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Thermodynamic Properties of Rare Earth Complexes

XVII. The Partial Molar Heat Capacities of Rare Earth Perchlorates and Oxydiacetate Complexes

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The partial molar heat capacities of some rare earth perchlorates and rare earth oxydiacetate complexes have been determined by direct calorimetry at 25°C using aqueous 1.000 mol/kg $NaClO_4$ as the solvent. From the near constancy of the $\bar{C}_P°$-values obtained for the various rare earth perchlorates it may be concluded that no ionic radius dependent hydration equilibria of the type

$$M(H_2O)_x^{3+} \rightleftharpoons M(H_2O)_y^{3+}$$

are present for the hydrated rare earth ions. This finding is in agreement with NMR data obtained by other authors. The previous interpretations of maxima in $\Delta C_P°$ *vs.* Z data for the formation of rare earth EDTA and oxydiacetate complexes as beeing due to hydration equilibria for the species $M(EDTA)^-$ and $M(oxydiacetate)_2^-$, have been confirmed.

The consistency of the partial molar heat capacity data has been checked by a comparison of the experimental $\Delta C_P°$-values for the formation of the complexes $Na_3M(oxydiacetate)_3$, $M = Pr$ and Gd, with the same quantity calculated from the partial molar heat capacities of reactants and products. The agreement was satisfactory.

The observed variations of thermodynamic quantities such as $\Delta H_j°$ and $\Delta S_j°$ for various rare earth complexation reactions have frequently been interpreted in terms of changes of hydration of the species participating in the reactions.[1,2] The fact that the variations throughout the rare earth series are very similar for a number of different ligands has been taken as evidence that the variation is due to some property of the central ion, *viz.* its state of hydration. Spedding and his coworkers[3] have studied various properties such as molar volumes, activity coefficients, transference numbers, partial molar heat capacities, *etc.* for a number of simple rare earth salts, and claim that their results indicate a change of hydration of the hydrated rare earth ions within the lanthanoid series. On the other hand, the observation of Reuben and Fiat[4] of a linear proportionality between the oxygen-17 chemical shifts and the molal concentration of lanthanoid perchlorate solutions, indicates that only a single hydrated species exists over a wide range of concentrations, *i.e.* no hydration equilibrium of the type

$$M(H_2O)_x^{3+} \rightleftharpoons M(H_2O)_y^{3+} \tag{1}$$

is present.

Most molecular interpretations (at least by solution chemists) of rare earth complexation reactions are based on thermodynamic data. There are two main obstacles to the interpretation of such thermodynamic data. Firstly, it is difficult to decide whether an observed variation in a "Δ" quantity is due to one or several of the species participating in the reaction studied. Secondly, at investigations of complex formation equilibria in solution one cannot, in general, obtain information about the complexes formed between the reaction species and the ions and molecules of the medium and the solvent. One possible way to circumvent these difficulties is to obtain further information on the systems by non-thermodynamic methods, *e.g.* by spectroscopic [4,5] or kinetic studies. The spectroscopic method has been used successfully by Geier *et al.*[5] in a study of hydration equilibria among rare earth EDTA complexes. Spectroscopic [6] and kinetic [7] methods have also been used to determine the relative amounts of inner and outer sphere complexes among the lanthanoids.

The molecular interpretation of the properties of a system obtained, *e.g.*, from spectroscopic studies must not contradict the thermodynamic properties of the macroscopic system, so thermodynamics can be used as a guide in the development of molecular theories. In the previous parts of this series [8–10] we have discussed the use of ΔC_p data to obtain information on the presence of equilibria of the type discussed above. Our experimental results from the rare earth oxydiacetate and EDTA systems gave strong evidence for the occurrence of hydration equilibria in these complexes. These measurements have now been extended by a study of partial molar heat capacities of a number of rare earth perchlorates and some rare earth oxydiacetate complexes. We have two aims with this study. The first is to establish, by the methods outlined in Ref. 11, whether hydration equilibria of the type (1) are present for the hydrated rare earth ions or not. The second is to decide whether the previously observed variations in ΔC_p° throughout the rare earth series are due to a variation in the partial molar heat capacity of the central ion and/or the various complexes.

