S^E = molar excess entropy, J mol^{-1} K^{-1}
T = absolute temperature, K
V^E = molar excess volume, cm^3 mol^{-1}
V_i° = molar volume of pure liquid component i, cm^3 mol^{-1}
X^E = typical molar excess property
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase

Greek Letters

γ_i = activity coefficient of component i in liquid phase
δ = difference of virial coefficients = $2B_{12} - B_{11} - B_{22}$
Φ_i = ratio of fugacity coefficients of pure component i and component i in the vapor-phase mixture, both evaluated at temperature and pressure of the mixture
σ = standard error

Subscripts

1 = cycloalkane component
2 = cycloalkanol component

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

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Specific heats of aqueous solutions of the stoichiometric trivalent rare earth perchlorates (La, Pr, Nd, Sm, Gd, Eu, Tb, Dy, Ho, Er, Tm, Yb, and Lu) were measured over the concentration range of 0.1m 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. From these equations the partial molal heat capacities of the solvent, $\bar{C}_{p1}$, and solute, $\bar{C}_{p2}$, were calculated. The $\bar{C}_{p1}$ data at given molalities exhibit a two-series effect across the rare earth series over the whole concentration range. For the lighter rare earths through Gd, ϕ_{cp} increases almost linearly with molality above 2.5m, whereas for the heavier rare earths, $\partial\phi/\partial m$ decreases with increasing concentration.

This investigation is part of an extensive research program to accurately determine thermodynamic and transport properties of aqueous solutions of the stoichiometric rare earth salts to aid in better understanding the behavior of solutions of higher valent salts. The regular decrease of the radii of the chemically similar trivalent rare earth ions, varying from 1.061 Å for La^{3+} to 0.848 Å for Lu^{3+} (*14*), provides a means of studying the effect of ionic radius upon solution properties.

Earlier work has shown that the properties of dilute aqueous rare earth salt solutions are not smooth monotonic functions of rare earth ionic radius. Rather, volume data (*8, 11–13*) and relative apparent molal heat content data (*1, 4, 7*) indicate that the rare earths, as they exist in dilute solution, are divided into two series. It has been proposed (*11*) that one series consisting of the larger light rare earths has a constant number of water molecules coordinated in the first sphere, and the other series consisting of the smaller heavy rare earths has a different and smaller number of water molecules coordinated in the first sphere. Furthermore, it was proposed that the intermediate rare earths exist in solution as an equilibrium of the two coordination types with the equilibrium shifting with decreasing ionic radius from the higher to the lower coordination type. However, the rare earth ion in dilute solution is hydrated beyond the first sphere and is the center of a large associated system.

When a water molecule is displaced because of steric hindrance from the first coordination sphere of the rare earth ion, the changes in size and symmetry of that sphere alter the environment beyond it. This results in the rearrangement of a large number of water molecules. Thus, a major portion of the observed effect on the macroscopic properties of solutions from the coordination change is probably due to the summation of a large number of small differences rather than simply the effect of a single water molecule, and an equation of the form $RE(H_2O)_x + H_2O \rightleftarrows RE(H_2O)_{x+1}$ would be an inadequate description of this equilibrium.

This study was undertaken to further investigate the two-series effect and to explore the effects of possible perchlorate ion–water and perchlorate ion–rare earth ion interactions on the heat capacities of these solutions. In

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addition, partial molal heat capacities determined in this work are of practical value in calculating the temperature dependence of heats of dilution and activities for the rare earth perchlorate solutions.

Many of the heat capacity determinations reported in the literature have been made for solutions of 1-1 electrolytes with less work being done on polyvalent electrolytes. Most 3-1 electrolytes hydrolyze considerably or are not very soluble. The rare earths, however, form several soluble salts with a low degree of hydrolysis in solution. Spedding and Miller (*10*) have determined the relative apparent molal heat capacities of dilute solutions of neodymium and cerium chloride, whereas Jekel et al. (*3*) have reported the partial molal heat capacity of gadolinium chloride at infinite dilution as a function of temperature. Spedding and Jones (*9*) have measured the apparent molal heat capacities of five rare earth chlorides from 0.1*m* to saturation. This paper presents the specific heats and the apparent and partial molal heat capacities of solutions of 13 rare earth perchlorates from 0.1*m* to saturation at 25°C. Data for the rare earth chlorides and nitrates, with comparisons to data for perchlorates, will be presented in later papers.

Experimental

Apparatus and procedure. Specific heat measurements were made using an adiabatic single can solution calorimeter. With the exception of the replacement of the on-off water bath temperature controller during the course of this work with a Leeds and Northrup proportional control system, the apparatus and experimental procedure are those described in detail elsewhere (*9*). In brief, the heat capacity of the calorimeter, plus appendages, was determined, and the value checked before each different series of rare earth perchlorate solutions were run.

To determine the heat capacity of the calorimeter, the total heat capacity of the calorimeter plus a known amount of air-saturated water was measured for numerous water samples. The heat capacity of the calorimeter was taken as the average of from 15 to 21 values for the difference between the total heat capacity and the heat capacity of the water, computed from its mass and specific heat of 0.9989 cal deg^{-1} g^{-1}. Because it is not possible to completely isolate the calorimeter from the surroundings, the heat capacity of the calorimeter was slightly dependent on the volume of liquid the calorimeter contained; therefore, samples were weighed such that their volume was equal to that of the water used in calibration. A typical value for the heat capacity of the calorimeter plus appendages was 16.95 ± 0.02 cal deg^{-1}. Since the sample size was such that the sample's heat capacity was about 100 cal deg^{-1}, an error of 0.02 cal deg^{-1} in the determination of the heat capacity of the calorimeter plus appendages would only result in a 0.02% error in the specific heat of the sample.

