Thermodynamic Properties of Rare Earth Complexes

XII. Enthalpy and Heat Capacity Changes for the Formation of Rare Earth Diglycolate Complexes at 5, 20, 35, and 50°C

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The changes in enthalpy and heat capacity for the formation of Pr(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), and Lu(III) diglycolate complexes have been determined at 5.00, 20.00, 35.00, and 50.00°C. All data refer to an aqueous sodium perchlorate medium with the sodium ion concentration equal to 1.00 M. The enthalpy changes were obtained from a direct calorimetric determination using the calorimeter and titration procedure described in a previous communication. The experimental results have been fitted to equations of the type:

$$\Delta H_j^\circ = A + BT + CT^2 + DT^3$$

from which the corresponding heat capacity changes have been obtained. The heat capacity data indicate the presence of a hydration equilibrium of the type $MA_2(H_2O)_x \rightleftharpoons MA_2(H_2O)_y$ for the second rare earth diglycolate complexes.

The data available in the literature on the temperature dependence of the enthalpy changes on complex formation are rather scarce. The results published indicate that the $\Delta C_{p_j}^\circ$-values for reactions of this type are fairly large and moreover that these values vary significantly with temperature in the range $0-100°C$.[1] One of the aims of the present investigation has been to obtain information of this kind for a series of rare earth diglycolate complexes. Another object has been to decide whether hydration equilibria of the type

$$MA_j(H_2O)_x \rightleftharpoons MA_j(H_2O)_y + (x-y)H_2O \qquad (1)$$
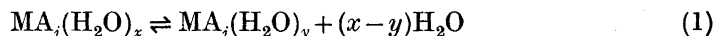
are present or not, in the systems studied. A preliminary discussion of how ΔC_p° data can be of use in the latter context is given in the preceding publication[2] of this series. The presence of an equilibrium of the type (1) implies differences in the number of coordinated donor atoms from the ligands A and H_2O, *i.e.* differences in the geometry of the coordination sphere. Spectro-

scopic methods can in some cases, *e.g.* for the *d*-type transition elements, give information of the point symmetry at the central ion site in the coordination compounds. However, such information can usually not be obtained for *f*-type transition elements, as changes in the surroundings normally show only small influence on the $f-f$ transitions (a possible exception is the so called hypersensitive transitions). Geier *et al.* [3] and Anderegg and Wenk[4] have interpreted the temperature dependence of the spectra of various rare earth aminopolycarboxylates in terms of an equilibrium of the type (1). The method will only be useful if the spectral changes are fairly large and this is not always the case as indicated by measurements on the diglycolate and dipicolinate spectra of various rare earths (see p. 1240).

The stepwise enthalpy changes, ΔH_j°, have been determined by a direct calorimetric method at 5, 20, 35, and 50°C. Nine rare earth diglycolate systems have been investigated, *viz.* Pr(III), Sm(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Yb(III), and Lu(III), for four of which the temperature dependences of the stepwise free energy changes have already been reported (preceding publication). The various heats of reaction were determined by use of the calorimeter and titration procedure described earlier.[5] All measurements refer to an aqueous sodium perchlorate medium with 1.00 M total sodium ion concentration. All concentrations, volumes and additions given in this investigation refer to 25°C as discussed in a preceding publication.

NOTATION AND CALCULATION

The notation used here is the same as before.[6]

The enthalpy changes for the various reactions were determined by graphical and numerical methods. The graphical method, outlined earlier,[6] was used to determine the enthalpies of protonation of the diglycolate ion, while the numerical methods were used in all other cases.

Two different numerical methods were used, one developed by Arnek[7] and the other by Ekström. Both methods give a set of "best" least-squares constants. The differences between the two methods lie in the type of input data used. Refs. 7 and 8 give details of the computing procedures. The enthalpy changes obtained from the two computing methods were essentially the same.

The stability constants, β_j, needed for the calculations were known at all four temperatures only for the Pr(III), Sm(III), Dy(III), and Yb(III) systems. On the basis of these results the following iterative procedure was used to calculate the stability constants and the enthalpy changes for the five remaining systems, for which β_j-values were known only at 20°C.[9]

A first guess was made of the stability constants at the various temperatures from the known behaviour of the Pr, Sm, Dy, and Yb systems. The over-all enthalpy changes were then calculated. All stepwise complexes are strong and fairly well separated one from another and an error in the stability constants will thus only have a small influence on the enthalpy changes. Improved stability constants were then calculated from the log $K_j(T)$ functions obtained from $\Delta H_j^\circ(T)$-data and the stability constants at 20°C. A re-calculation of the various enthalpy changes using the new set of stability constants did not lead to any significant changes.

The stability constants at 20°C used for the calculations have been recalculated from data in Ref. 9. The corrected values are given in Table 8. The reasons for the corrections have been outlined in the preceding publication.

EXPERIMENTAL

Chemicals. Rare earth oxides were obtained from the American Potash & Chemical Corp. Stock solutions of the rare earth perchlorates were prepared and standardized as described before.[10] The diglycolic acid (Fluka) was recrystallized from ethyl acetate. Stock solutions of the disodium salt of the acid were prepared by neutralization with sodium hydroxide. Sodium perchlorate was prepared as described earlier.[8]

Calorimetric titrations. The calorimeter and the experimental procedure used were the same as described before.[5] The measurements have been performed at 5.00, 20.00, 35.00, and 50.00°C. The calorimeter was filled with 100.24 ml (V_0) of a solution S. From a calibrated piston burett known volumes (v) were added of a solution T. For the rare earth diglycolate measurements the solutions S and T had the following composition:

$$S \begin{cases} C_M & M(ClO_4)_3 \\ C_H & HClO_4 \\ 1.00 \text{ M} & NaClO_4 \end{cases} \qquad T \begin{cases} C_{Na_2A} & \text{diglycolate} \\ (1.00 \text{ M} - 2C_{Na_2A}) \text{ NaClO}_4 \end{cases}$$
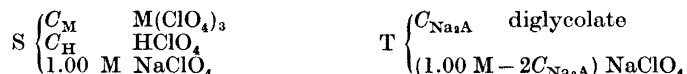
The sodium ion concentration was 1.00 M in all the measurements. The concentrations in the various rare earth perchlorate solutions S are given in Table 3. C_{Na_2A} in solution T was 0.3000 M. The compositions of the S and T solutions used for determining the enthalpies of protonation of the diglycolate ion are given in Tables 1 and 2.

