution, and S° (0.9989 cal deg^{-1} g^{-1}) is the specific heat of pure liquid water as determined by Osborne et al. (*7*). Empirical polynomial equations of the form:

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

Salt	A (0)	A (1)	A (2)	A (3)	A (4)
Praseodymium chloride	−121.36	100.730	−85.391	59.5617	−12.9533
Samarium chloride	−124.14	126.700	−129.140	87.9856	−19.1966
Europium chloride	−115.63	121.103	−131.466	91.8997	−20.5198
Gadolinium chloride	−117.80	119.362	−121.432	82.7956	−18.4807
Terbium chloride	−113.74	120.535	−126.387	87.0900	−19.9319
Holmium chloride	−114.79	123.367	−128.620	87.8105	−20.0228
Thulium chloride	−106.52	93.985	−90.081	66.8670	−16.0079
Lutetium chloride	−103.65	79.672	−71.556	56.3495	−13.9014

Table II. Specific Heats, Apparent Molal, and Partial Molal Heat Capacities of $RECl_3$ Solutions at 25° C

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p_2}$	$\bar{C}_{p_1}$
Praseodymium chloride						
0.3139	563.4	0.9660	−95.1	−96.4	−86.5	17.98
0.3906	363.8	0.9492	−91.0	−91.8	−80.4	17.96
0.4961	225.5	0.9216	−86.2	−85.9	−72.6	17.94
0.5993	154.6	0.8908	−80.7	−80.5	−65.1	17.90
0.6942	115.2	0.8597	−76.3	−75.7	−58.0	17.84
0.7999	86.7	0.8236	−70.3	−70.2	−49.5	17.76
0.9064	67.6	0.7864	−64.2	−64.6	−40.1	17.63
1.0046	55.0	0.7518	−59.0	−59.1	−30.5	17.48
1.1073	45.3	0.7164	−53.2	−53.1	−19.7	17.26
1.2057	38.2	0.6845	−47.0	−47.0	−8.6	16.99
1.3085	32.4	0.6534	−40.2	−40.3	3.6	16.64
1.4084	28.0	0.6255	−33.6	−33.4	15.8	16.24
1.4697	25.7	0.6100	−29.2	−29.1	23.2	15.96
1.6034	21.6	0.5802	−19.4	−19.5	38.8	15.30
1.7032	19.1	0.5611	−12.2	−12.2	49.3	14.78
1.7983	17.2	0.5453	−5.4	−5.4	57.6	14.32
1.8867	15.6	0.5324	0.6	0.6	63.4	13.97
1.9477	14.6	0.5244	4.6	4.6	66.0	13.79
1.9726[c]	14.3	0.5212	6.1	6.1	66.7	13.75
Samarium chloride						
0.3116	571.6	0.9658	−92.9	−94.7	−83.9	17.98
0.3995	347.9	0.9460	−88.7	−89.0	−76.9	17.96
0.5184	206.6	0.9137	−82.5	−82.3	−68.5	17.93
0.6003	154.0	0.8884	−78.6	−78.1	−63.0	17.90
0.7182	107.6	0.8491	−72.5	−72.3	−54.7	17.83
0.8187	82.8	0.8139	−67.1	−67.3	−46.8	17.75
0.9235	65.1	0.7760	−62.2	−61.9	−37.6	17.62
1.0308	52.2	0.7383	−55.7	−56.1	−26.8	17.43
1.0664	48.8	0.7256	−54.1	−54.0	−22.9	17.36
1.1988	38.6	0.6817	−45.7	−45.9	−7.5	17.00
1.2909	33.3	0.6532	−39.8	−39.8	4.0	16.68