To check the accuracy of each calibration of the heat capacity of the calorimeter, the specific heat of one or more NaCl solutions was determined and compared with data of Randall and Rossini (*6*) (corrected to defined calories and carbon-12 based atomic weights). This also provided a check on the integrity of the method. An average deviation of −0.05% for multiple determinations of 14 different NaCl solutions during these studies implies an accuracy of that amount. Because the very small differences between this work and that of Randall and Rossini were consistently negative (the standard deviation around the −0.05 value was 0.02), which indicates a very small systematic error in either this work or that of Randall and Rossini (*6*), the relative error in the heat capacities of the rare earth perchlorate solutions should be less than 0.05%. Heat capacity measurements on three NaCl solutions by Epiken and Stakhanova (*2*) show very nearly the same deviations from Randall and Rossini as this work.

Materials. The stock solutions of rare earth perchlorates were prepared by adding an excess of the appropriate rare earth oxide to reagent-grade perchloric 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 (*11*). The rare earths used were prepared using ion-exchange methods by the Rare Earth Separation Group of the Ames Laboratory of the U.S. Atomic Energy Commission. The purity of the oxides was established by spectroscopic analysis. In all cases, the total impurities of iron, calcium, and adjacent rare earths were certainly less than 0.15%, with less than 0.05% being iron and calcium.

Concentrations of the stock solutions were checked by two or more of gravimetric oxide, gravimetric sulfate, and EDTA methods. The average deviation of the concentration determined by the various methods from the mean was about 0.1%. Solutions were prepared at 0.1 intervals in $m^{1/2}$ from 0.09*m* to saturation. Because the solutions were made from weighted portions of the stock solutions and water, the relative concentrations of a series of solutions for a particular rare earth perchlorate were at least an order of magnitude more accurate than the absolute concentration. Water used had a specific conductance of less than 1.0×10^{-6} ohm^{-1} cm^{-1}. All weights were corrected to vacuum.

Saturated solutions were prepared by concentrating portions of stock solution over $Mg(ClO_4)_2$. The saturated solution was stored in contact with crystals formed during

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)
Lanthanum perchlorate	−53.15	95.951	−47.594	13.8815	−1.1379
Praseodymium perchlorate	−64.59	130.265	−87.803	34.2039	−4.6601
Neodymium perchlorate	−53.54	92.140	−38.050	7.6346	0.2582
Samarium perchlorate	−60.14	127.734	−88.755	35.6035	−4.9032
Europium perchlorate	−51.77	112.108	−73.954	29.5032	−3.9898
Gadolinium perchlorate	−49.72	110.236	−70.323	25.5108	−3.0186
Terbium perchlorate	−55.47	138.398	−103.560	41.7978	−5.9257
Dysprosium perchlorate	−50.67	124.473	−87.443	34.8403	−4.9875
Holmium perchlorate	−55.29	146.360	−116.337	50.7796	−8.0859
Erbium perchlorate	−53.09	131.262	−93.982	38.0937	−5.5823
Thulium perchlorate	−50.73	130.494	−98.088	42.3543	−6.6213
Ytterbium perchlorate	−67.00	173.816	−143.335	63.3309	−10.2540
Lutetium perchlorate	−50.96	119.040	−76.823	29.3410	−4.1424

preparation for two weeks or more at 25.00° ± 0.01°C. Samples were decanted from the crystals. The concentration of the saturated solutions was determined by one or more of the above three methods. Determinations of concentration were always made on multiple samples.

Results

The specific heat capacities of aqueous rare earth perchlorate solutions were measured at 0.1 intervals of $m^{1/2}$ from 0.1m to saturation at 25°C. 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 molality, M_2 is the molecular weight of the salt calculated from IUPAC (1969) atomic weights, S is the measured specific heat of the solution, and S° is the specific heat of pure liquid water (0.9989 cal deg^{-1} g^{-1}) as determined by Osborne et al. (*5*). Empirical polynomial equations of the form:

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

were obtained for each salt by a least-squares method. Fourth-order equations adequately represent the apparent molal heat capacity data for each of the salts. In performing the least-squares calculation, each ϕ_{cp} value was weighted proportionately to the square of the inverse of the probable error, assuming a probable error of 0.05% in specific heat over the whole concentration range and probable errors in molality resulting from a probable error of 0.1% in the molality of the stock solution.

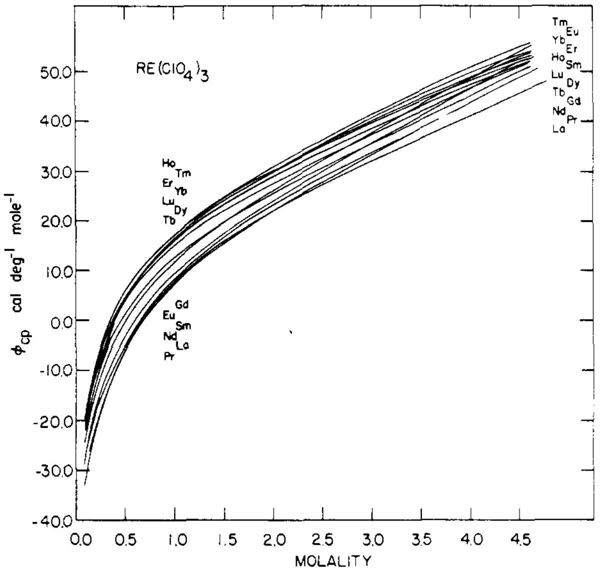

Figure 1. Apparent molal heat capacities of RE(ClO$_4$)$_3$ solutions vs. molality at 25°C