The solution T was normally added in portions of 1.50 ml at 5°C and 50°C and 2.00 ml at 20°C and 35°C. Two runs were made for each system at each temperature with about ten additions in each run. The first, third *etc.* points in Table 4 belong to one titration and the second, fourth etc. points to the second titration. The highest $\bar{n}$-values reached in the titrations were approximately 2.85.

In order to obtain the heat equivalent of the various systems at least two electrical calibrations were performed in each run. The temperature changes in the calorimeter were small enough to be put proportional to the changes in the resistance of the thermistor.

The heats of dilution of the perchloric acid solutions and the sodium diglycolate solutions were small and at most 0.03 cal/2 ml. The heats of dilution of the rare earth perchlorate solutions (S) and the complexes have been neglected.[6]

The thermodynamic standard state for the solute species in this study is a hypothetical ideal one molar solution in which the concentration of neutral salt (sodium perchlorate) is equal to 1.0 M.

Spectroscopic measurements. Spectra were recorded at four different temperatures *viz.* 2, 25, 45, and 65°C for the diglycolate and dipicolinate complexes of Eu, Dy, Ho, and Er by using a Cary 14 spectrophotometer. The solutions studied had the values of $\bar{n}$ equal to 0.5, 1.5 (for the diglycolate solutions only), and 2.5. The complexes formed are so strong, that the relative amounts of the dominating species (M and MA at $\bar{n} = 0.5$, MA and MA$_2$ at $\bar{n} = 1.5$, and MA$_2$ and MA$_3$ at $\bar{n} = 2.5$) do not change significantly with a change of temperature. Possible changes in the spectra can thus not be referred to a change in the relative amounts of the species MA$_j$.

Experimental absorbance curves at the highest and lowest temperatures are shown in Fig. 3. There are no pronounced changes in the spectra with temperature, apart from a slight shift towards lower wave length, followed by a small decrease of the absorption maximum. Hence, the $f-f$ spectra are not suitable as indicators of environmental changes for these particular systems.

RESULTS

The experimental Q-values given in this study are positive for exothermal and negative for endothermal reactions.

The proton diglycolate system. The experimental data are given in Tables 1 and 2. The values of Q_{corr} in Table 1 have been obtained from the measured Q-values by correction for the dilution of the perchloric acid solutions. The heats of dilution of the S solutions (Na$_2$A) are small and can be neglected.

Table 1. Corresponding values of v_{tot} and Q_{corr} for the proton diglycolate system at 5, 20, 35, and 50°C. S: $C_A = 0.0300$ M; $C_{Na} = 1.00$ M. T: $C_H = 0.1014$ M; $C_{Na} = 1.00$ M.

Temp.:	5°C	20°C	35°C	50°C
$\dfrac{v_{tot}}{ml}$	$\dfrac{Q_{corr}}{cal}$	$\dfrac{Q_{corr}}{cal}$	$\dfrac{Q_{corr}}{cal}$	$\dfrac{Q_{corr}}{cal}$
1.50	− 0.014			− 0.247
2.00		− 0.117	− 0.220	
3.00	− 0.009			− 0.242
4.00		− 0.129	− 0.216	
4.50	− 0.022			− 0.245
6.00	− 0.020	− 0.121	− 0.212	− 0.234
7.50	− 0.014			− 0.234
8.00		− 0.120	− 0.201	
9.00	− 0.001			− 0.225
10.00		− 0.114	− 0.206	
10.50	± 0.000			− 0.212
12.00	0.006	− 0.102	− 0.191	− 0.215
13.50	0.007			− 0.202
14.00		− 0.094	− 0.183	
15.00	0.014			− 0.197
16.00		− 0.086	− 0.162	
18.00		− 0.084	− 0.158	
20.00		− 0.062	− 0.146	

In this titration, the highest $\bar{n}_H$-value reached was 0.6 and, consequently, only $\Delta H_1°$ could be evaluated.

In the second series, an S-solution of perchloric acid was titrated with a sodium diglycolate solution. The measured Q-values have been corrected for the dilution of the sodium diglycolate solutions and the corrected values are given in Table 2. In this case the heats of dilution of the perchloric acid solutions were neglected. The final $\bar{n}_H$-values in this titration were all close to 2 and the data were used to determine $\Delta H_2°$.

Table 2. Corresponding values of v_{tot} and Q_{corr} for the proton diglycolate system at 5, 20, 35, and 50°C. S: $C_H = 0.0916$ M, $C_{Na} = 1.00$ M. T: $C_A = 0.0300$ M, $C_{Na} = 1.00$ M.

Temp.:	5°C	20°C	35°C	50°C
$\dfrac{v_{tot}}{ml}$	$\dfrac{Q_{corr}}{cal}$	$\dfrac{Q_{corr}}{cal}$	$\dfrac{Q_{corr}}{cal}$	$\dfrac{Q_{corr}}{cal}$
1.50	0.038			− 0.101
2.00		− 0.015	− 0.069	
3.00	0.036			− 0.099
4.00		− 0.013	− 0.066	
4.50	0.035			− 0.098
6.00		− 0.012	− 0.061	

Table 3. The composition of the various rare earth perchlorate solutions (solutions S) at 5, 20, 35, and 50°C.