1.3947	28.5	0.6237	−32.8	−32.6	17.4	16.25
1.4547	26.2	0.6082	−28.5	−28.2	25.0	15.97
1.5885	22.0	0.5785	−18.1	−18.3	41.0	15.30
1.6925	19.4	0.5583	−10.5	−10.6	51.5	14.79
1.7829	17.5	0.5429	−4.1	−4.1	58.4	14.42
1.8727	15.8	0.5293	2.0	2.0	62.3	14.18
1.9082[c]	15.2	0.5242	4.2	4.2	62.8	14.15
Europium chloride						
0.3165	554.0	0.9652	−87.0	−87.8	−77.8	17.98
0.4005	346.0	0.9464	−82.8	−82.8	−71.9	17.96
0.5009	221.2	0.9199	−77.2	−77.7	−65.6	17.94
0.6013	153.5	0.8893	−73.4	−73.0	−59.6	17.91
0.7018	112.7	0.8560	−69.0	−68.6	−53.2	17.86
0.8029	86.1	0.8209	−64.1	−64.1	−45.9	17.78
0.9055	67.7	0.7842	−59.3	−59.3	−37.5	17.67
1.0049	55.0	0.7488	−54.2	−54.4	−28.2	17.52
1.1060	45.4	0.7138	−48.7	−48.9	−17.6	17.31
1.2002	38.5	0.6825	−43.3	−43.4	−6.9	17.05
1.3041	32.6	0.6504	−36.9	−36.8	5.6	16.70
1.3998	28.3	0.6232	−30.7	−30.4	17.3	16.31
1.5058	24.5	0.5969	−23.1	−23.1	29.7	15.84
1.6057	21.5	0.5750	−15.9	−16.1	40.1	15.39
1.6950	19.3	0.5571	−9.9	−9.9	47.6	15.02
1.8006	17.1	0.5383	−3.0	−3.0	53.1	14.72
1.8595	16.1	0.5283	0.4	0.5	54.2	14.65
1.8944[c]	15.5	0.5232	2.6	2.5	54.0	14.66
Gadolinium chloride						
0.3148	560.0	0.9648	−89.7	−89.9	−79.6	17.98
0.3992	348.4	0.9457	−84.6	−84.7	−73.3	17.96
0.4984	223.5	0.9190	−79.5	−79.4	−66.7	17.94
0.5992	154.6	0.8881	−74.5	−74.4	−60.3	17.90
0.6670	124.8	0.8657	−71.2	−71.3	−56.0	17.87
0.7993	86.9	0.8192	−65.3	−65.2	−46.8	17.78
0.8993	68.6	0.7830	−60.6	−60.5	−38.9	17.68
0.9877	56.9	0.7510	−56.1	−56.2	−31.2	17.56
1.1082	45.2	0.7084	−49.8	−49.8	−19.6	17.33
1.2345	36.4	0.6661	−42.8	−42.7	−6.2	17.00
1.3632	29.9	0.6273	−34.6	−34.8	7.9	16.57
1.4656	25.8	0.5987	−28.5	−28.3	18.8	16.17
1.5972	21.8	0.5670	−19.8	−19.8	31.2	15.65
1.6936	19.4	0.5463	−13.8	−13.8	38.2	15.31
1.7890	17.3	0.5276	−8.2	−8.1	42.5	15.08
1.8536	16.2	0.5159	−4.6	−4.6	43.4	15.02
1.8947[c]	15.5	0.5084	−2.6	−2.6	43.0	15.05
Terbium chloride						
0.3168	553.2	0.9646	−85.9	−85.7	−75.5	17.98
0.4019	343.7	0.9457	−78.6	−80.6	−69.3	17.96
0.5015	220.7	0.9185	−76.0	−75.4	−63.0	17.94
0.5987	154.8	0.8889	−71.0	−70.7	−57.1	17.91
0.6999	113.3	0.8552	−66.4	−66.2	−50.7	17.86
0.7974	87.3	0.8209	−62.1	−61.9	−44.1	17.79
0.8994	68.6	0.7844	−57.1	−57.2	−36.3	17.69
1.0073	54.7	0.7457	−51.7	−52.1	−27.1	17.54
1.1008	45.8	0.7126	−47.2	−47.3	−18.4	17.36