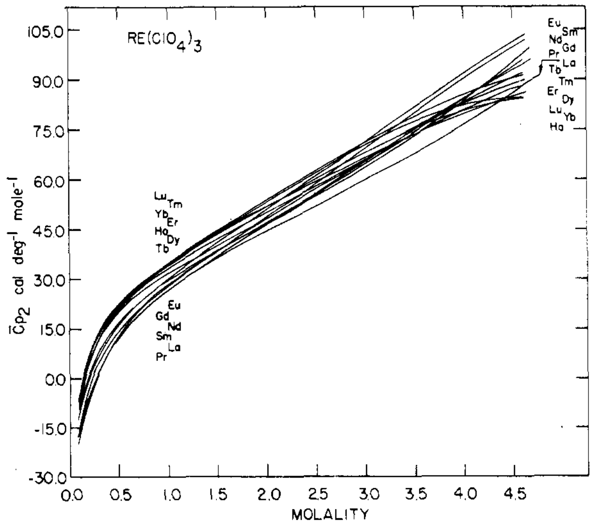

Figure 2. Partial molal heat capacities of solute for RE(ClO$_4$)$_3$ solutions vs. molality at 25°C

$\bar{C}_{p1}$ and $\bar{C}_{p2}$ were calculated from Equations 3 and 4, respectively:

$$\bar{C}_{p1} = \bar{C}_{p1}^\circ - \frac{M_1}{2000} m^{3/2} \left(\frac{\partial \phi_{cp}}{\partial m^{1/2}}\right)_{P,T,n_1} = 17.996 - (9.0077 \times 10^{-3}) \sum_{k=0}^{4} k A_k m^{(k+2)/2} \qquad (3)$$

$$\bar{C}_{p2} = \phi_{cp} + \frac{1}{2} m^{1/2} \left(\frac{\partial \phi_{cp}}{\partial m^{1/2}}\right)_{P,T,n_1} = \sum_{k=0}^{4} (1 + k/2) A_k m^{k/2} \qquad (4)$$

where M_1 is the molecular weight of water, $\bar{C}_{p1}^\circ$ is the molal heat capacity of pure water, and the A_k from Equation 2 are given in Table I.

The square root of molality, ratio of moles of water to moles of Re(ClO$_4$)$_3$, specific heat, experimental and smoothed apparent molal heat capacities calculated from Equation 1 and Equation 2, respectively, partial molal heat capacity of the solute, and the partial molal heat capacity of the solvent are listed in Table II for each solution run. Figures 1–3 illustrate the heat capacity properties of the rare earth perchlorate solutions as a function of molality. Figures 4–6 illustrate the trends in ϕ_{cp}, $\bar{C}_{p2}$, and $\bar{C}_{p1}$ across the rare earth series at even molalities as a function of ionic radius.

Table II. Specific Heats, Apparent Molal, and Partial Molal Heat Capacities of RE(ClO$_4$)$_3$ Solutions at 25°C

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
			Lanthanum perchlorate			
0.2985	622.9	0.9593	−24.9	−28.4	−17.8	17.98
0.4014	344.5	0.9303	−19.0	−21.4	−8.6	17.96
0.5000	222.0	0.8968	−16.2	−15.4	−0.9	17.93
0.5919	158.4	0.8629	−10.8	−10.3	5.5	17.90
0.7028	112.4	0.8193	−5.4	−4.7	12.2	17.85
0.8030	86.1	0.7791	−0.2	−0.1	17.6	17.79
0.9037	68.0	0.7384	3.9	4.2	22.5	17.73
1.0031	55.2	0.6995	8.3	8.1	27.0	17.65
1.1015	45.7	0.6621	11.9	11.7	31.2	17.57
1.2090	38.0	0.6234	15.7	15.4	35.8	17.46
1.3168	32.0	0.5868	18.9	18.9	40.3	17.33
1.4098	27.9	0.5576	21.8	21.9	44.3	17.19
1.5065	24.5	0.5299	25.1	25.0	48.7	17.03
1.5944	21.8	0.5061	27.4	27.8	52.9	16.84
1.7042	19.1	0.4798	31.1	31.2	58.6	16.56
1.8175	16.8	0.4560	35.0	34.9	65.1	16.20
1.8915	15.5	0.4418	37.5	37.4	69.7	15.92
2.0193	13.6	0.4204	42.0	41.9	78.3	15.32
2.1129	12.4	0.4072	45.5	45.4	85.3	14.78
2.1888[c]	11.6	0.3973	48.1	48.3	91.4	14.28

(Continued on page 192)

Table II. Continued

Praseodymium perchlorate

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
0.2987	622.0	0.9585	−31.6	−32.6	−19.7	17.97
0.3993	348.1	0.9302	−22.4	−24.5	−9.5	17.95
0.4996	222.4	0.8964	−17.0	−17.5	−1.0	17.92
0.5975	155.5	0.8600	−11.2	−11.4	5.9	17.88
0.6987	113.7	0.8199	−6.5	−5.9	12.0	17.84
0.7951	87.8	0.7806	−2.4	−1.2	17.1	17.79
0.8953	69.2	0.7406	3.1	3.2	22.0	17.72
0.9955	56.0	0.7011	7.4	7.2	26.5	17.65
1.0956	46.2	0.6630	11.4	11.0	31.0	17.56
1.1934	39.0	0.6274	14.8	14.5	35.5	17.46
1.2922	33.2	0.5937	18.1	17.9	40.2	17.33
1.3906	28.7	0.5625	21.5	21.3	45.2	17.16
1.4906	25.0	0.5333	24.7	24.8	50.7	16.96
1.5874	22.0	0.5074	27.8	28.2	56.4	16.72
1.6865	19.5	0.4838	31.4	31.7	62.6	16.42
1.7836	17.4	0.4637	35.5	35.3	69.0	16.07
1.8822	15.7	0.4449	39.1	39.1	75.8	15.66
1.9085	15.2	0.4405	40.2	40.1	77.6	15.54
1.9993	13.9	0.4262	44.0	43.8	84.1	15.09
2.0993	12.6	0.4122	48.0	47.9	91.3	14.55
2.1671[c]	11.8	0.4036	50.5	50.7	96.1	14.16