Temp.:	5 and 50°C		20 and 35°C	
Metal ion	$C_{Na} = 1.00$ M			
	$\dfrac{C_M \times 10^3}{M}$	$\dfrac{C_H \times 10^3}{M}$	$\dfrac{C_M \times 10^3}{M}$	$\dfrac{C_H \times 10^3}{M}$
Pr	13.59	0.852	18.12	1.136
Sm	14.16	1.080	18.88	1.440
Gd	12.05	0.852	16.07	1.136
Tb	13.94	1.568	18.58	2.090
Dy	14.22	0.426	18.96	0.568
Ho	14.25	1.611	19.00	2.148
Er	12.47	0.681	16.63	0.908
Yb	14.40	0.783	19.20	1.044
Lu	13.07	0.941	17.41	1.254

The stepwise enthalpy changes with their estimated errors are given in Table 5. The temperature dependence of the enthalpy changes was described by functions of the type:

$$\Delta H_j^\circ = A + BT + CT^2 + DT^3 \qquad (2)$$

and the various constants are given in Table 6. Expressions for the heat capacity changes, ΔC_{pj}°, are obtained by derivation of relation (2) and the values at 25.0°C are given in Table 7.

The rare earth diglycolate systems. All the experimental Q-values corrected for the heats of dilution of the ligand are given in Table 4. Values of the differences $(Q_{corr,calc} - Q_{corr,obs})$ are also given. The stepwise enthalpy changes, ΔH_j°, for the various systems with their corresponding standard deviations are shown in Table 5. The standard deviations in the individual measurements, $Sig\ Q_{corr}$, are included in the last column in this table.

The temperature dependence of the enthalpy changes for the rare earth complexes was described by the same type of relations as for diglycolic acid (eqn. 2). The constants for the various systems are given in Table 6. The heat capacity changes ΔC_{pj}° at 25.0°C, obtained from these functions are shown in Table 7.

Precision of the results. The values of $Sig\ Q_{corr}$, given in Table 5, are useful for an estimate of the precision of the enthalpy titrations. It is obvious that some results are more precise than others.

There are several possible reasons for the deviations, *e.g.* errors in the concentrations of the reacting species, errors in the stability constants used and temperature errors in the heat exchange device. We do not think that any of these errors alone can be large enough to cause differences in the precision between the various systems investigated. A combination of error sources seems to be a possible explanation of the observed variations in $Sig\ Q_{corr}$.

Table 4. Corresponding values of v_{tot}, Q_{corr}, and $(Q_{calc} - Q_{corr}) = \Delta Q$ for the various rare earth diglycolate systems at 5, 20, 35 and 50°C.

All values are given as $Q_{corr} \cdot 10^5$ (cal.) and $\Delta Q \cdot 10^5$ (cal.) for each metal ion.

5 °C

V_{tot} (ml)	Pr Q_{corr}	Pr ΔQ	Sm Q_{corr}	Sm ΔQ	Gd Q_{corr}	Gd ΔQ	Tb Q_{corr}	Tb ΔQ	Dy Q_{corr}	Dy ΔQ	Ho Q_{corr}	Ho ΔQ	Er Q_{corr}	Er ΔQ	Yb Q_{corr}	Yb ΔQ	Lu Q_{corr}	Lu ΔQ
0.75	288	-1	379	-2	259	-8	14	-8	-124	+21	-164	-18	-189	-18	-174	-3	-154	-5
1.50	570	+6	749	+9	494	-4	62	+6	-171	+19	-306	+7	-347	-14	-352	+11	-286	-8
2.25	569	+7	768	-2	546	+5	180	-1	-49	+11	-172	-1	-256	+2	-317	+8	-238	-6
3.00	581	-5	784	-7	614	+11	286	+10	107	-20	-44	-1	-145	+8	-261	-5	-181	-5
3.75	580	-4	794	+0	711	-3	421	-7	232	-13	81	+2	-28	+15	-203	-9	-123	+3
4.50	580	-4	814	+3	795	+1	541	-7	378	-20	204	+9	108	+11	-136	-9	-48	-1
5.25	581	-6	844	-2	883	-3	647	+6	515	-15	341	+2	250	+8	-57	-7	10	+17
6.00	566	+2	864	+0	960	-12	769	-1	645	-5	478	-4	404	+3	-14	+0	88	+17
6.75	545	+9	873	+2	982	+3	879	-6	761	+13	604	+2	587	-16	91	+8	156	+17
7.50	531	-5	873	-6	960	+7	971	-9	884	+13	741	-2	773	-11	178	+14	260	+16
8.25	480	-1	829	+6	870	+9	1012	+8	989	+10	879	-9	989	-1	301	+12	463	-28
9.00	405	+2	773	-2	758	-11	1030	+6	1070	+4	1004	-6	1226	-2	522	-3	801	-28
9.75	317	+2	674	+2	630	-2	996	+4	1120	-7	1109	+2	1396	+7	883	-18	1175	-24
10.50	252	+4	575	-2	540	-6	934	-1	1124	-5	1190	+10	1477	-1	1257	-7	1333	-24
11.25	179	-6	483	+3	434	+4	860	+1	1086	-1	1254	+17	1418	-11	1486	-8	1259	+1
12.00	130	-1	424	-8	310	+9	792	-5	1055	+0	1257	-5	1139	+14	1517	-3	1091	+11
12.75	95	+3	347	+2			692	+0	966	-11	1208	-15			1400	+7	857	+32
13.50	71	+3	273	+4											1177	+9	613	+31
14.25	57	-2	205	-2											881	+18	444	+31
15.00	45	-4	131	+4													333	+1