Some experimental determinations of partial molar heat capacities for a number of simple rare earth salts in water solution have previously been reported by Spedding *et al.*[3,12] In order to obtain heat capacities which were compatible with our other thermodynamic data, we have chosen to use an aqueous 1.000 mol/kg $NaClO_4$ solution as the solvent. An advantage with this solvent as compared to pure water is the decreased concentration dependence of the apparent and partial molal heat capacities of the solute.

The most accurate heat capacity data for solutions are probably obtained by using a twin calorimeter as described, *e.g.*, by Gucker *et al.*[13] However, our previous experience with isothermal jacket calorimeters indicated that determinations of partial molar heat capacities in 0.1 mol/kg solutions were possible with an accuracy of 10 – 15 J/K mol. This was considered to be sufficient in order to establish whether a maximum in the partial molar heat capacity, $\overline{C}_p$, occurred within the lanthanoid series or not; *cf.* Ref. 8, p. 1218. The height of the maximum is expected to be approx. 80 J/K mol.

EXPERIMENTAL

Description of the calorimeter. The calorimeter used is of the isothermal jacket type and is a development of the previously described reaction calorimeter.[14] The main changes are the removal of the addition unit (capillaries and heat exchange system) and the use of a larger calibration resistance. The inner vessel has a total volume of 115 cm^3. It is made of 18 carat gold in order to ensure a rapid temperature equilibration. The calorimeter is heated electrically by using a manganin resistance enclosed in a gold spiral. The temperature is measured by a thermistor enclosed in a gold thimble. The two bladed stirrer is operated at 750 rpm. The calorimeter is thermostated at 25.00°C by using a thermostat bath similar to the LKB 7603 A. The stability is within 2.5×10^{-4} K/h. The calorimeter system and part of the electronic equipment was placed in an air thermostat at 25.00 ± 0.05°C.

The calorimeter heater has a resistance of 250 Ω. Electrical energy is supplied from a constant current source (Guildline 9770 B). A four-lead system is used by which a simultaneous measurement of voltage and current can be made. The voltage was measured with an accuracy better than 30 ppm by a digital voltmeter (S.E. Laboratories, SM 213 Mk 2).

The current was determined by measuring the voltage drop over a thermostated standard resistance (Tinsley 3504 B). This voltage was measured with an accuracy of 25 ppm by a differential voltmeter (Fluke, model 885 AB) which had been calibrated against a voltage standard.

The current through the heater is switched on and off *via* a timer (Elesta Digital Counter) and a relay. The timer has a quartz crystal as frequency standard, the accuracy of which is better than 10 ppm. All electrical calibrations are made over 240 s and the total error in this quantity, including the errors in closing and releasing the relay (at most 650 μs), is less than 12 ppm. From the above quantities, we estimate the maximum error in the added energy quantity to be less than 50 ppm.

The bridge circuit. The bridge described in Ref. 14 has been modified as described by Ginstrup.[15] After several tests we found that an increased precision could be obtained by feeding the bridge with a square-wave voltage instead of the original DC voltage. This method has been used previously by Faulkner *et al.*[16] A frequency of 120 Hz was chosen for the square wave source and the unbalance voltage was detected by a phase sensitive detector (Brookdeal Electronics Ltd, Type 411). In this way we were able to decrease noise and drift by a factor of ten as compared with the DC bridge. The unbalance voltage from the phase sensitive detector is recorded on a Mosley 680 recorder to give a resistance *vs.* time curve. The bridge, except the thermistor and the 100 – 0.01 Ω decades, is made as a micro circuit placed on a card and immersed in a thermostated oil bath. By thermostating the large resistance (6 000 Ω in our case) in the decade one can get a substantial reduction of the resistance errors due to fluctuations in the ambient temperature.

Calculation of the partial molar heat capacities. The apparent molar heat capacity ϕ_{C_P} is obtained from the experimental heat capacity of the solution by using the expression

$$\phi_{C_P} = [c_P(1\,000 + mM) - 1\,000 c_P{}^{\circ}]/m \qquad (2)$$

where c_P and $c_P{}^{\circ}$ are the specific heat capacities of solution and solvent, respectively, m is the molality of the solute with the formula weight M.