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Table II. Continued

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p_2}$	$\bar{C}_{p_1}$
			Terbium chloride			
1.2068	38.1	0.6768	−41.6	−41.6	−7.8	17.11
1.3035	32.7	0.6463	−36.1	−36.0	2.0	16.83
1.3959	28.5	0.6192	−30.6	−30.6	11.3	16.53
1.4667	25.8	0.5998	−26.4	−26.3	17.9	16.28
1.6007	21.7	0.5669	−18.2	−18.3	28.4	15.84
1.6999	19.2	0.5449	−12.6	−12.7	33.4	15.60
1.7964	17.2	0.5246	−7.8	−7.8	34.8	15.52
1.8643	16.0	0.5110	−4.8	−4.8	33.2	15.62
1.8898[c]	15.5	0.5061	−3.7	−3.8	32.0	15.70
			Holmium chloride			
0.3162	555.3	0.9641	−86.6	−86.1	−75.7	17.98
0.4003	346.4	0.9450	−80.0	−80.9	−69.4	17.96
0.5017	220.6	0.9173	−75.4	−75.5	−62.8	17.94
0.6021	153.1	0.8860	−71.1	−70.6	−56.6	17.90
0.7018	112.7	0.8524	−66.2	−66.1	−50.3	17.86
0.8038	85.9	0.8162	−61.3	−61.5	−43.3	17.78
0.9034	68.0	0.7798	−56.9	−56.9	−35.7	17.68
0.9969	55.9	0.7459	−52.2	−52.4	−27.8	17.55
1.1046	45.5	0.7073	−47.1	−46.9	−17.8	17.36
1.2049	38.2	0.6735	−41.4	−41.5	−7.9	17.12
1.3031	32.7	0.6423	−35.8	−35.9	2.1	16.83
1.4014	28.3	0.6131	−30.1	−30.1	11.8	16.51
1.5039	24.5	0.5855	−23.9	−23.9	21.1	16.16
1.6005	21.7	0.5618	−18.2	−18.2	28.3	15.85
1.7041	19.1	0.5387	−12.3	−12.4	33.3	15.60
1.7963	17.2	0.5194	−7.7	−7.7	34.6	15.54
1.9220[c]	15.0	0.4941	−2.6	−2.6	29.5	15.86
			Thulium chloride			
0.3240	528.9	0.9625	−81.9	−83.4	−74.6	17.98
0.4001	346.7	0.9444	−80.4	−79.5	−69.5	17.97
0.4973	224.4	0.9180	−74.4	−74.8	−63.3	17.94
0.6254	141.9	0.8772	−69.7	−69.1	−55.3	17.90
0.7043	111.9	0.8504	−65.3	−65.6	−50.0	17.86
0.8089	84.8	0.8124	−61.4	−60.9	−42.5	17.78
0.9063	67.6	0.7773	−55.8	−56.4	−34.7	17.67
1.0076	54.7	0.7399	−51.4	−51.4	−25.9	17.53
1.1095	45.1	0.7037	−46.1	−46.1	−16.3	17.34
1.2128	37.7	0.6686	−40.5	−40.4	−6.2	17.09
1.3086	32.4	0.6383	−34.9	−34.9	3.2	16.82
1.4004	28.3	0.6111	−29.5	−29.5	12.0	16.53
1.5072	24.4	0.5820	−23.3	−23.2	21.2	16.18
1.6098	21.4	0.5571	−17.1	−17.2	28.4	15.87
1.7111	19.0	0.5345	−11.5	−11.7	33.0	15.64
1.8117	16.9	0.5130	−6.8	−6.8	34.2	15.57
1.9236	15.0	0.4903	−2.5	−2.3	30.4	15.82
1.9691[c]	14.3	0.4818	−0.7	−0.9	26.9	16.06
			Lutetium chloride			
0.3170	552.3	0.9632	−84.2	−83.9	−76.1	17.98
0.4036	340.7	0.9427	−79.8	−79.8	−70.6	17.97
0.5037	218.8	0.9146	−75.0	−75.4	−64.4	17.95
0.6279	140.8	0.8743	−70.0	−70.0	−56.6	17.90
0.7050	111.7	0.8470	−67.4	−66.7	−51.5	17.86
0.8056	85.5	0.8106	−62.1	−62.3	−44.2	17.78
0.9020	68.2	0.7746	−57.8	−57.9	−36.5	17.68
1.0042	55.0	0.7368	−52.6	−52.9	−27.7	17.54
1.1089	45.1	0.6989	−47.4	−47.5	−18.1	17.34
1.2109	37.9	0.6634	−42.2	−41.9	−8.3	17.11
1.3111	32.3	0.6312	−36.3	−36.3	1.3	16.83
1.4079	28.0	0.6021	−30.8	−30.7	10.2	16.54
1.5116	24.3	0.5738	−24.6	−24.7	18.8	16.20
1.6082	21.5	0.5496	−19.1	−19.2	25.4	15.92
1.7069	19.1	0.5269	−13.8	−13.9	29.9	15.69
1.8196	16.8	0.5025	−8.6	−8.5	31.5	15.61
1.8980	15.4	0.4864	−5.4	−5.3	29.6	15.73
2.0289[c]	13.5	0.4601	−1.4	−1.5	19.6	16.43