20 °C

V_{tot} (ml)	Pr Q_{corr}	Pr ΔQ	Sm Q_{corr}	Sm ΔQ	Gd Q_{corr}	Gd ΔQ	Tb Q_{corr}	Tb ΔQ	Dy Q_{corr}	Dy ΔQ	Ho Q_{corr}	Ho ΔQ	Er Q_{corr}	Er ΔQ	Yb Q_{corr}	Yb ΔQ	Lu Q_{corr}	Lu ΔQ
1.00	214	+13	352	-3	164	-9	-141	+6	-297	+4	-374	-8	-405	-9	-376	-6	-529	-10
2.00	459	-4	701	+3	340	+4	-210	+3	-553	+16	-706	+9	-759	-12	-730	-6	-640	-7
3.00	470	-11	715	+2	423	+0	-71	-4	-359	-9	-546	-10	-654	-12	-669	-5	-580	+1
4.00	462	+2	754	+3	527	+1	83	-4	-184	-14	-388	-10	-504	+7	-593	-6	-489	-6
5.00	464	+11	767	+2	659	-1	251	-2	-10	-2	-239	+13	-340	+13	-505	-5	-593	-5
6.00	499	-6	795	+18	797	+9	424	+8	189	+2	-38	-1	-150	+12	-418	+12	-295	+7
7.00	519	-3	882	-15	957	-7	625	-6	403	-2	145	+9	47	+17	-300	+7	-185	+10
8.00	525	+8	940	-23	1077	-11	795	-9	611	+4	351	+4	278	+4	-187	+14	-77	+20
9.00	538	-3	976	-27	1126	+6	974	+3	820	+1	554	+4	523	+0	-60	+9	37	+21
10.00	511	+5	957	-3	1129	+3	1110	+4	1015	+4	779	-12	839	-12	64	+15	181	+6
11.00	471	+3	894	+34	1055	+9	1218	-1	1205	-6	985	+0	1252	-50	258	-10	460	-30
12.00	403	+1	841	+28	964	-7	1272	-1	1348	+4	1226	-10	1653	+7	584	-15	1020	-24
13.00	336	-15	786	-3	861	-10	1275	-10	1479	-6	1446	+4	1961	+13	1165	-10	1590	-25
14.00	254	-10	698	-7	753	-9	1255	-7	1539	+10	1652	+2	2069	-1	1776	-26	1755	-29
15.00	195	-6	616	-4	581	+20	1194	+4	1575	+0	1771	+11	1923	+18	2017	-8	1599	+3
16.00	138	+5	552	-15			1126	-10	1538	-15	1809	+1	1439	+23	1977	-8	1334	+20
17.00	104	+6	460	-9			951	+13	1544	+8	1701	-9			1742	+7	1023	+35
18.00	74	+8	316	+26											1375	+28	743	+31
19.00	43	+17													975	+43	518	+52
20.00	36	+8															366	+23

35 °C

V_{tot} (ml)	Pr Q_{corr}	Pr ΔQ	Sm Q_{corr}	Sm ΔQ	Gd Q_{corr}	Gd ΔQ	Tb Q_{corr}	Tb ΔQ	Dy Q_{corr}	Dy ΔQ	Ho Q_{corr}	Ho ΔQ	Er Q_{corr}	Er ΔQ	Yb Q_{corr}	Yb ΔQ	Lu Q_{corr}	Lu ΔQ
1.00	89	-4			15	-11	-274	+0	-422	+4	-502	-8	-518	-21	-492	-4	-451	-9
2.00	172	+1	407,410	-2,-5	59	-15	-493	-2	-806	+19	-953	-13	-1008	-21	-977	+8	-878	-11
3.00	183	-4	226	-10	128	+5	-372	-6	-679	+7	-847	-2	-901	-15	-907	-10	-809	-9
4.00	185	+8	456	-7	247	+5	-228	-3	-515	-9	-695	-10	-765	-7	-851	-14	-734	+7
5.00	207	+5	465	+27	393	+11	-55	-1	-314	-28	-544	+8	-652	+36	-734	-15	-620	+5
6.00	259	-9	550	+8	577	+2	146	+2	-115	-9	-355	+11	-406	+15	-621	-4	-493	+3
7.00	300	+0	658	-18	746	+6	355	+9	120	-6	-150	+15	-205	+34	-487	+5	-372	+17
8.00	349	-2	716	+6	901	-3	574	+6	350	+13	71	+14	37	+24	-362	+30	-237	+16
9.00	373	+2	792	-12	993	+4	768	+9	586	+14	301	+5	311	-1	-256	+44	-99	+1
10.00	379	+0	806	-13	1039	-2	946	+1	815	+9	531	+4	661	-25	-88	+29	19	+10
11.00	364	+0	795	+17	1087	-1	1036	+0	1036	+0	793	-11	1158	-50	73	+20	279	-22
12.00	329	+2	782	+2	985	-15	1196	-8	1260	-10	1089	-19	1671	-56	473	-74	883	-22
13.00	290	-2	765	-24	921	-17	1270	-7	1465	-10	1408	-17	2062	-5	1096	-47	1520	-28
14.00	241	+3	688	+1	820	-6	1521	-15	1611	+5	1688	+3	2155	-1	1766	-31	1668	-8
15.00	208	-3	624	+14	662	+7	1504	+3	1698	-1	1884	+5	1957	+4	1985	+7	1516	+11
16.00	172	-2	576	+0	423	+44	1249	-2	1676	-8	1944	+2	1475	+43	1892	+17	1284	+8
17.00	125	+11	500	-9			1071	+22	1469	+13	1817	+10			1651	+22	1003	+28
18.00	108	-3	367	+13											1346	+20	775	+13
19.00	86	-8	273	-11											1039	+11	567	+20
20.00	60	-2													762	+12	435	+2