Two methods can be used to determine the specific heat capacity. In one the thermistor is calibrated against a platinum resistance thermometer so that its resistance directly can be converted to temperature. In the other, which is the method we have used, solutions of known specific heat capacities are used to calibrate the system in the following way:

A quantity of energy Q which corresponds to a certain change of state (27.000 Ω as measured by the change in resistance, ΔR, of the thermistor) is added to the system. The heat capacity of the system is

$$Q/\Delta T = C_{PC} + gc_P \tag{3}$$

where ΔT is the change in temperature of the system, C_{PC} and c_P are the heat capacity of the calorimeter and the specific heat capacity of the solution, respectively, while g is the mass of the solution. In systems where the change of state, as measured by ΔR, always is the same, $\Delta T = k\Delta R$. Eqn. (3) can then be written as

$$Q/\Delta R = kC_{PC} + kgc_P \tag{4}$$

From experimental values of Q, ΔR, and g in solutions with known values of c_P, the constants k and kC_{PC} can be determined. These constants can then be used to calculate unknown specific heat capacities. We have used Randall and Rossinis' [17] specific heat capacity data on NaCl and KCl solutions to calculate the constants. A comparison of our specific heat capacity data using experimental calorimeter constants with those obtained by Randall and Rossini is given in Table 1. The agreement is in general within 0.008 J/K g which is satisfactory. An equally satisfactory agreement is obtained for the specific heat capacity of water where our experimental value was 4.1769 ± 0.0002 J/K g as compared to 4.1769 J/K g given by Osborne, Stimson and Ginnings.[18]

Experimental procedure. All solutions were weighed into the calorimeter which then was allowed to stand over night in the thermostat bath. Five to ten electrical calibrations were made with a rate of 1 calibration/1.5 h. In each calibration the calorimeter was brought to a predetermined temperature and an initial period of about 10 min duration was then recorded. At a given temperature energy was added to the system from the constant current source for a period of 240.00 s. The current was adjusted to give a change in the thermistor resistance of 27.000 Ω. This figure corresponds to a temperature change of approx. 0.1 K. The after period was recorded over a period of 30 min. From this record of resistance *vs.* time the value of ΔR was obtained.

Analysis and preparation of solutions. Stock solutions of the various rare earth perchlorates were prepared by dissolving the corresponding oxides (American Potash and Chemical Co, purity better than 99.9 %) in warm concentrated perchloric acid. The excess of acid was removed by evaporation with a heat lamp. The rare earth and hydrogen ion concentrations were determined as described before.[19] The sodium perchlorate molality in the stock solutions was 1.000 mol/kg and the rare earth and hydrogen ion molalities had values in the ranges 0.8 – 1.0 mol/kg and $5 \times 10^{-3} - 10 \times 10^{-3}$ mol/kg, respectively. The solutions in the calorimeter were prepared from these stock solutions and a 1.000 mol/kg sodium perchlorate stock solution by weighing. A stock solution of oxydiacetate was prepared by partial neutralization of oxydiacetic acid with sodium hydroxide.

Table 1. A comparison of specific heat capacities at 25°C of aqueous sodium chloride and potassium chloride solutions obtained in this study with the corresponding values obtained by Randall and Rossini (R & R).

Molality of NaCl	c_P/J K^{-1} g^{-1} R & R	c_P/J K^{-1} g^{-1} this work	Molality of KCl	c_P/J K^{-1} g^{-1} R & R	c_P/J K^{-1} g^{-1} this work
0.0500	4 1585	4 1601	0.1604	4 1141	4.1133
0.1010	4.1430	4.1442	0.1609	4.1137	4.1141
0.1498	4.1284	4.1288	0.1628	4.1129	4.1125
0.4995	4.0296	4.0313	0.5029	3.9853	3.9878
0.7495	3.9656	3.9664	0.5032	3.9848	3.9849
1.0028	3.9066	3.9083	1.0047	3.8187	3.8177
1.5095	3.8003	3.7991	1.0050	3.8187	3.8166
			1.5065	3.6694	3.6702
			1.5068	3.6694	3.6710

Oxydiacetic acid was purified by recrystallization from ethyl acetate and had an equivalent weight of 67.10, calcd. 67.03. The solution had the following composition $C_{NaClO_4} = 1.0000$ mol/kg, $C_{Na_2A} = 2.3093$ mol/kg and $C_{NaHA} = 0.0480$ mol/kg. The solutions containing the complexes Na_3MA_3 were prepared from the metal and ligand stock solutions with addition of water to make the sodium perchlorate molality equal to 1.000 mol/kg. These solutions had an excess of ligand sufficiently large to make the concentrations of the first and second complexes negligible.