[a] Moles of water per mole of $RECl_3$. [b] Computed from Equation 2 using the parameters given in Table I. [c] Saturated solutions.

$$\phi_{cp} = \sum_{k=0}^{4} A_k m^{k/2} \tag{2}$$

were obtained for each salt by a least-squares method. These fourth-order equations represent the apparent molal heat capacity data within experimental accuracy for each of the salts. In obtaining the A_k's, ϕ_{cp} values 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 assuming a probable error of 0.05% in specific heat over the whole concentration range 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

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

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

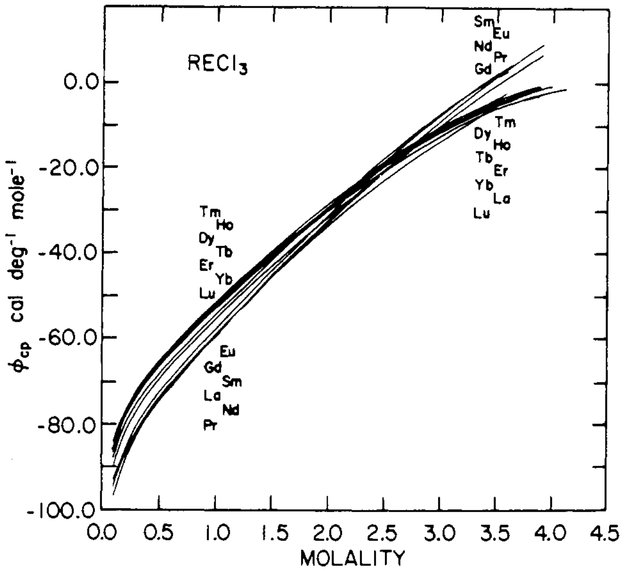

Figure 1. Apparent molal heat capacities of $RECl_3$ solutions vs. molality at 25°C

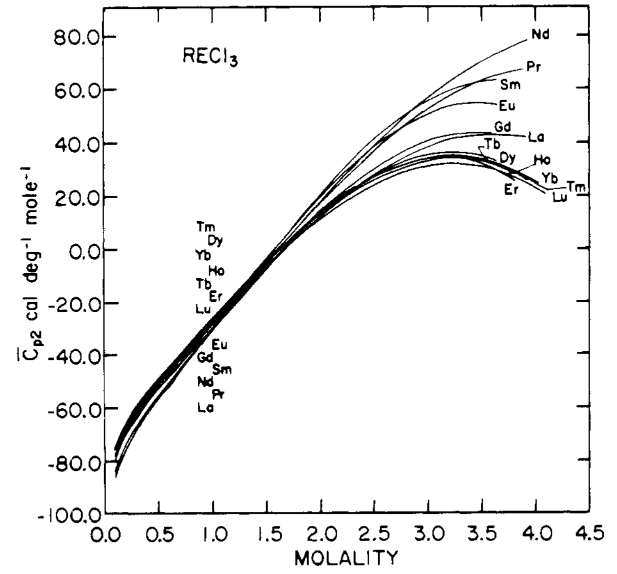

Figure 2. Partial molal heat capacities of solute for $RECl_3$ solutions vs. molality at 25°C

where M_1 (18.015 g mol^{-1}) is the molecular weight of water, and $\bar{C}^\circ_{p1}$ (17.996 cal deg^{-1} mol^{-1}) is the molal heat capacity of pure water (*7*). The derivatives were computed from Equation 2 using the coefficients given in Table I.

