

## Thermodynamic Properties of Rare Earth Complexes

### XVI. Thermodynamic Model for the Description of Hydration Equilibria among Rare Earth EDTA and Oxydiacetate Complexes

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A model is used to describe the variation of  $\Delta C_P^\circ$  with both  $Z$  and  $T$  in rare earth complexation reactions where hydration equilibria are involved. The results from both the EDTA and oxydiacetate investigations are discussed according to this model.

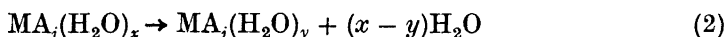
In a previous communication,<sup>1</sup> we have given a qualitative description of the effect of an equilibrium between two different states of hydration in a certain complex and the changes in some thermodynamic functions for the over-all reaction. In the following we will elaborate this description and eventually make a quantitative comparison between model and experiment.

The enthalpy change  $\Delta H^\circ$  for the over-all reaction



is obtained experimentally.  $(1-n)$  and  $n$  denote the number of mol (properly the fraction of mol) of the two different states of hydration, "x" and "y", of the complex  $MA_j$ .

If the enthalpy change for the reaction



is denoted  $\Delta H_H^\circ$ , one obtains

$$\Delta H^\circ = \Delta H^{o(x)} + n\Delta H_H^\circ \quad (3)$$

where  $\Delta H^{o(x)}$  is the change in enthalpy for the formation of one mol of the complex  $MA_j$  in the "x"-form and  $n$  is the number of mol of the complex in the "y"-form.

Derivation of expression (3) gives

$$\frac{d\Delta H^\circ}{dT} = \frac{d\Delta H^{\circ(x)}}{dT} + n \frac{d\Delta H_{\text{H}}^\circ}{dT} + \Delta H_{\text{H}}^\circ \frac{dn}{dT}$$

or

$$\Delta C_{\text{P}}^\circ = \Delta C_{\text{P}}^{\circ(x)} + n\Delta C_{\text{PH}}^\circ + \Delta H_{\text{H}}^\circ \frac{dn}{dT} \quad (4)$$

$\Delta C_{\text{P}}^\circ$  is a quantity which is obtained experimentally from the temperature variation of  $\Delta H^\circ$ .  $\Delta C_{\text{P}}^{\circ(x)}$  is the heat capacity change in a reaction where only the species  $\text{MA}_j(\text{H}_2\text{O})_x$  is formed and  $\Delta C_{\text{PH}}^\circ$  is the heat capacity change for reaction (2).  $dn/dT$  is the temperature derivate of  $n$  for the element "M".

The equilibrium constant for a possible hydration equilibrium of type (2) will be a function of both the ionic radius (or the atomic number  $Z$ ) and the temperature. As will be discussed below, the second term in the right hand of eqn. (4) will be mainly dependent on  $Z$  while the third term will be strongly dependent on  $T$ .

It is obvious that the observed non-monotonic variation of  $\Delta H^\circ$  through the rare earth series for a number of rare earth complexation reactions might be a result of a hydration equilibrium with a positive value of  $\Delta H_{\text{H}}^\circ$ , if  $n$  is gradually increasing with  $Z$  (see eqn. (3)). Regarding the terms in eqn. (4), we then know that the third term is positive as both  $\Delta H_{\text{H}}^\circ$  and consequently also  $dn/dT$  are positive. The second term must be negative as all molecular theories will give  $\Delta C_{\text{PH}}^\circ$  a negative value for  $x > y$ . The opposite signs of the last two terms in eqn. (4) result in the appearance of a maximum in  $\Delta C_{\text{P}}^\circ$  plotted as a function of  $Z$  if a hydration equilibrium is present. The maximum is situated at the element for which  $dn/dT$  is largest.

A derivation of eqn. (4) gives the following result after rearranging:

$$\frac{d\Delta C_{\text{P}}^\circ}{dT} - \frac{d\Delta C_{\text{P}}^{\circ(x)}}{dT} = 2\Delta C_{\text{PH}}^\circ \frac{dn}{dT} + n \frac{d\Delta C_{\text{PH}}^\circ}{dT} + \Delta H_{\text{H}}^\circ \frac{d^2n}{dT^2} \quad (5)$$

This expression is a measure of the contribution to the temperature variation of  $\Delta C_{\text{P}}^\circ$  caused by the presence of hydration equilibria. Thus, the difference on the left hand side in eqn. (5) represents the difference in curvature between the  $\Delta C_{\text{P}}^\circ(T)$ - and  $\Delta C_{\text{P}}^{\circ(x)}(T)$ -functions, since  $\Delta C_{\text{P}}^{\circ(x)}$  is the heat capacity change for a reaction where only the species  $\text{MA}_j(\text{H}_2\text{O})_x$  is formed (see p. 2358).