RESULTS AND DISCUSSION

The accuracy of the specific heat capacity values is in general within 0.02 % as indicated by the data given in Table 1. The errors in the specific heat capacity values are in our case not influenced significantly by analytical errors. They are instead dominated by the errors in Q and ΔR. However, the error in Q is not large enough to explain the observed spread in the c_p values. The two main sources of error in ΔR are due to temperature dependent variations in the decade resistance, an error we have tried to decrease by keeping the large resistances well thermostated, and errors due to a slow (and not sufficiently reproducible) attainment of thermal equilibrium within the calorimeter. From the graphs of the after period we have reason to believe that the second factor is the most important source of error.

The rare earth perchlorate solutions. The specific heat capacities of the various solutions with their estimated errors, equal to 3σ, are given in Table 2.

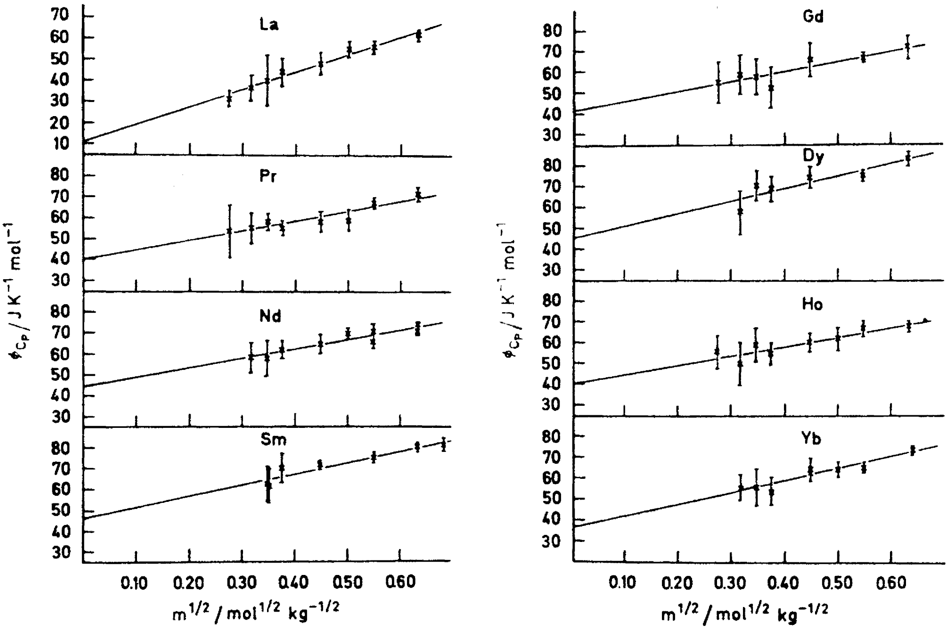

Fig. 1. ϕc_p *versus* the square root of the molality for the various rare earth perchlorates.

Table 2. c_P and ϕ_{CP} for $M(ClO_4)_3$, Na_2A, $NaClO_4$ and Na_3MA_3. The difference in the specific heat capacity of the solvent (1.000 m $NaClO_4$) between the various systems is due to the use of different stock solutions.

La, $c_{P\,solv.}$ = 3.7887±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
[illegible]	3.2416±0.0010	62.3±0.7
[illegible]	[illegible]±0.0008	56.1±1.1
[illegible]	[illegible]	[illegible]
0.1994	[illegible]	48.4±5.4
[illegible]	[illegible]	44.2±6.9
[illegible]	3.5041±0.0014	40.4±10.7
[illegible]	3.6307±0.0006	36.9±6.3
[illegible]	3.6704±0.00[illegible]	31.7±1.1

Pr, $c_{p\,.solv.}$ = 3.7887±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.4002	3.2446±0.0010	71.5±3.[illegible]
0.3001	3.3553±0.0007	67.4±2.7
0.2499	3.4073±0.0010	53.2±5.2
0.1999	3.4976±0.0009	59.4±4.9
0.1502	3.5762±0.0009	55.3±3.8
0.1202	3.6054±0.0005	58.4±4.4
0.0909	3.6347±0.0007	55.2±7.[illegible]
0.07[illegible]	3.6718±0.0009	[illegible].9±10.[illegible]