Neodymium perchlorate

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
0.3169	552.9	0.9539	−26.0	−27.9	−16.8	17.98
0.3999	347.1	0.9295	−22.5	−22.3	−9.2	17.96
0.4996	222.4	0.8960	−15.7	−16.0	−1.1	17.93
0.6005	153.9	0.8582	−10.4	−10.2	6.2	17.89
0.6964	114.5	0.8204	−5.0	−5.2	12.4	17.84
0.7994	86.9	0.7780	−1.4	−0.2	18.4	17.78
0.8977	68.9	0.7390	4.6	4.2	23.5	17.72
0.9969	55.9	0.6995	8.3	8.3	28.3	17.64
1.0996	45.9	0.6606	12.6	12.3	32.9	17.55
1.1992	38.6	0.6244	16.0	15.9	37.3	17.44
1.3005	32.8	0.5900	19.4	19.5	41.7	17.32
1.4015	28.3	0.5585	23.0	22.9	46.2	17.17
1.4995	24.7	0.5300	26.0	26.1	50.9	16.99
1.5972	21.8	0.5044	29.4	29.3	55.9	16.78
1.6991	19.2	0.4800	32.7	32.8	61.7	16.49
1.7921	17.3	0.4601	35.9	36.0	67.6	16.17
1.9024	15.3	0.4397	40.1	40.0	75.5	15.68
2.0183	13.6	0.4211	44.5	44.5	85.2	15.01
2.1235	12.3	0.4071	48.9	48.9	95.3	14.23
2.1645[c]	11.8	0.4022	50.6	50.7	99.6	13.87

Samarium perchlorate

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
0.3034	603.0	0.9569	−27.0	−28.6	−16.0	17.97
0.4002	346.5	0.9289	−19.9	−21.1	−6.6	17.95
0.4991	222.8	0.8953	−14.0	−14.4	1.4	17.92
0.5990	154.7	0.8576	−9.0	−8.5	8.2	17.89
0.6976	114.0	0.8184	−3.6	−3.3	13.9	17.84
0.7993	86.9	0.7768	0.9	1.4	19.0	17.79
0.8966	69.1	0.7374	5.5	5.5	23.6	17.73
0.9987	55.7	0.6967	9.5	9.5	28.2	17.66
1.0998	45.9	0.6580	13.4	13.2	32.8	17.57
1.1995	38.6	0.6217	16.8	16.7	37.4	17.46
1.2972	33.0	0.5885	20.2	20.0	42.3	17.32
1.3960	28.5	0.5574	23.5	23.4	47.7	17.14
1.4982	24.7	0.5278	27.0	27.0	53.7	16.92
1.5963	21.8	0.5020	30.2	30.6	59.9	16.65
1.6980	19.3	0.4786	34.3	34.4	66.9	16.31
1.7970	17.2	0.4585	38.4	38.3	74.1	15.91
1.8961	15.4	0.4407	42.4	42.3	81.6	15.45
1.9938	14.0	0.4250	46.4	46.4	89.2	14.93
2.0794	12.8	0.4136	50.2	50.1	96.0	14.42
2.1541[c]	12.0	0.4045	53.4	53.5	101.9	13.95

Europium perchlorate

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
0.2996	618.4	0.9581	−23.1	−24.1	−12.8	17.98
0.4015	344.4	0.9293	−13.3	−16.9	−3.6	17.96
0.4990	222.9	0.8959	−10.1	−10.8	3.7	17.93
0.5996	154.4	0.8573	−7.8	−5.3	10.2	17.89
0.6978	114.0	0.8192	−0.2	−0.5	15.8	17.85
0.8005	86.6	0.7770	3.7	4.1	21.0	17.80
0.9004	68.5	0.7365	8.0	8.1	25.7	17.74
0.9998	55.5	0.6973	12.3	11.9	30.3	17.66
1.0975	46.1	0.6592	14.8	15.4	34.8	17.58
1.2008	38.5	0.6228	19.6	19.0	39.7	17.46
1.3010	32.8	0.5886	22.7	22.4	44.8	17.31
1.4009	28.3	0.5572	25.9	25.9	50.2	17.14
1.5024	24.6	0.5282	29.3	29.5	56.2	16.91
1.6009	21.7	0.5027	32.8	33.0	62.4	16.64
1.7033	19.1	0.4791	36.6	36.8	69.3	16.30
1.8048	17.0	0.4588	40.8	40.8	76.6	15.90
1.9035	15.3	0.4412	44.8	44.8	84.0	15.44
2.0055	13.8	0.4256	49.1	49.1	91.9	14.89
2.0416	13.3	0.4209	50.9	50.6	94.8	14.68
2.1525[c]	12.0	0.4066	55.3	55.5	103.6	13.98