*Test of the model.* Let us now investigate how well the experimental  $\Delta C_{\text{P}}^\circ(T, Z)$ -data can be described with this model. Unfortunately, there is no possibility of making any *a priori* statements about the various quantities in eqns. (4) and (5). They have instead to be determined from the experimental data. The procedure we will follow is to determine the quantities in the equations from the  $\Delta H^\circ$ -data obtained at only one temperature, supplemented with the temperature variation of  $\Delta H^\circ$  for two elements in the series chosen so that the form  $\text{MA}_j(\text{H}_2\text{O})_x$  dominates for one element and  $\text{MA}_j(\text{H}_2\text{O})_y$  for the other at all the investigated temperatures.

*The EDTA-system.* In Fig. 1 we have plotted the enthalpy changes for the formation of the various rare earth EDTA complexes against  $Z$ .<sup>2</sup> The plots have been made for all four temperatures investigated. The basis for our test

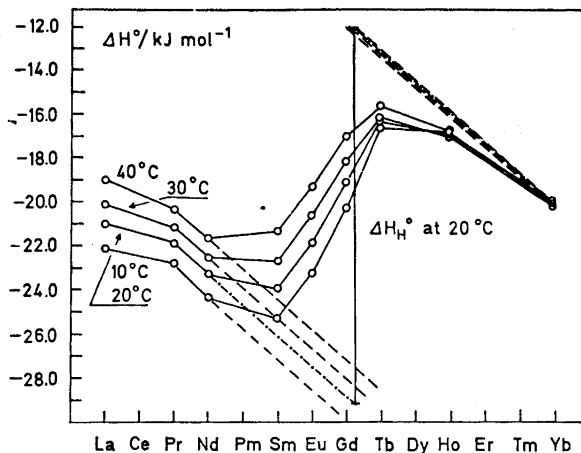


Fig. 1. The enthalpy changes  $\Delta H^\circ$  versus  $Z$  for the formation of rare earth EDTA complexes at 10, 20, 30, and 40°C. The figure demonstrates the determination of  $\Delta H_H^\circ$ . The full-drawn curves at 10, 30, and 40°C are calculated according to the model.

is the  $\Delta H^\circ - Z$  curve at 20°C. The enthalpy change,  $\Delta H_H^\circ$ , for reaction (2) is determined on the following assumptions:

1. There is a linear dependence of both  $\Delta H^{\circ(x)}$  and  $\Delta H^{\circ(y)}$  on  $Z$ .  $\Delta H^{\circ(y)}$  is the enthalpy change for the formation of one mol of the complex  $MA_n$  in the "y" form (*i.e.*  $n = 1$  in eqn. (3)).
2. The two lines are parallel, *i.e.* the  $\Delta H_H^\circ$ -value is the same for all elements in the series.
3. The slopes of the lines  $\Delta H^{\circ(x)} - Z$  and  $\Delta H^{\circ(y)} - Z$  are constant in the temperature range studied.

These assumptions are supported by empirical findings, *e.g.* a large number of investigations on the complex formation between rare earth ions and various ligands.

Under these conditions, the  $\Delta H_H^\circ$ -value at 20°C is determined as shown in Fig. 1. As indicated by the  $\Delta H^\circ - Z$  curve at 20°C in this figure, the dominating species for Pr is the "x"-form and for Yb the "y"-form. From the temperature variation of  $\Delta H^\circ$  for these two elements, the  $\Delta H_H^\circ$ -values at 10, 30, and 40°C are obtained on the same assumptions as above, *i.e.* parallel lines are drawn to the lines at 20°C. The  $\Delta H_H^\circ$ -values are given in Table 1. Normally, these values should have been fitted to the same type of function as in the preceding publication<sup>2</sup> (*i.e.* a polynomial of the third degree; Ref. 2, p. 2346), but for simplicity the temperature variation of  $\Delta H_H^\circ$  is described by a polynomial of only the second degree. This can be done without any significant loss in accuracy. From this function the value at 25°C given in Table 1 is obtained. The  $\Delta C_{PH}^\circ$ - and  $d\Delta C_{PH}^\circ/dT$ -values in the same table are obtained from the  $\Delta H_H^\circ$ -function by derivation.