Nd, $c_{p\,.solv.}$ = 3.7887±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.4017	3.2413±0.000[illegible]	74.[illegible]
0.4003	3.2424±0.000[illegible]	73.8±[illegible]
0.3000	3.3623±0.001[illegible]	73.7±[illegible]
0.2997	3.3630±0.000[illegible]	66.3±[illegible].4
0.2507	3.4258±0.000[illegible]	69.9±[illegible]
0.2001	3.4917±0.000[illegible]	64.9±[illegible]
0.1400	3.5755±0.000[illegible]	62.1±1.[illegible]
0.1202	3.6039±0.001	57.2±[illegible]
0.1000	3.6337±0.000[illegible]	58.[illegible]

Sm, $c_{p\,.solv.}$ = 3.7887±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
[illegible]	[illegible]27±0.[illegible]	[illegible]
[illegible]	[illegible]±0.[illegible]	[illegible]
[illegible]	[illegible]8±0.[illegible]	[illegible].8±[illegible]
[illegible]	[illegible].4895±0.[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible].5989±0.0009	[illegible].7±8.[illegible]
[illegible]	[illegible]±0.[illegible]	[illegible].6±8.[illegible]

Gd, $c_{p\,.solv.}$ = 3.7887±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.3934	3.2307±0.0019	71.3±5.7
0.2995	3.3512±0.0006	66.6±2.2
0.2002	3.4840±0.0015	65.4±8.3
0.1400	3.5683±0.0015	52.3±10.[illegible]
0.1200	3.5988±0.0010	57.3±8.7
0.0999	3.6293±0.0012	53.7±9.4
0.0777	3.6670±0.00[illegible]	[illegible]

Dy, $c_{p\,.solv.}$ = 3.7887±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.4003	3.2266±0.0012	82.9±3.6
0.3006	3.3475±0.0007	73.0±2.8
0.2007	3.4815±0.0011	74.0±5.4
0.1497	3.5676±0.0008	68.7±6.2
0.1200	3.5978±0.0008	70.2±7.2
0.1000	3.6269±0.0010	[illegible]

Ho, $c_{p\,.solv.}$ = 3.7878±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.4004	3.2181±0.0009	67.5±[illegible]
0.3003	3.2428±0.0010	66.9±[illegible]
0.2505	3.4079±0.0012	62.[illegible]
0.1998	3.4779±0.001[illegible]	60.[illegible]
0.1599	3.5645±0.000[illegible]	54.[illegible]
0.1199	3.5950±0.0009	58.[illegible]
0.1001	3.6247±0.001[illegible]	49.2±[illegible]
0.0759	3.6646±0.0006	55.2±8.1

Yb, $c_{p\,.solv.}$ = 3.7887±0.0008 J·K.$^{-1}$·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.4099	3.2017±0.0008	[illegible].7±[illegible]
0.3005	3.3362±0.0006	65.6±2.[illegible]
0.2502	3.4035±0.0009	64.5±5.6
[illegible]	3.4736±0.001	64.5±5.[illegible]
[illegible]	3.4[illegible]1±0.0006	62.8±[illegible]
0.1400	3.5610±0.0009	54.2±[illegible]
0.1201	3.5921±0.001[illegible]	56.2±8.[illegible]
0.1000	3.6232±0.0006	56.1±6.[illegible]

Na_2A, $c_{p\,.solv.}$ = 3.7900±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
[illegible].1912	3.3987±0.0006	265.2±1.0
[illegible]	3.5060±0.0004	249.[illegible]±1.0
[illegible]	3.5867±0.0008	232.1±1.9
[illegible]	3.6795±0.0011	213.7±4.0
[illegible]	3.7[illegible]54±[illegible]	194.8±9.[illegible]

$NaClO_4$, $c_{p\,.solv.}$ = 3.7877±0.0008 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
1.[illegible]	3.3540±0.0006	136.1±0.6
0.9937	3.4964±0.0009	135.6±0.9
0.6999	3.5734±0.0012	131.4±1.9
0.4699	3.6386±0.0005	128.3±1.8
0.2500	3.7050±0.0012	125.0±5.1
0.1000	3.7528±0.0007	111.0±7.3

$NaClO_4$(rel. H_2O), $c_{p\,.H_2O}$ = 4.1769 J·K^{-1}·g^{-1}

m / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
2.4524	3.3340±0.00[illegible]	11[illegible].8±0.3
2.1228	3.4964±0.00[illegible]	10[illegible].9±0.5
1.7875	3.5734±0.00[illegible]	10[illegible].0±0.5
1.5302	3.6386±0.00[illegible]	[illegible].1±0.7
1.2811	3.7050±0.00[illegible]	[illegible].2±1.0
1.1130	3.7528±0.00[illegible]	78.2±2.0
1.0000	3.7637±0.0008	7[illegible].6±1.4