50 °C

V_{tot} (ml)	Pr Q_{corr}	Pr ΔQ	Sm Q_{corr}	Sm ΔQ	Gd Q_{corr}	Gd ΔQ	Tb Q_{corr}	Tb ΔQ	Dy Q_{corr}	Dy ΔQ	Ho Q_{corr}	Ho ΔQ	Er Q_{corr}	Er ΔQ	Yb Q_{corr}	Yb ΔQ	Lu Q_{corr}	Lu ΔQ
0.75	-66	+13	11	+9	-121	-5	-325	+4	-437	-6	-478	-9	-487	-12	-472	-6	-449	-2
1.50	-113	+10	66	-19	-216	-9	-593	-16	-834	-15	-929	-10	-944	-21	-934	-2	-870	-7
2.25	-96	+0	82	-16	-162	+3	-526	-8	-767	+5	-850	-13	-877	-11	-884	-9	-804	-14
3.00	-73	-11	96	-1	-58	-8	-429	-5	-640	-10	-768	+4	-779	-4	-819	-12	-743	+2
3.75	-49	-12	126	+14	29	+30	-308	+5	-520	+11	-638	-2	-661	+13	-737	-13	-645	+3
4.50	-18	-2	194	+11	214	-5	-164	+19	-543	+5	-509	+16	-504	+19	-655	+11	-525	+2
5.25	36	+2	269	+18	374	-9	31	+2	-162	+15	-358	+10	-353	+43	-529	+7	-404	+8
6.00	82	+13	360	+11	509	-11	194	+18	47	+4	-172	+18	-166	+35	-416	+23	-292	+20
6.75	125	+10	444	-6	600	-5	373	+4	231	+13	11	+7	76	-26	-313	+37	-193	+29
7.50	161	-5	476	+6	621	+38	510	+9	427	-1	186	+4	294	-18	-205	+34	-88	+18
8.25	170	-3	507	-3	702	-9	656	-13	609	+0	378	-3	663	-27	-80	+10	97	-45
9.00	174	-4	519	-7	723	-15	773	-12	830	-20	629	-24	1134	-18	136	-36	425	-21
9.75	181	-13	520	-12	724	-26	895	-22	1033	-7	909	-14	1492	-8	603	-66	902	-30
10.50	166	-5	512	-14	671	-17	966	+2	1219	-1	1210	-13	1578	+6	1149	-44	1090	-29
11.25	148	+2	489	-11	558	+6	1026	-6	1338	-11	1404	+7	1437	+29	1369	+2	1008	-9
12.00	123	+9	444	+1	400	+51	1015	-5	1538	-9	1489	+3			1312	+23	850	+24
12.75	111	+3	401	-8	250	+42	915	+11	1225	-8	1419	+14			1176	+20	698	+38
13.50	99	-5	306	+19			738	+21	939	+50					1003	+20	573	+51
14.25	79	-3	231	+19											855	+15	467	+22
15.00	42	+18	157	+24											678	+10	386	+7

Table 5. The stepwise values of ΔH_i° with their corresponding standard deviations for the various rare earth diglycolates at 5, 20, 35, and 50°C. At each temperature the standard deviations *Sig Q* in the Q_{corr} values are also given.

Temp.:	5°C				20°C			
Metal ion	$-\Delta H_1^\circ$ kcal mol^{-1}	$-\Delta H_2^\circ$ kcal mol^{-1}	$-\Delta H_3^\circ$ kcal mol^{-1}	$\dfrac{Sig}{Q \times 10^3}$ cal	$-\Delta H_1^\circ$ kcal mol^{-1}	$-\Delta H_2^\circ$ kcal mol^{-1}	$-\Delta H_3^\circ$ kcal mol^{-1}	$\dfrac{Sig}{Q \times 10^3}$ cal
Pr	1.280 ± 0.005	1.362 ± 0.005	0.335 ± 0.006	5	0.757 ± 0.008	1.039 ± 0.006	0.331 ± 0.010	9
Sm	1.673 ± 0.005	2.163 ± 0.005	1.033 ± 0.004	5	1.160 ± 0.015	1.825 ± 0.012	1.070 ± 0.015	17
Gd	0.976 ± 0.011	2.706 ± 0.005	1.339 ± 0.009	8	0.476 ± 0.010	2.361 ± 0.007	1.482 ± 0.007	10
Tb	-0.094 ± 0.009	3.049 ± 0.004	1.982 ± 0.007	6	-0.544 ± 0.009	2.625 ± 0.004	2.251 ± 0.007	9
Dy	-0.574 ± 0.020	2.833 ± 0.009	2.598 ± 0.014	14	-1.084 ± 0.009	2.397 ± 0.004	2.976 ± 0.005	9
Ho	-0.953 ± 0.014	2.468 ± 0.005	3.350 ± 0.008	9	-1.382 ± 0.009	1.866 ± 0.004	3.793 ± 0.007	9
Er	-1.027 ± 0.017	1.658 ± 0.006	4.140 ± 0.013	12	-1.466 ± 0.017	1.120 ± 0.006	4.449 ± 0.013	16
Yb	-0.816 ± 0.013	0.538 ± 0.007	4.507 ± 0.012	11	-1.311 ± 0.016	0.360 ± 0.008	4.489 ± 0.016	17
Lu	-0.753 ± 0.027	0.734 ± 0.011	4.091 ± 0.026	20	-1.176 ± 0.022	0.430 ± 0.010	4.102 ± 0.023	22
Diglycolic acid	-0.143 ± 0.010	0.988 ± 0.030	—	—	-0.644 ± 0.010	0.420 ± 0.030	—	—

Temp.:	35°C				50°C			
Metal ion	$-\Delta H_1^\circ$ kcal mol^{-1}	$-\Delta H_2^\circ$ kcal mol^{-1}	$-\Delta H_3^\circ$ kcal mol^{-1}	$\dfrac{Sig}{Q \times 10^3}$ cal	$-\Delta H_1^\circ$ kcal mol^{-1}	$-\Delta H_2^\circ$ kcal mol^{-1}	$-\Delta H_3^\circ$ kcal mol^{-1}	$\dfrac{Sig}{Q \times 10^3}$ cal
Pr	0.284 ± 0.004	0.791 ± 0.004	0.452 ± 0.005	5	-0.234 ± 0.011	0.494 ± 0.009	0.545 ± 0.014	10
Sm	0.658 ± 0.011	1.593 ± 0.010	1.225 ± 0.010	13	0.081 ± 0.016	1.361 ± 0.014	1.370 ± 0.015	14
Gd	-0.034 ± 0.016	2.127 ± 0.010	1.714 ± 0.013	15	-0.602 ± 0.029	1.759 ± 0.020	1.955 ± 0.025	22
Tb	-0.984 ± 0.007	2.224 ± 0.004	2.651 ± 0.004	7	-1.479 ± 0.015	1.711 ± 0.010	3.057 ± 0.012	12
Dy	-1.468 ± 0.012	1.830 ± 0.007	3.450 ± 0.010	13	-2.040 ± 0.021	1.424 ± 0.012	3.893 ± 0.018	17
Ho	-1.788 ± 0.012	1.340 ± 0.007	4.260 ± 0.010	12	-2.222 ± 0.016	0.864 ± 0.010	4.670 ± 0.016	13
Er	-1.868 ± 0.028	0.730 ± 0.013	4.815 ± 0.024	27	-2.278 ± 0.033	0.374 ± 0.019	5.111 ± 0.034	25
Yb	-1.683 ± 0.026	0.136 ± 0.015	4.792 ± 0.029	30	-2.158 ± 0.032	$-.040 \pm 0.019$	5.048 ± 0.042	28
Lu	-1.599 ± 0.016	0.230 ± 0.006	4.210 ± 0.017	16	-2.050 ± 0.030	0.101 ± 0.016	4.131 ± 0.040	24
Diglycolic acid	-1.089 ± 0.010	0.027 ± 0.030	—	—	-1.641 ± 0.010	$-.574 \pm 0.050$	—	—

The increase of *Sig* Q_{corr} with increasing temperature is another characteristic feature. This is caused by the decrease in the sensitivity of the thermistor with increasing temperature and hence a decreased accuracy. This has been observed earlier.[5] It should be noticed, that errrors discussed here are all very small.