The square root of molality, ratio of moles of water to moles of $RECl_3$, specific heat, experimental and smoothed apparent molal heat capacities calculated from Equations 1 and 2, respectively, partial molal heat capacity of the solute, and the partial molal heat capacity of the solvent calculated from Equations 4 and 3, respectively, are listed in Table II for each solution run. Figures 1–3 illustrate the heat capacity properties of the rare earth chloride solutions, including those reported earlier (*13*) as a function of molality. Figures 4–6 illustrate the trends of ϕ_{cp}, $\bar{C}_{p2}$, and $\bar{C}_{p1}$ across the rare earth series, at even molalities, as a function of ionic radius (*18*). Curves in Figures 7–9 are typical for the rare earth salt solutions and compare the heat capacity properties of Pr, Gd, and Tm chloride solutions with those reported for the corresponding perchlorate solutions (*10*).

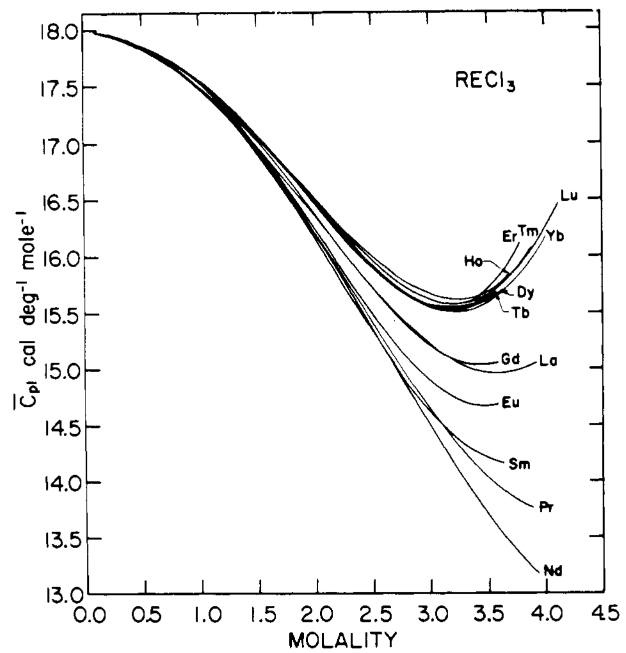

Figure 3. Partial molal heat capacity of water for $RECl_3$ solutions vs. molality at 25°C

Discussion

Values for ϕ_{cp} and $\bar{C}_{p2}$ for rare earth chloride solutions, like those for the perchlorate solutions (*10*), are negative at low concentrations because of the ions' disruptive effect on the hydrogen bonding of water. This is illustrated in Figures 1 and 2. Upon addition of salt to a dilute solution, the decrease in heat capacity associated with the breaking or distortion of hydrogen bonds is larger than the heat capacity of the ion hydrates formed. Due to the overlap of hydration spheres with increasing concentration, the decrease in heat capacity due to loss of solvent structure becomes less per mole of salt added, and ϕ_{cp} and $\bar{C}_{p2}$ increase with concentration. The $\bar{C}_{p2}$ data indicate that between 1.55 and 1.70*m*, the heat capacity gained in formation of the ion hydrates dominates and $\bar{C}_{p2}$ becomes positive.

Values for $\bar{C}_{p1}$ across the rare earth series at various concentrations do not show a monotonic trend with rare earth ionic radius but rather the two series effect as discussed in the introduction. This is shown in Figure 6.

From Figures 7 and 8, both ϕ_{cp} and $\bar{C}_{p2}$ values for the most dilute rare earth chloride solutions are about 70 cal deg^{-1} mol^{-1} less than for the corresponding rare earth perchlorate solutions. Per mole of anion this would be 23 cal deg^{-1}. It is not unexpected that the difference in the ϕ_{cp}