Gadolinium perchlorate

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
0.3182	548.2	0.9529	−20.1	−21.0	−9.4	17.97
0.4004	346.3	0.9290	−12.8	−15.3	−2.2	17.96
0.5029	219.5	0.8937	−8.9	−9.0	5.4	17.93
0.5998	154.3	0.8567	−4.9	−3.8	11.5	17.90
0.6992	113.5	0.8172	0.7	1.0	16.8	17.86
0.8003	86.7	0.7757	5.0	5.3	21.5	17.81
0.9004	68.5	0.7349	9.2	9.2	25.7	17.75
1.0016	55.3	0.6944	12.9	12.7	29.8	17.69
1.1025	45.7	0.6556	16.3	16.1	33.7	17.61
1.2021	38.4	0.6192	19.4	19.2	37.7	17.51
1.3017	32.8	0.5849	22.1	22.2	41.9	17.40
1.4022	28.2	0.5531	25.3	25.2	46.4	17.25
1.5017	24.6	0.5241	28.2	28.3	51.3	17.06
1.6041	21.6	0.4970	31.4	31.5	56.9	16.82
1.6992	19.2	0.4744	34.5	34.5	62.6	16.54
1.7981	17.2	0.4533	37.8	37.9	69.0	16.18
1.8959	15.4	0.4352	41.5	41.4	75.9	15.76
1.9964	13.9	0.4187	45.2	45.1	83.4	15.24
2.0505	13.2	0.4108	47.3	47.2	87.7	14.93
2.1468[c]	12.0	0.3981	51.0	51.1	95.7	14.29

Terbium perchlorate

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
0.3045	598.6	0.9565	−20.1	−21.8	−8.7	17.97
0.4048	338.8	0.9273	−12.9	−13.8	1.1	17.95
0.5018	220.5	0.8943	−6.5	−7.2	8.6	17.92
0.6054	151.5	0.8550	−1.7	−1.2	15.1	17.89
0.7017	112.7	0.8165	2.9	3.7	20.0	17.85
0.8047	85.7	0.7747	8.0	8.1	24.5	17.81
0.9057	67.7	0.7335	11.9	12.0	28.3	17.75
1.0053	54.9	0.6938	15.4	15.4	31.9	17.70
1.1082	45.2	0.6545	18.9	18.7	35.6	17.62
1.2112	37.8	0.6173	22.1	21.8	39.5	17.53
1.3118	32.3	0.5830	24.9	24.7	43.7	17.41
1.4127	27.8	0.5511	27.6	27.6	48.3	17.25
1.5155	24.2	0.5213	30.4	30.7	53.4	17.05
1.6167	21.2	0.4946	33.3	33.7	58.9	16.81
1.7179	18.8	0.4715	36.9	37.0	64.9	16.51
1.8207	16.7	0.4507	40.8	40.4	71.2	16.15
1.9235	15.0	0.4316	44.1	43.9	77.8	15.74
2.0268	13.5	0.4148	47.5	47.6	84.5	15.27
2.0903	12.7	0.4058	49.8	50.0	88.5	14.96
2.1464[c]	12.0	0.3988	52.1	52.0	91.9	14.69

Table II. Continued

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
		Dysprosium perchlorate				
0.3044	598.9	0.9566	−16.1	−19.9	−7.7	17.98
0.4017	344.0	0.9281	−11.4	−12.7	1.4	17.95
0.4996	222.4	0.8945	−5.8	−6.3	8.9	17.93
0.5987	154.9	0.8569	−1.2	−0.7	15.2	17.89
0.6999	113.3	0.8163	3.5	4.4	20.6	17.85
0.7999	86.8	0.7756	8.4	8.7	25.2	17.81
0.8988	68.7	0.7350	12.1	12.6	29.3	17.75
0.9982	55.7	0.6956	16.1	16.1	33.2	17.69
1.0991	46.0	0.6574	20.2	19.5	37.1	17.61
1.1997	38.6	0.6205	23.1	22.6	41.0	17.52
1.2985	32.9	0.5866	25.8	25.6	45.1	17.41
1.3992	28.4	0.5544	28.4	28.6	49.4	17.26
1.4986	24.7	0.5254	31.3	31.6	54.1	17.09
1.5991	21.7	0.4986	34.1	34.6	59.0	16.87
1.6963	19.3	0.4759	37.5	37.6	64.1	16.62
1.7984	17.2	0.4544	41.1	40.8	69.6	16.32
1.8975	15.4	0.4355	44.3	44.0	75.0	15.99
1.9982	13.9	0.4182	47.3	47.4	80.5	15.61
2.0867	12.7	0.4050	50.2	50.3	85.1	15.26
2.1459[c]	12.1	0.3970	52.3	52.3	88.1	15.03
		Holmium perchlorate				
0.2991	620.3	0.9576	−17.9	−20.6	−7.2	17.97
0.4060	336.8	0.9266	−9.3	−11.9	3.3	17.95
0.5071	215.8	0.8915	−4.8	−4.9	11.2	17.92
0.6086	149.9	0.8526	0.1	1.0	17.4	17.89
0.7109	109.8	0.8115	5.3	6.1	22.6	17.85
0.8134	83.9	0.7696	10.0	10.6	27.0	17.80
0.9144	66.4	0.7286	14.3	14.4	31.0	17.75
1.0224	53.1	0.6860	18.5	18.2	35.1	17.68
1.1179	44.4	0.6499	21.8	21.2	38.8	17.60
1.2220	37.2	0.6123	24.8	24.5	43.1	17.49
1.3260	31.6	0.5772	27.5	27.6	47.7	17.36
1.4311	27.1	0.5449	30.7	30.8	52.7	17.19
1.5353	23.6	0.5154	33.7	34.0	58.0	16.98
1.6263	21.0	0.4923	36.5	36.9	62.7	16.77
1.7391	18.4	0.4674	40.8	40.5	68.6	16.46
1.8524	16.2	0.4446	44.4	44.2	74.3	16.13
1.9585	14.5	0.4255	47.6	47.6	79.0	15.83
2.0675	13.0	0.4083	51.0	51.0	82.7	15.56
2.1504[c]	12.0	0.3966	53.5	53.5	84.5	15.41
		Erbium perchlorate				
0.3104	576.3	0.9543	−19.1	−20.3	−7.4	17.97
0.3991	348.5	0.9284	−10.6	−13.4	1.2	17.95
0.4986	223.3	0.8938	−6.5	−6.6	9.1	17.92
0.5983	155.1	0.8558	−1.2	−0.8	15.7	17.89
0.6973	114.2	0.8159	3.5	4.3	21.1	17.85
0.7981	87.2	0.7746	8.5	8.9	25.9	17.80
0.8994	68.6	0.7331	12.8	13.0	30.3	17.74
0.9986	55.7	0.6936	16.8	16.7	34.3	17.68
1.0957	46.2	0.6562	20.1	20.0	38.1	17.60
1.1980	38.7	0.6193	23.8	23.3	42.3	17.50
1.2966	33.0	0.5853	26.5	26.4	46.5	17.39
1.3952	28.5	0.5541	29.5	29.4	50.9	17.24
1.4980	24.7	0.5239	32.3	32.6	55.9	17.05
1.6011	21.7	0.4965	35.2	35.8	61.1	16.83
1.6914	19.4	0.4758	38.7	38.7	66.0	16.59
1.7917	17.3	0.4547	42.2	42.0	71.5	16.29
1.8894	15.5	0.4363	45.5	45.2	76.8	15.96
1.9871	14.1	0.4193	48.4	48.5	82.1	15.61
2.0887	12.7	0.4039	51.7	51.9	87.2	15.22
2.1491[c]	12.0	0.3963	54.1	54.0	90.0	15.00