Table 1.  $\Delta H_{\text{H}}^{\circ}$ ,  $\Delta C_{\text{PH}}^{\circ}$  and  $\frac{d(\Delta C_{\text{PH}}^{\circ})}{dT}$  for reaction (2) at 5, 10, 20, 25, 30, 35, 40, and 50°C for the EDTA and diglycolate complexes obtained from the functions of the type

$$\begin{aligned} \text{EDTA: } \Delta H_{\text{H}}^{\circ} &= A + BT + CT^2 \\ \text{Diglyc.: } \Delta H_{\text{H}}^{\circ} &= A + BT + CT^2 + DT^3 \end{aligned}$$

$\frac{T}{\text{K}}$	EDTA			Diglyc.	
	$\frac{\Delta H_{\text{H}}^{\circ}}{\text{J mol}^{-1}}$	$\frac{\Delta C_{\text{PH}}^{\circ}}{\text{J K}^{-1} \text{mol}^{-1}}$	$\frac{d(\Delta C_{\text{PH}}^{\circ})}{dT}$ $\text{J K}^{-2} \text{mol}^{-1}$	$\frac{\Delta H_{\text{H}}^{\circ}}{\text{J mol}^{-1}}$	$\frac{\Delta C_{\text{PH}}^{\circ}}{\text{J K}^{-1} \text{mol}^{-1}}$
278.15				15900	-67
283.15	18200	-115	1.3		
293.15	17175	-102	1.3	15350	-15
298.15	16650	-95	1.3	15300	-9
303.15	16150	-89	1.3		
308.15				15200	-13
313.15	15375	-76	1.3		
323.15				14700	-62

If the equilibrium constant for reaction (2) is  $K$ , we can apply the relation

$$\frac{d \ln K}{dT} = \frac{d}{dT} \ln \frac{n}{1-n} = \frac{\Delta H_{\text{H}}^{\circ}}{RT^2} \quad (6)$$

and calculate the  $n$ -values for each element in the series at any temperature in the range 10–40°C, provided that the  $n$ -values at one temperature are known. The necessary information can be obtained from the  $\Delta H^{\circ} - Z$  curve at 20°C in Fig. 1. This is done by calculation of that fraction of the total enthalpy change,  $\Delta H_{\text{H}}^{\circ}$ , which each of the experimental  $\Delta H^{\circ}$ -values constitutes. The  $n$ -values obtained from eqn. (6) are used for the determinations of the derivatives  $dn/dT$  and  $d^2n/dT^2$  which are necessary for the calculations according to eqns. (4) and (5).

Relation (6) can be transformed to

$$\frac{dn}{dT} = \frac{\Delta H_{\text{H}}^{\circ} n (1-n)}{RT^2} \quad (7)$$

which describes the variation of  $dn/dT$  with temperature. The values of  $n$  and  $dn/dT$  at 10, 20, 25, 30, and 40°C are given in Table 2. From these data the second and third terms on the right in eqn. (4) can be calculated at the above temperatures. The consequence of the three assumptions (p. 2353), under which the temperature dependence of  $\Delta H_{\text{H}}^{\circ}$  was determined, is that the  $\Delta C_{\text{P}}^{\circ(x)}$ -values vary with temperature but are at each temperature equal for all elements within the rare earth series. As the temperature variation of  $\Delta H^{\circ}$  for Pr is known (Ref. 2, p. 2347), the  $\Delta C_{\text{P}}^{\circ(x)}$ -values in (4) can be calculated from the experiment. The values used are 118, 76, 69, 71, and 102 J/K<sup>-1</sup> mol<sup>-1</sup> at 10, 20, 25, 30, and 40°C, respectively.

Table 2. The values of  $n$  and  $dn/dT$  for the various rare earth EDTA complexes at 10, 20, 25, 30, and 40°C.