Na_3PrA_3, $c_{p\,.solv.}$ = 3.7900 J·K^{-1}·g^{-1}

$m_{complex}$ / mol·kg^{-1}	m_{Na_2A} / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
[illegible]	0.2893	3.4527±0.0006	541.0±6.9
[illegible]	0.2893	3.4902±0.0008	538.5±7.8
[illegible]	0.2893	3.5[illegible]10±0.0010	[illegible].5±11.[illegible]
[illegible]	0.2893	3.5474±0.0006	[illegible]
[illegible]	0.2894	3.[illegible]15±0.0006	[illegible]3.8±6.7

Na_3GdA_3, $c_{p\,.solv.}$ = 3.7900±0.0008 J·K^{-1}·g^{-1}

$m_{complex}$ / mol·kg^{-1}	m_{Na_2A} / mol·kg^{-1}	c_p / J·K^{-1}·g^{-1}	ϕ_{cp} / J·K^{-1}·mol^{-1}
0.1516	0.2872	3.4410±0.0006	557.7±4.2
0.1200	0.2844	3.4810±0.0002	549.8±2.[illegible]
0.1022	0.2844	3.5127±0.0005	534.7±5.4
0.08091	0.2843	3.5441±0.0009	528.9±11.[illegible]
0.06079	0.2843	3.5741±0.0008	[illegible]2.5±8.4

The relation between the apparent molal heat capacity (also given in Table 2) and the square root of the molality is assumed to be linear. It is a well established experimental fact that $\bar{C}_p$ and many other partial molar properties of strong electrolytes vary linearly with $m^{\frac{1}{2}}$ over a concentration range far beyond that at which the limiting laws might be expected to hold.[20] Thus, the experimental ϕ_{C_p} data in Table 2 were fitted to functions of the type

$$\phi_{C_P} = a + bm^{\frac{1}{2}} \tag{5}$$

by a least-squares method.

The constants a and b with their corresponding standard deviations are given in Table 3. The ϕ_{C_p} data are very sensitive towards systematic errors, particularly in the most dilute solutions.[21] The fact that the slope b turns out to have about the same values for all the investigated rare earth perchlorate solutions is a good indication that the experimental procedure is not seriously affected by such errors.

Table 3. Least-squares refined parameters from eqn. (5). a is the partial molal heat capacity of the solute at infinite dilution.

Metal ion	a J K^{-1} mol^{-1}	b J K^{-1} mol^{-1} $m^{-\frac{1}{2}}$
La	10.7 ± 2.4	84.2 ± 5.3
Pr	39.9 ± 3.6	46.6 ± 8.0
Nd	43.9 ± 3.1	45.9 ± 6.3
Sm	46.2 ± 3.8	52.8 ± 7.6
Gd	41.2 ± 4.8	47.3 ± 10.9
Dy	44.9 ± 7.2	59.7 ± 15.6
Ho	40.4 ± 3.9	44.6 ± 8.8
Yb	36.5 ± 3.5	56.7 ± 7.5
Na_2A	170.5 ± 1.0	87.5 ± 1.3
$NaClO_4$	75.6 ± 1.4	–
Na_3PrA_3	477.9 ± 7.5	170.9 ± 22.6
Na_3GdA_3	438.3 ± 8.1	308.6 ± 25.1

Since the parameters in eqn. (5) are not evaluated from data at high dilution, the intercept and slope may differ numerically from the correct values at infinite dilution in the solvent 1.000 mol/kg $NaClO_4$. For the intercept this difference is usually small,[20] while it can be fairly large for the slope. Small errors in the $\bar{C}_p°$ values at infinite dilution due to errors in the extrapolation procedure should be nearly equal for all the rare earth perchlorates. Hence, the variation of the extrapolated ϕ_{C_p}-values ought to be very nearly the same as the variation of the "true" $\bar{C}_p°$-values at infinite dilution.

An experimental finding worth mentioning is that the slope b is smaller in 1.000 mol/kg $NaClO_4$ than in pure water (see Ref. 12), thus making the solution appear more "ideal" in the former case. This is a well known fact, at least to solution chemists who often use an ionic medium to keep activity coefficients approximately constant for moderate variations in the composition of a solution.