$m^{1/2}$	Mole ratio[a]	S	ϕ_{cp}, expt	ϕ_{cp}, calc[b]	$\bar{C}_{p2}$	$\bar{C}_{p1}$
		Thulium perchlorate				
0.2997	618.1	0.9571	−18.1	−19.3	−7.0	17.98
0.3986	349.3	0.9286	−8.5	−11.8	2.3	17.96
0.4975	224.3	0.8942	−5.4	−5.3	9.9	17.93
0.5956	156.5	0.8570	0.5	0.3	16.1	17.89
0.6942	115.2	0.8169	4.1	5.2	21.4	17.85
0.7936	88.1	0.7760	8.6	9.6	26.1	17.81
0.8951	69.3	0.7346	13.3	13.6	30.5	17.75
0.9933	56.3	0.6956	17.7	17.2	34.6	17.69
1.0914	46.6	0.6579	21.1	20.5	38.7	17.61
1.1899	39.2	0.6217	24.1	23.7	43.0	17.50
1.2886	33.4	0.5877	27.0	26.9	47.5	17.38
1.3851	28.9	0.5570	30.0	30.0	52.3	17.23
1.4844	25.2	0.5278	32.8	33.2	57.4	17.03
1.5822	22.2	0.5018	35.9	36.4	62.8	16.81
1.6793	19.7	0.4791	39.6	39.7	68.2	16.55
1.7771	17.6	0.4590	43.5	43.1	73.7	16.25
1.8744	15.8	0.4401	46.6	46.4	79.0	15.93
1.9702	14.3	0.4235	49.7	49.8	83.9	15.61
2.0677	13.0	0.4089	53.0	53.1	88.2	15.29
2.1307	12.2	0.3999	55.0	55.2	90.6	15.11
2.1488[c]	12.0	0.3984	56.1	55.8	91.1	15.06
		Ytterbium perchlorate				
0.3152	558.7	0.9524	−18.9	−24.6	−8.6	17.97
0.3985	349.6	0.9272	−14.5	−16.7	0.6	17.95
0.4980	223.8	0.8918	−11.2	−8.8	9.4	17.91
0.5976	155.4	0.8545	−1.7	−2.1	16.3	17.88
0.7027	112.4	0.8115	3.0	3.8	22.1	17.83
0.7998	86.8	0.7715	8.2	8.5	26.6	17.79
0.9007	68.4	0.7300	12.6	12.8	30.7	17.73
1.0006	55.4	0.6900	16.8	16.6	34.6	17.67
1.1010	45.8	0.6515	20.4	20.1	38.7	17.59
1.1998	38.6	0.6153	23.5	23.3	42.9	17.49
1.2979	33.0	0.5820	26.8	26.5	47.4	17.36
1.4008	28.3	0.5494	29.9	29.8	52.5	17.20
1.4992	24.7	0.5208	32.7	33.0	57.7	17.00
1.5977	21.7	0.4947	35.7	36.3	63.1	16.76
1.6998	19.2	0.4716	39.8	39.7	68.7	16.49
1.7997	17.1	0.4510	43.4	43.2	73.9	16.20
1.8997	15.4	0.4323	46.7	46.6	78.6	15.92
1.9973	13.9	0.4154	49.6	49.8	82.1	15.67
2.0387	13.4	0.4095	51.2	51.1	83.2	15.59
2.1458[c]	12.1	0.3939	54.3	54.3	84.6	15.48
		Lutetium perchlorate				
0.3143	561.8	0.9527	−16.7	−20.3	−7.9	17.97
0.3931	359.1	0.9289	−13.2	−14.3	−0.3	17.96
0.4996	222.4	0.8917	−7.4	−7.3	8.3	17.93
0.5988	154.8	0.8534	−1.9	−1.5	15.0	17.89
0.6998	113.3	0.8121	3.0	3.8	20.9	17.84
0.8005	86.6	0.7705	8.3	8.5	26.0	17.79
0.8982	68.8	0.7301	12.4	12.6	30.5	17.73
0.9957	56.0	0.6910	16.5	16.3	34.7	17.67
1.1006	45.8	0.6505	20.3	20.0	39.0	17.58
1.2011	38.5	0.6139	23.7	23.4	43.1	17.48
1.3023	32.7	0.5793	26.8	26.7	47.3	17.37
1.4010	28.3	0.5480	29.7	29.8	51.5	17.23
1.4968	24.8	0.5200	32.4	32.7	55.7	17.07
1.5956	21.8	0.4942	35.7	35.7	60.2	16.87
1.6989	19.2	0.4695	38.8	38.9	65.1	16.63
1.7908	17.3	0.4501	41.9	41.8	69.5	16.39
1.8983	15.4	0.4293	45.1	45.1	74.7	16.07
2.0098	13.7	0.4104	48.6	48.6	80.0	15.71
2.0932	12.7	0.3981	51.3	51.2	83.8	15.42
2.1528[c]	12.0	0.3896	52.9	53.0	86.3	15.22