In Fig. 1, Δh_v has been plotted as a function of $\bar{n}$ for the praseodymium diglycolate systems at four temperatures. The Q-values, used for the calcula-

Table 6. The stepwise enthalpy changes for the various rare earth diglycolates as functions of temperature: $\Delta H_j^\circ = A + BT + CT^2 + DT^3$. The number of figures in the constants $A - D$ have been chosen in order to describe the experimental data within 1 cal at the four different temperatures.

	ΔH_1°				ΔH_2°			
Constants	$-A$	B	$-C \times 10^3$	$D \times 10^6$	$-A$	B	$-C \times 10^3$	$D \times 10^6$
Metal ion	kcal mol^{-1}	kcal mol^{-1} K^{-1}	kcal mol^{-1} K^{-2}	kcal mol^{-1} K^{-3}	kcal mol^{-1}	kcal mol^{-1} K^{-1}	kcal mol^{-1} K^{-2}	kcal mol^{-1} K^{-3}
Pr	137.928	1.306856	4.237067	4.691358	174.819	1.694176	5.552124	6.123457
Sm	119.900	1.142185	3.759520	4.246914	159.179	1.505553	4.839253	5.234568
Gd	68.001	0.631253	2.062471	2.370370	333.248	3.280608	10.887279	12.098765
Tb	90.724	0.869571	2.845244	3.209877	182.606	1.774823	5.914311	6.666667
Dy	63.978	0.604455	1.956622	2.222222	14.249	0.052939	0.056764	0.049383
Ho	74.458	0.706580	2.266098	2.518519	59.668	0.467373	1.298098	1.283951
Er	69.661	0.648694	2.036622	2.222222	179.921	1.673979	5.280036	5.629630
Yb	101.812	0.984906	3.217138	3.604938	88.148	0.836912	2.686880	2.913580
Lu	41.837	0.384392	1.216071	1.382716	66.168	0.572103	1.664338	1.629630
Diglycolic acid	221.569	2.178046	7.203716	8.049383	307.695	3.002863	9.867164	10.913580

	ΔH_3°			
Constants	$-A$	B	$-C \times 10^3$	$D \times 10^6$
Metal ion	kcal mol^{-1}	kcal mol^{-1} K^{-1}	kcal mol^{-1} K^{-2}	kcal mol^{-1} K^{-3}
Pr	212.924	2.105303	6.922738	7.555556
Sm	180.570	1.775654	5.821404	6.320988
Gd	114.090	1.121153	3.672267	3.950617
Tb	175.850	1.738528	5.720000	6.172840
Dy	170.854	1.712268	5.729084	6.271605
Ho	100.000	1.031351	3.571253	4.000000
Er	166.338	1.667354	5.642418	6.271605
Yb	519.676	5.090126	16.695982	18.172840
Lu	373.891	3.735225	12.549991	14.024691

tions, have been corrected for both the heats of dilution and protonation. The smooth curves have been calculated from the enthalpy changes given in Table 5 and the stability constant given in the preceding publication. The radii of the circles in the figure do not represent error limits; the errors estimated from the experiments are approximately three times smaller.

The enthalpy changes at 25°C, obtained from the temperature functions in this study, agree fairly well with those determined earlier.[6] The deviations

Table 7. The stepwise heat capacity changes $\Delta C_{p_j}°$ at 25.0°C. The errors in the values given are approx. 2 cal mol^{-1} K^{-1}.

Metal ion	$\Delta C_{P1}°$ cal mol^{-1} K^{-1}	$\Delta C_{P2}°$ cal mol^{-1} K^{-1}	$\Delta C_{P3}{}^3$ cal mol^{-1} K^{-1}
Pr	31.4	16.4	-7.8
Sm	33.0	15.9	-10.0
Gd	33.5	15.0	-15.1
Tb	29.0	26.0	-26.1
Dy	30.3	32.3	-31.5
Ho	26.9	35.7	-31.5
Er	26.9	26.8	-24.7
Yb	27.9	11.7	-19.4
Lu	28.0	14.2	-8.2
Diglyc. acid	29.1	29.5	$-$

Table 8. Stability constants, β_j, at 20°C recalculated from data in Ref. 9.

Constants Metal ion	$\beta_1 \times 10^{-5}$ M^{-1}	$\beta_2 \times 10^{-10}$ M^{-2}	$\beta_3 \times 10^{-13}$ M^{-3}
Gd	3.09	1.08	1.66
Tb	2.64	1.20	2.56
Ho	2.49	1.18	2.91
Er	2.95	1.44	2.55
Lu	6.21	5.66	2.64

in the over-all $\Delta H_2°$-values between the two studies are all within three standard deviations (3σ). The deviations in the over-all $\Delta H_3°$-values, however, are larger and of the magnitude 0.3 kcal mol^{-1}.