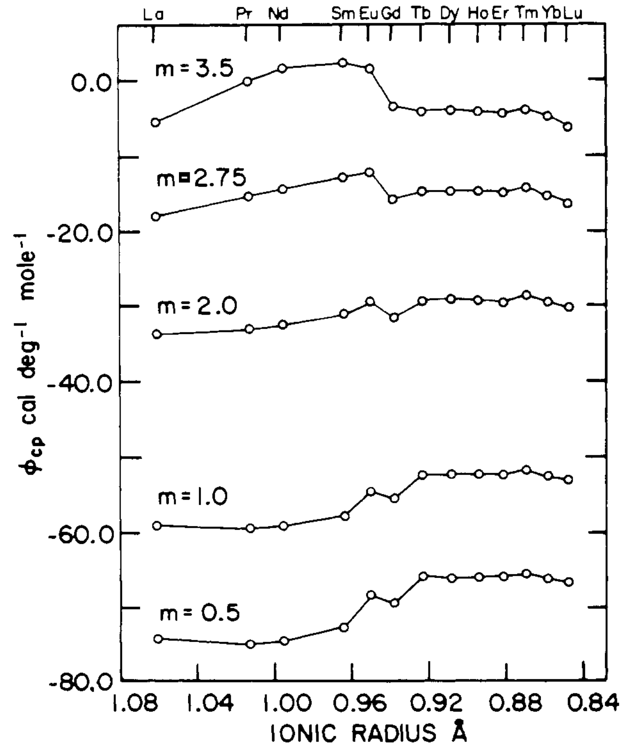

Figure 4. Apparent molal heat capacities of $RECl_3$ solutions at given molalities vs. RE ionic radius at 25°C

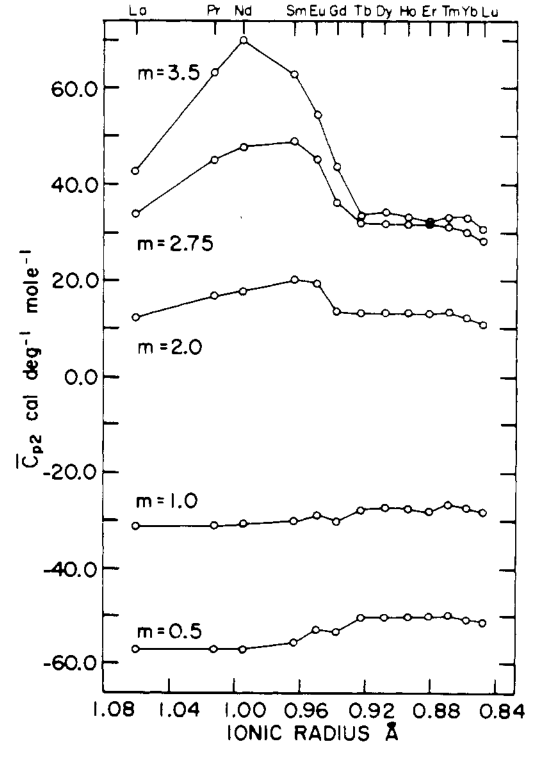

Figure 5. Partial molal heat capacities of solute for $RECl_3$ solutions at given molalities vs. RE ionic radius at 25°C

values for the most dilute solutions of two salts approximately equals the difference in the $\bar{C}_{p2}$ values because at infinite dilution ϕ_{cp} equals $\bar{C}_{p2}$.

Additivity of ionic heat capacities is strictly only valid at infinite dilution. However, the 23 cal deg^{-1} mol^{-1} can, to a good approximation, be attributed to the difference in the partial molal heat capacity of the chloride and perchlorate ions, assuming no cation–anion interactions. Furthermore, the partial molal heat capacities of the chloride and perchlorate ions include the intrinsic heat capacity of the ions and the heat capacity change due to anion water interactions. The perchlorate ion has internal degrees of freedom, whereas the chloride ion has none. However, the additional vibrational heat capacity at 25°C for the perchlorate ion is only about 7 cal deg^{-1} mol^{-1}, calculated assuming harmonic oscillators and using frequencies and assignments given by Herzberg (*4*).