As seen in Fig. 3 the values of $\bar{C}_P°$ for the perchlorates are very nearly constant from praseodymium to ytterbium. Spedding *et al.*[12] found this behaviour for rare earth nitrates while the corresponding chlorides and perchlorates seemed to form two groups with a region of transition in between. The authors interpreted the latter finding in terms of an equilibrium between rare earth ions with different hydration numbers. However, it follows from our arguments in the preceding publications that an equilibrium of the type (1), where the equilibrium constant varies through the rare earth series, must give rise to a maximum in $\bar{C}_P°$. Such a maximum is found neither in our data nor in Spedding's.

Hence, one may conclude that these thermodynamic data give no indications for the presence of a Z-dependent hydration equilibrium for the hydrated rare earth ions. This conclusion is supported by the previously mentioned NMR study of Reuben and Fiat.[4] The differences between our data for the rare earth perchlorates and those of Spedding *et al.*[12] might be due to the difference in solvents, *viz.* 1.000 mol/kg $NaClO_4$ *vs.* pure water.

The tris-(oxydiacetato)lanthanoidate(III) complexes. The reaction in which the third rare earth oxydiacetate complex is formed can be written as

$$M(ClO_4)_3(aq) + 3\ Na_2A(aq) \rightarrow Na_3MA_3(aq) + 3\ NaClO_4(aq)$$

The change in heat capacity $\Delta C_P°{}_{III}$, for this reaction is

$$\Delta C_P°{}_{III} = \bar{C}_P°{}_{Na_3MA_3} + 3\ \bar{C}_P°{}_{NaClO_4} - 3\ \bar{C}_P°{}_{Na_2A} - \bar{C}_P°{}_{M(ClO_4)_3} \qquad (6)$$

The value of $\Delta C_P°{}_{III}$ is known from previous calorimetric determinations. The partial molar heat capacities of the various reactants and products can, as we have described above, be determined experimentally. In this section we will report values of $\bar{C}_P°{}_{NaClO_4}$, $\bar{C}_P°{}_{Na_2A}$ and $\bar{C}_P°{}_{Na_3MA_3}$. A comparison between the experimental values of $\Delta C_P°{}_{III}$ and the corresponding quantity calculated from eqn. (6) will give a check of the consistency of our partial molal heat capacity data.

The values of $C_P°{}_{Na_3MA_3}$, with M = Pr and Gd, were determined in solutions containing an excess of ligand sufficiently large to make the concentrations of lower oxydiacetate complexes negligible. From eqn. (2) one obtains

$$\phi c_P = \frac{c_P(1\,000 + m_{Na_2A}M_{Na_2A} + m_{Na_3MA_3}M_{Na_3MA_3}) - m_{Na_2A}\bar{C}_{PNa_2A} - 1\,000c_P°}{m_{Na_3MA_3}} \qquad (7)$$

where the meaning of the various symbols is evident from the context.

The apparent molar heat capacity values for Na_2A are given in Table 2 and in Fig. 2. The $\bar{C}_P$-values at the various molalities, m_{Na_2A}, were calculated from the eqn.

$$\bar{C}_{PNa_2A} = \phi c_{PNa_2A} + 1/2\sqrt{m_{Na_2A}}\,\frac{d\phi c_{PNa_2A}}{d\sqrt{m_{Na_2A}}} \qquad (8)$$

The variation of $\bar{C}_{PNa_2A}$ with $\sqrt{m_{Na_2A}}$ is shown in Fig. 2.

The experimental results for the praseodymium and gadolinium complexes are shown in Table 2, while the corresponding partial molar heat capacities at infinite dilution are given in Table 3.

In order to calculate a value of $\Delta C_p{}^\circ{}_{\mathrm{III}}$ from eqn. (6) we must also determine the partial molar heat capacity of sodium perchlorate *referred to* 1.000 mol/kg $NaClO_4$ *as the solvent.* The experimental data for sodium perchlorate in Table 2 have been given relative to both 1.000 mol/kg $NaClO_4$ ($\phi' c_p$) and pure water ($\phi'' c_p$) as the solvent. These data are also shown in Fig. 2. The value of $\bar{C}_p{}^\circ{}_{\mathrm{NaClO_4}}$ in 1.000 mol/kg $NaClO_4$ is given in Table 3.