[a] Moles of water per mole of $RE(ClO_4)_3$. [b] Computed from Equation 2 by use of the parameters given in Table I. [c] Saturated solutions.

Discussion

As shown in Figures 1 and 2, values for ϕ_{cp} and $\bar{C}_{p2}$ for rare earth perchlorate solutions are negative at low concentrations but become positive with increasing concentration. Pure liquid water, with its nine degrees of freedom, three of which (vibrational) are not excited at 25°C, has an abnormally high heat capacity of 18 cal deg^{-1} mol^{-1}. Part of the extra heat capacity is considered due to the breaking or distortion of hydrogen bonds in the short-range structure of water with increasing temperature. The addition to water of highly charged rare earth ions, with strong electric fields acting on the dipoles of water, weakens the average hydrogen bonding in the vicinity of the ion.

In dilute solutions the negative contributions to the heat capacity from the weakening of hydrogen bonding is greater than the positive contribution of the solute in its

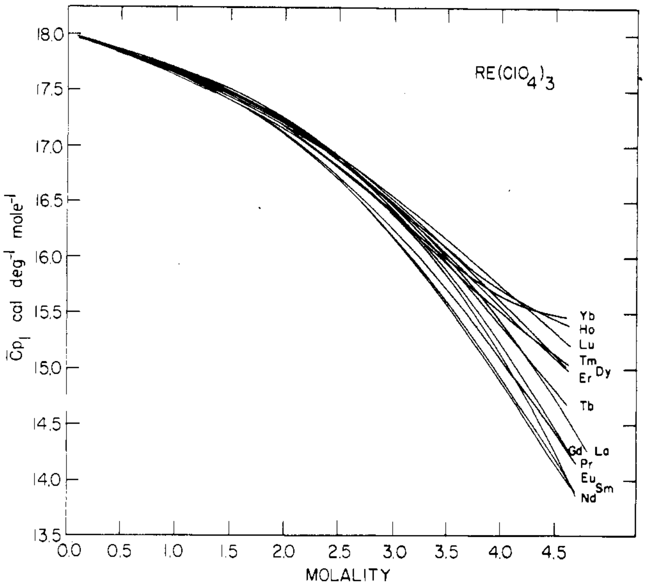

Figure 3. Partial molal heat capacity of water for $RE(ClO_4)_3$ solutions vs. molality at 25°C

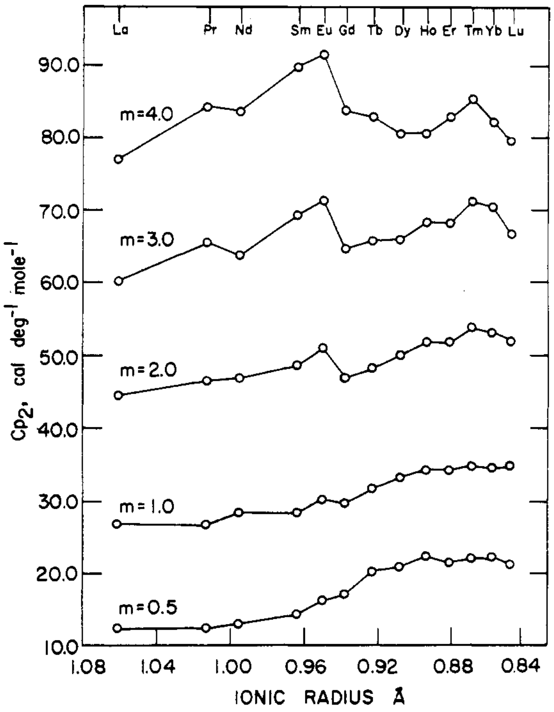

Figure 5. Partial molal heat capacities of solute for $RE(ClO_4)_3$ solutions at given molalities vs. RE ionic radius at 25°C

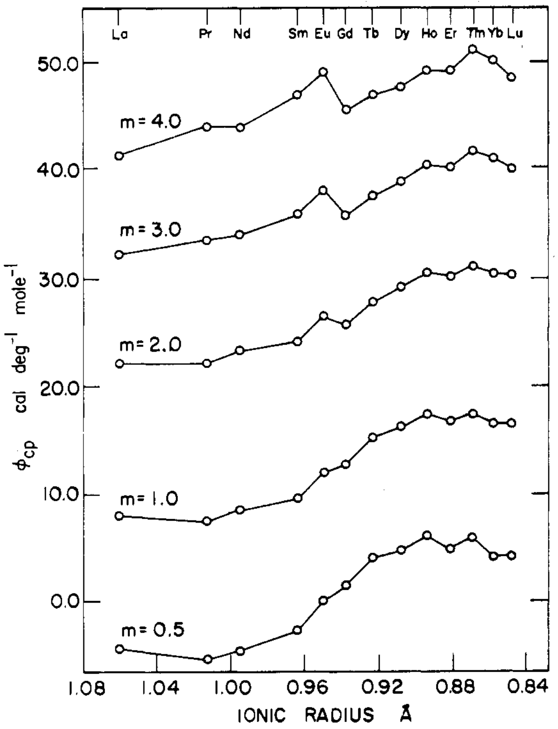

Figure 4. Apparent molal heat capacities of $RE(ClO_4)_3$ solutions at given molalities vs. RE ionic radius at 25°C