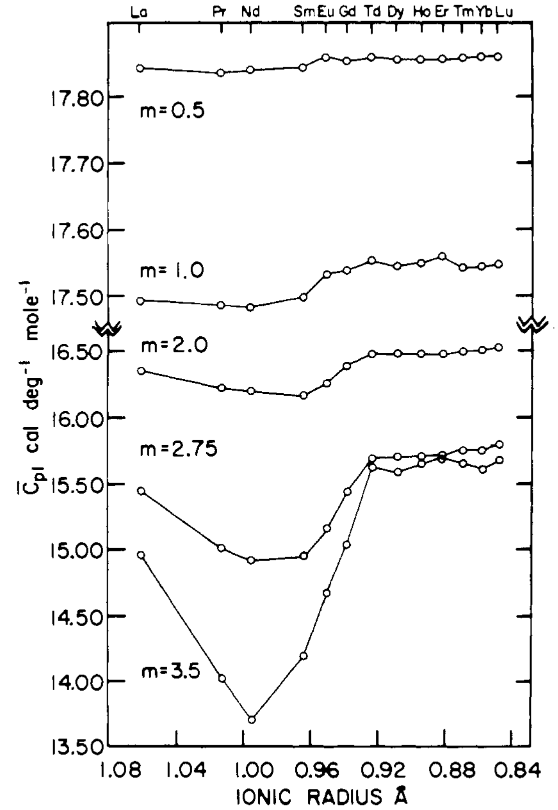

Figure 6. Partial molal heat capacity of water for $RECl_3$ solutions at given molalities vs. RE ionic radius at 25°C

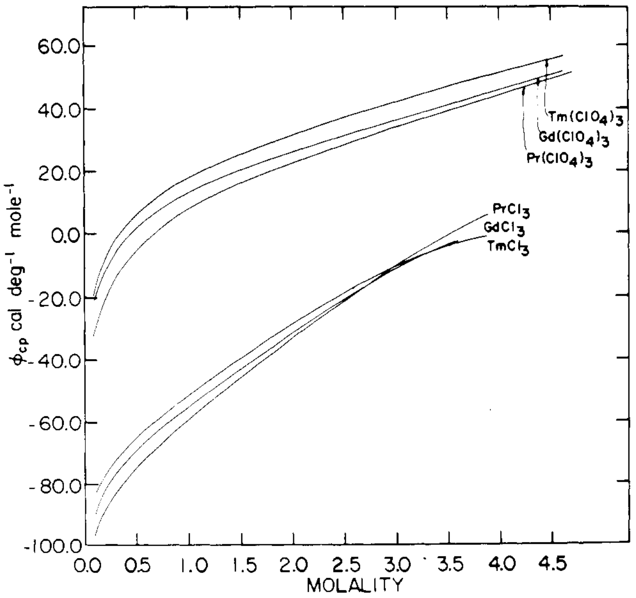

Figure 7. Comparison of concentration dependence of apparent molal heat capacities for solutions of typical rare earth chlorides and perchlorates

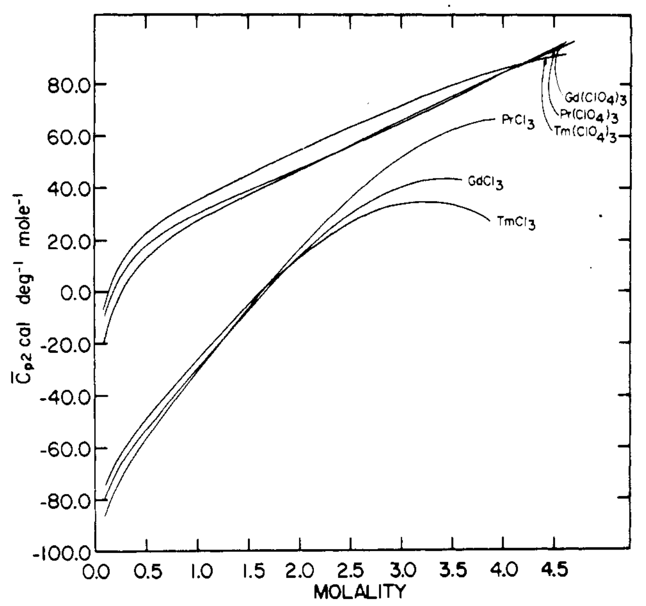

Figure 8. Comparison of concentration dependence of solute partial molal heat capacities for solutions of typical rare earth chlorides and perchlorates