Determination of the $\Delta H°(T)$ functions. The temperature dependences of the stepwise enthalpy changes for the systems investigated have all been described by the same type of relations (eqn. 2). The experimental enthalpy data could not be fitted to polynomials of lower than third degree with preservations of the accuracy given by the experiments. The corresponding heat capacity data are thus described by second degree polynomials. Plots of ΔC_{p_j} vs. T show in most cases minima around 30°C. It may be remarked that even very slight errors in the enthalpy changes are enough to cause a substantial shift of the position of the inflection points of the $\Delta H(T)$-curves. The estimated errors in the temperature dependence of the various ΔC_p-values are thus fairly large. On the other hand, the errors in the averages of ΔC_p in the given temperature range are smaller and of the magnitude 2 cal mol^{-1} K^{-1}.
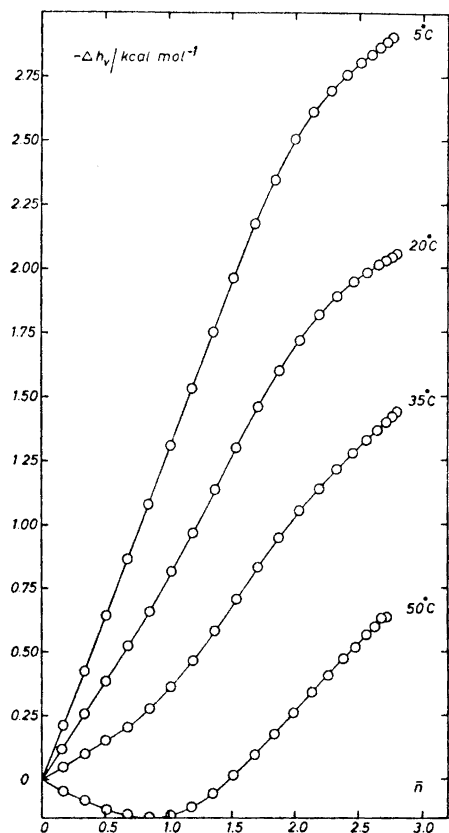
Fig. 1. The total molar enthalpy change, Δh_v, as a function of the average ligand number, $\bar{n}$, for the praseodymium diglycolate system at 5, 20, 35, and 50°C.
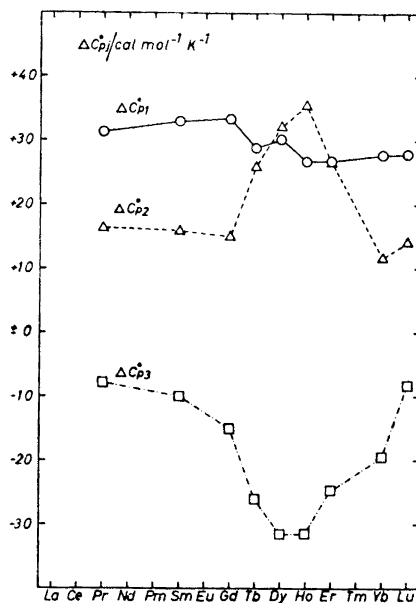
Fig. 2. The stepwise heat capacity changes, ΔC_{pj}°, at 25°C for the formation of rare earth diglycolate complexes.

DISCUSSION

The changes in enthalpy and entropy for the reactions investigated show fairly large variations with temperature. The temperature dependence of the various stepwise enthalpy changes is, for instance, illustrated by the corresponding heat capacity changes shown in Fig. 2. The variations of ΔG_j°, ΔH_j°, ΔS_j°, and ΔC_{pj}° with the atomic number of the central ion are changed slightly with a change in temperature, *e.g.* both the minimum in ΔH_2° and the maximum in $\Delta C_{p_2}^{\circ}$ are shifted towards the elements with smaller atomic numbers when the temperature increases. There are large differences between the various stepwise complex formation reactions, which is most obvious from the ΔC_{pj}° *vs.* Z values, shown in Fig. 2. ΔC_{p1}° is fairly constant for all the elements investigated, while the values of ΔC_{p2}° pass through a pronounced

maximum. This maximum occurs in that part of the rare earth series, where the change in ΔH_2° is also largest. We suggest, for reasons outlined in the preceding communication, that the maximum in the plot of ΔC_{p2}° vs. Z is due to the presence of a hydration equilibrium of the type (1) for the complex MA_2. On the other hand the variation of ΔH_1°, which is about as large as the variation of ΔH_2, is not reflected in ΔC_{p1}°. Hence, no equilibrium of the type (1) seems probable for the formation of the first complex and the change of $\Delta H_1^\circ(Z)$ cannot be explained in the same way as the corresponding change of ΔH_2° (Z) (cf. part XI, p. 1219). This fact does not exclude gradual changes in the structure of the hydration shell, neither for the central ion nor for the first complex (as indicated by the variation of ΔH_1° and ΔS_1°). However, for each element only one species of both M and MA must be dominating.

The maximum value of $\Delta C_{p_2}^\circ$ for Ho is about 20 cal mol^{-1} K^{-1} higher than the approximately constant values of $\Delta C_{p_2}^\circ$ at the beginning and the end of the lanthanoid series. This is of the expected magnitude if the change is caused by a reaction (1) in which K for Ho equals unity and ΔH° is 2 kcal mol^{-1}.

The variation of $\Delta C_{p_3}^\circ$ with Z is opposite that of $\Delta C_{p_2}^\circ$. The complex MA_3 is coordinatively saturated by the nine donor atoms from the tridentate ligands A. Hence no hydration equilibrium of the type (1) seems probable for this species. The observed behaviour of $\Delta C_{p_3}^\circ$ vs. Z is then a natural result of the stepwise formation of the complex MA_3 from MA_2 (aq) if it is again supposed that MA_2(aq) is a mixture of two species of comparable concentrations when M is an element between Gd and Yb in the lanthanoid series.

Spectra of rare earth diglycolate and dipicolinate complexes. Spectra of solutions, containing different rare earth complexes showed only small variations with temperature (see Fig. 3). Hence, no positive evidence for an equilibrium of the type (1) can be obtained from spectral data alone.

The temperature dependence of ΔC_{pj}°. From the model presented above one would expect a positive contribution to $\Delta C_{p_3}^\circ$ from the equilibrium (1). This contribution passes through a maximum in a given temperature range for those elements, where the constant K is near unity. The values of ΔC_{pj}° in the present investigation are dependent of temperature – we have described the temperature variation of the various ΔH_j°-values with a polynomial of third degree. Because of the small number of temperatures investigated, it is difficult to decide whether the temperature dependence of ΔC_{p2} for say, Ho is different from that of Pr and Lu. However, the data indicate a contribution from (1) to the temperature variation of ΔC_{p2} for Ho; a further discussion will be given in a following communication.