The changes in heat capacity calculated from eqn. (6) are 153 J/K mol and 113 J/K mol for the praseodymium and gadolinium complexes, respectively. The same quantities obtained from the temperature variation of the corresponding enthalpy changes [9] are 167 J/K mol and 139 J/K mol, respectively. The fair agreement between the two sets of data is a good criterion of the reliability of the various $\bar{C}_p{}^\circ$-values obtained in this study. However, it must be pointed out that the agreement for the gadolinium system is less satisfactory at finite concentrations of solute. This is probably due to a small error in the slope b for this system. Small errors in this quantity do not affect the $\bar{C}_p{}^\circ$-values very much, but will lead to fairly large errors in the $\bar{C}_p$-data at finite concentrations (see p. 2549 and Ref. 20).

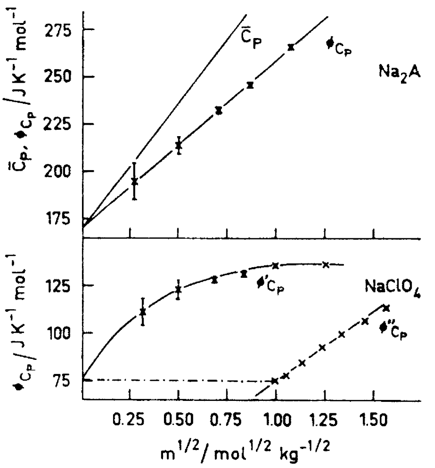

Fig. 2. ϕc_p and $\bar{C}_p$ *versus* the square root of the molality for Na_2A. For $NaClO_4$ two different curves are shown. $\phi' c_p$ refers to a 1.000 mol/kg $NaClO_4$ solution as the solvent, whereas for $\phi'' c_p$ pure water is used as the solvent (see above).

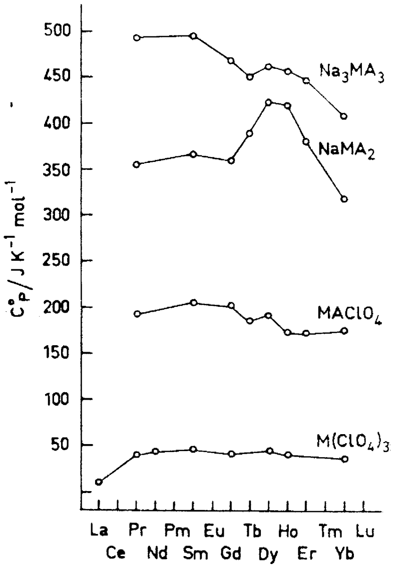

Fig. 3. The partial molar heat capacities at infinite dilution for the various rare earth perchlorates and the corresponding oxydiacetate complexes.

A better agreement with the previously found ΔC_P-values [9] would be obtained for Gd by using a smaller slope for the complex. This would also make the magnitudes of the *b*-values for the praseodymium and gadolinium complexes more equal (see Table 3).

By use of the $\bar{C}_p$-values for the rare earth perchlorates, Na_2A and $NaClO_4$, together with the $\Delta\bar{C}_p°$-data for the complexation reactions from the preceding investigation, one can calculate the $\bar{C}_p°$-values for all the various rare earth oxydiacetate complexes. These values given in Table 4 and in Fig. 3. The $\bar{C}_p°$-values for the terbium and erbium perchlorates were obtained by interpolation between the corresponding values for the adjacent elements in the rare earth series. The $\bar{C}_p°$-data show conclusively that the maximum found in $\Delta C_P°_2$ for the formation of the second rare earth oxydiacetate complex is due to the second complex alone, thus confirming the conclusion drawn previously.[9]

Table 4. The partial molar heat capacities at infinite dilution for the various rare earth perchlorates and the corresponding oxydiacetate complexes.

Metal ion	$C_P°_{M(ClO_4)_3}$ / J K^{-1} mol^{-1}	$C_P°_{MAClO_4}$ / J K^{-1} mol^{-1}	$C_P°_{NaMA_2}$ / J K^{-1} mol^{-1}	$C_P°_{Na_3MA_3}$ / J K^{-1} mol^{-1}
Pr	40	191	354	492
Sm	46	204	365	494
Gd	41	201	358	466
Tb	43	184	387	449
Dy	45	191	421	460
Ho	40	172	417	455
Er	39	171	378	445
Yb	37	173	316	406

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