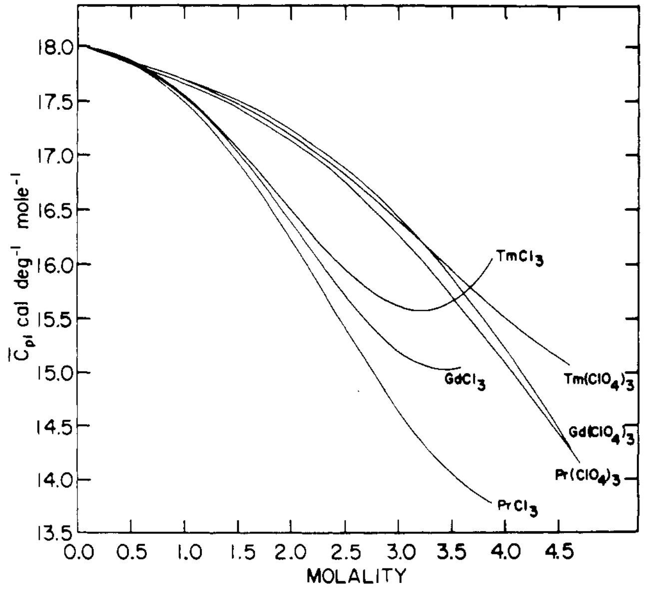

Figure 9. Comparison of concentration dependence of solvent partial molal heat capacities for solutions of typical rare earth chlorides and perchlorates

This is much less than the observed difference of 23 cal deg^{-1} mol^{-1}. The remaining difference must result from variations between chloride–water and perchlorate–water interactions.

A comparison, Figure 9, of the concentration dependence of $\bar{C}_{p1}$ for solutions of rare earth chlorides with solutions of perchlorates shows a divergence up to about 2m. In the case of the perchlorates, there is a slight tendency for the heavier rare earths to exhibit an upturn. This tendency is much more pronounced for the chlorides. Although it is generally believed that the complexes formed in these concentrated solutions are probably outer sphere, it is known from the stoichiometric ratio of water to ions that these outer sphere complexes must interact with each other. The upturns are probably related to these interactions. It would therefore be very helpful if we knew the formation constants for these complexes and understood how they interact.

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NEW COMPOUND SECTION

Tetrachlorobenzenethiols

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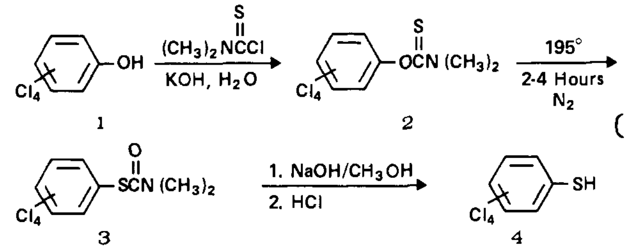
An unequivocal synthesis of the three isomeric tetrachlorobenzenethiols is described, and infrared and NMR spectral data for these compounds are presented.

Although the synthesis of the isomeric tetrachlorobenzenethiols from pentahalobenzenes has previously been reported (*1, 3*), positive structure identification has only been established for 2,3,5,6-tetrachlorobenzenethiol. In this paper we would like to present an unequivocal synthesis of the three isomeric tetrachlorobenzenethiols and a summary of their infrared and NMR spectral properties.

The thiols were synthesized by the method of Newman and Karnes (*2*), which is outlined in Equation 1:



(1)

The phenols (**1**) were converted to the corresponding *O*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamates (**2**, Table I) by reaction with dimethylthiocarbamoyl chloride in the presence of potassium hydroxide. The *O*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamates were converted to the corresponding *S*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamates (**3**) by thermal rearrangement in a nitrogen atmosphere at 195°. The progress of the rearrangement was conveniently followed by NMR, with the two singlets for the methyl groups of **2** disappearing and the broad singlet for the methyl groups of **3** appearing. The *S*-(tetrachlorophenyl)-*N,N*-dimethylthiocarbamates were not isolated but were hydrolyzed directly with sodium hydroxide in refluxing methanol, followed by acidification with hydrochloric acid, to give the tetrachlorobenzenethiols (**4**, Table II). The infrared spectra of the three isomeric tetrachlorobenzenethiols are given in Figures 1–3 (deposited with the ACS Microfilm Depository Service).

The chemical shift (7.509 δ) of the aromatic proton of *O*-(2,3,4,6-tetrachlorophenyl)-*N,N*-dimethylthiocarbamate and the chemical shift (7.507 δ) of the aromatic proton of *O*-(2,3,5,6-tetrachlorophenyl)-*N,N*-dimethylthiocarbamate are identical, indicating that these two protons are in identical environments and that the *N,N*-dimethylthiocarbamoyl group does not donate electron density to the aromatic ring system via resonance interaction. In the case of *O*-(2,3,4,5-tetrachlo-

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