Theoretical models. The interpretation of the experimental thermodynamic quantities is facilitated if one has access to a model. Various theoretical attempts have been made to describe the thermodynamics of complex formation and protonation reactions. Gurney [11] and Hammet [12] explained, *e.g.*, the minimum in log $K = f(T)$ for protonation reactions by assuming that the changes in free energy, enthalpy, and entropy were sums of terms, depending on electrostatic, covalent and cratic effects.[11] The only temperature dependent term, according to this model is that due to electrostatic effects, the temperature variation of which is given by the temperature variation of the macro-
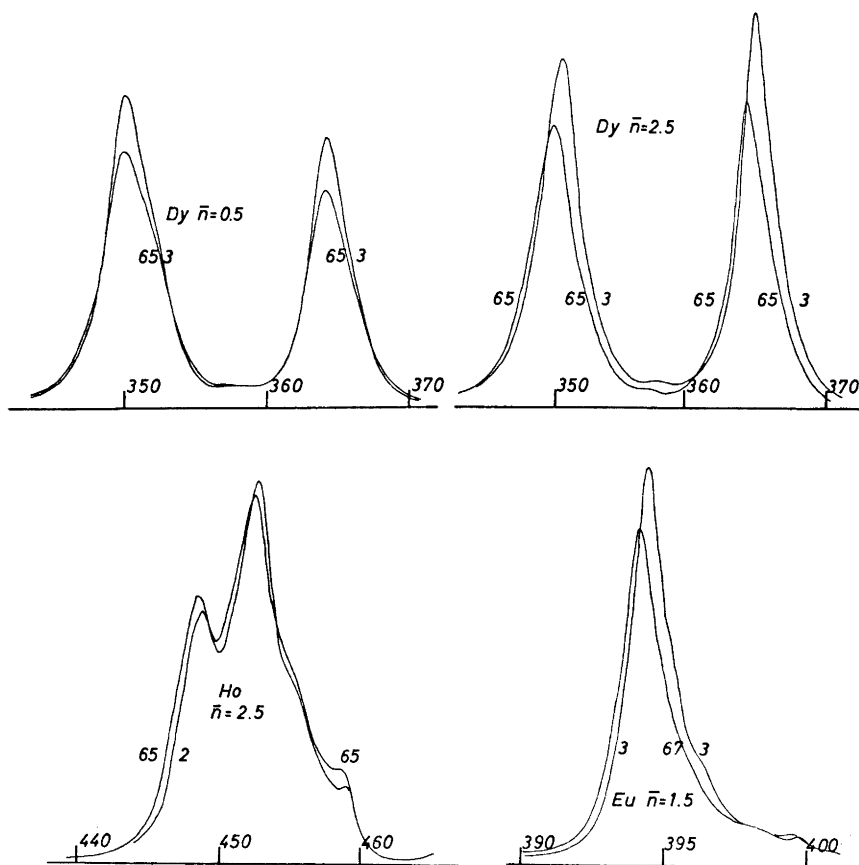
Fig. 3. Absorption spectra at the temperatures 2 – 3 and 65 – 67°C for some rare earth diglycolate solutions at varying values of $\bar{n}$. The concentrations of the solutions have been chosen so as to give a maximum absorbance of about 0.5. The absorption curves obtained at 25 and 45°C have been left out for clarity. The wave length is given in nm.

scopic dielectric constant, ε, of the medium.[12] Around room temperature, the dependence of temperature can be expressed by the empirical relation $\varepsilon = \varepsilon_0 \times e^{-T/\theta}$ for several common solvents (Ref. 11, pp. 16 and 28). The model has lately been used by Degischer and Nancollas [13] and Anderegg [14] for a number of complex formation reactions.

The following relation between the heat capacity change and the entropy change is valid, provided that all interactions are electrostatic.

$$\Delta C_p = (\Delta S - \nu \times 7.9) \times T/\theta \qquad (3)$$

If the interactions are covalent only, the value of ΔC_p is equal to zero (see Ref. 14, p. 1859, for further details).

The theory can roughly describe the magnitudes of $\Delta C_{p,}^{\circ}$ for the reactions in this study, if one assumes that the interactions are mainly electrostatic. The theory can on the other hand neither describe the variations of $\Delta C_{p_j}^{\circ}$ through the lanthanoid series nor the fact that $\Delta C_{p,}^{\circ}$ is negative. Hence it might be concluded that the quantitative success of the model is not too impressive. This might in part be due to the presence of complicating factors, such as changes in hydration, which are not included in the original model.

A quantitive explanation of the observed variations in $\Delta C_{p_j}^{\circ}$ through the lanthanoid series (or for other complexation reactions) cannot be obtained from the theoretical electrolyte models presently available. Hence, all interpretations are necessarily qualitative and must be made with full insight into the limitations of the discussions, based on the conversion from the macroscopic to the molecular level. A publication of Holzer and Emerson [15] is in this part instructive reading. Additional information on the causes to the observed variations in thermodynamic functions may be obtained by determination of the partial molal heat capacities for the ions, participating in the reactions. Work of this type is in progress and will be published in a following communication in this series.

Hydration equilibria and structure. The prevalent coordination numbers of the tervalent lanthanoids are 8 and 9 in the solid state. There are many reasons to believe, that this is the case in solution as well. The complex MA_3 is surrounded by nine coordinated oxygen atoms from three ligands.[18] Hence geometrical reasons exclude hydration equilibria of the type (1) for MA_3. The situation is different in the complex MA_2. From the known geometry of the eight- and nine-coordinated complexes [17] one expects both ligands to occupy positions in the same half of the coordination sphere with remaining coordination sites occupied by water. The configuration of the complex is thus similar to the one suggested by Hoard *et al.*[17] for EDTA-complexes. The similarity in geometry of MA_2 and MEDTA may be another reason for the presence of the same type of hydration equilibria in both complexes.

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