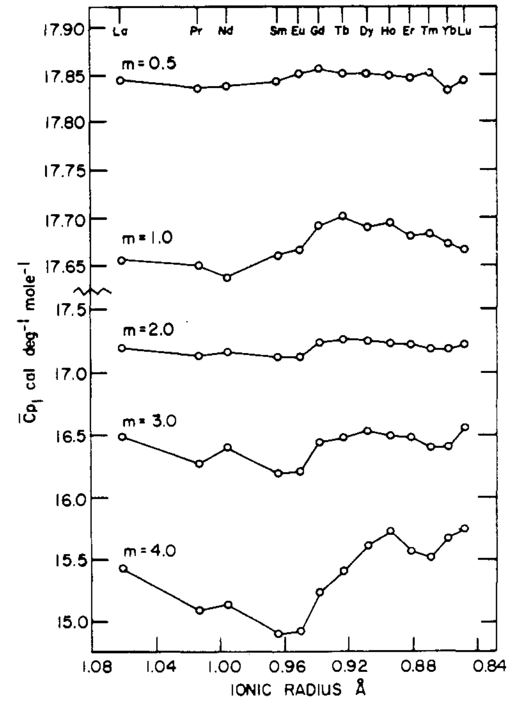

Figure 6. Partial molal heat capacity of water for $RE(ClO_4)_3$ solutions at given molalities vs. RE ionic radius at 25°C

hydrated form, resulting in negative $\bar{C}_{p2}$ values. Because there are a finite number of hydrogen bonds present in water, the extent to which hydrogen bonding is affected, and thus the negative contributions, decreases with increasing concentrations. When the positive contribution to the heat capacity from the hydrated ionic species exceeds the negative contribution, $\bar{C}_{p2}$ values become positive.

The radii of the trivalent rare earth ions are known to decrease monotonically from La to Lu; therefore, the charge density at the surface of the ions increases across the rare earth series. This higher charge density would exert a greater influence on the hydrogen bonding of water, and one might expect that $\bar{C}_{p1}$ would decrease across the rare earth series with decreasing ionic radii. As evident from Figure 6, $\bar{C}_{p1}$ values for dilute rare earth perchlorate solutions do not follow a monotonic trend across the rare earth series but rather illustrate the two-series effect owing to the change in inner sphere coordination plus resulting changes in outer spheres. It is interesting that the two-series effect is evident over the whole concentration range, although it does appear in Figure 4 that at high concentrations the break points in the curve shift to higher atomic numbers. It should be recalled however, that unlike the dilute solution where the outer spheres consist mainly of water molecules, in the concentrated solutions the outer spheres are made up mostly of outer sphere complexes with the perchlorate ion.

As illustrated in Figure 1, above 2.5 *m*, ϕ_{cp} for the lighter rare earths through Gd increases almost linearly with molality, whereas for the heavier rare earths, deviation from linear behavior is greater. At high concentrations this results in an increased separation in the $\bar{C}_{p1}$ curves of Figure 3 and in a distinct difference in the shape of the $\bar{C}_{p2}$ vs. *m* curves of Figure 2 for the heavy rare earths relative to the light.

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Adsorption of Hydrocarbons on Carbon Molecular Sieve—Application of Volume Filling Theory

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Adsorption data of methane, ethylene, ethane, propylene, and propane on a microporous carbon molecular sieve were examined by Dubinin's volume filling theory. The Dubinin-Astakhov three-parameter characteristic equation $W = W^\circ \exp\{-(A/E)^n\}$ (where W is the pore volume, W° is the total pore volume, A is the adsorption potential, E is the characteristic energy, and n is the integer constant), was applied to data reduction. The adsorption data were well characterized by the equation for $n = 3$. The total pore volume and the characteristic energy were obtained. The generalized characteristic curve for hydrocarbons was obtained by using an affinity coefficient. Isosteric heat, differential heat of adsorption at constant coverage, and distribution of adsorption potential were calculated. The effect of microporosity of the adsorbent is discussed and compared with reported data for charcoal.

This work is the second part of a continuing study of adsorption of gases and vapors on microporous adsorbent. In the previous paper (*7*), the experimental adsorption data were reported for hydrocarbons on commercial-grade carbon molecular sieve designated as Molecular Sieving Carbon-5A (MSC-5A) by Takeda Chemical Ind. Co. It has micropores of approximately 5 Å in diameter, and its physical properties were described in the previous paper (*7*). The reported experimental adsorption isotherms were for pure adsorbates methane and benzene at 5.4° and 30.0°C; ethylene, propylene, and propane at 5.4°, 30.0°, and 50.0°C; *n*-butane at 5.4°, 30.0°, and 51°C; and *n*-pentane and cyclohexane at 30.0°C, all at pressures up to 650 mm Hg.

Volume Filling Theory and Experimental Data Analysis

The adsorption force-field ranges over the inside of the entire volume of micropores for adsorbents such as MSC-5A. Therefore, adsorption of vapor in micropores leads to the volume filling rather than the layer-by-layer filling of micropore surface. The conception of volume filling theory developed by Dubinin (*3*) was in principle based on Polanyi's potential theory (*8*). The force of attraction at any given point in the adsorbed film is conveniently measured by the adsorption potential *A*, defined as the work done by the adsorption force in bringing a

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