Metal ion	283 K		293 K		298 K		303 K		313 K	
	$\frac{n}{\text{mol}}$	$\frac{dn}{dT} \times 10^3$ mol K <sup>-1</sup>	$\frac{n}{\text{mol}}$	$\frac{dn}{dT} \times 10^3$ mol K <sup>-1</sup>	$\frac{n}{\text{mol}}$	$\frac{dn}{dT} \times 10^3$ mol K <sup>-1</sup>	$\frac{n}{\text{mol}}$	$\frac{dn}{dT} \times 10^3$ mol K <sup>-1</sup>	$\frac{n}{\text{mol}}$	$\frac{dn}{dT} \times 10^3$ mol K <sup>-1</sup>
La	—	—	—	—	—	—	—	—	—	—
Pr	0	0	0	0	0	0	0	0	0	0
Nd	0	0	0	0	0	0	0	0	0	0
Sm	0.100	2.46	0.125	2.63	0.138	2.68	0.152	2.73	0.180	2.79
Eu	0.273	5.42	0.326	5.28	0.352	5.14	0.377	4.97	0.426	4.61
Gd	0.502	6.83	0.566	5.91	0.594	5.44	0.620	4.98	0.666	4.20
Tb	0.764	4.93	0.807	3.75	0.825	3.25	0.840	2.84	0.865	2.20
Ho	0.920	2.01	0.937	1.42	0.944	1.19	0.949	1.02	0.958	0.76
Yb	1.000	0	1.000	0	1.000	0	1.000	0	1.000	0

The values of  $\Delta C_p^\circ$  calculated from eqn. (4) using the data above show a satisfactory agreement with the experimental data at all temperatures (some values at 10°C are exceptions). In Fig. 2 the calculated  $\Delta C_p^\circ - Z$  curve at

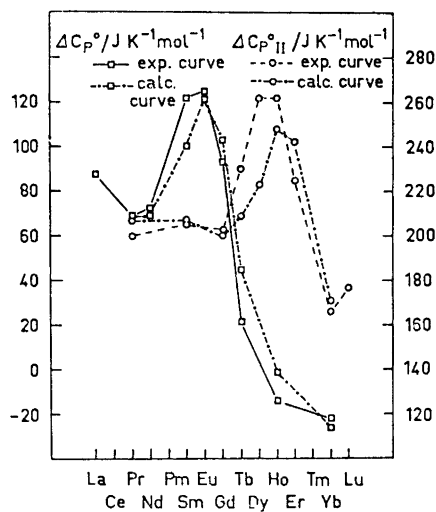


Fig. 2. The heat capacity changes at 25°C for the reactions  $\text{Ln}(\text{ClO}_4)_3 + \text{Na}_2\text{MgEDTA} \rightarrow \text{NaLnEDTA} + \text{NaClO}_4 + \text{Mg}(\text{ClO}_4)_2$  ( $-\square-$ ) and  $\text{Ln}(\text{ClO}_4)_3 + 2\text{Na}_2(\text{diglyc}) \rightarrow \text{NaLn}(\text{diglyc})_2 + 3\text{NaClO}_4$  ( $--\circ--$ ). The calculated curves for EDTA ( $-\square-\cdots-$ ) and diglycolate ( $-\circ-\cdots-$ ) are also included.

25°C is plotted together with the experimental data for the EDTA-system. It must be kept in mind that the deviations shown in Fig. 2 are a result both of errors in the model and in the experimental data. The satisfactory agreement between experimental and calculated data is a good indication for the validity of the assumptions made and consequently the model and the parameters used can be considered to be essentially correct. The same conclusion is obtained

by comparing the  $\Delta H^\circ$ -values calculated from eqn. (3), using the data in Tables 1 and 2, with the corresponding experimental quantities. (The  $\Delta H^{\circ(z)}$ -values are taken from Fig. 1). The deviation between the two quantities is in general less than 1 % ( $1\sigma$ ) at all temperatures.

*The oxydiacetate system.* A. From our previous investigations,<sup>1</sup> we know that hydration equilibria are present for the second rare earth diglycolate complexes. On the basis of the experimental determinations of the stepwise enthalpy changes,  $\Delta H_2^\circ$ , versus  $Z$  at 20°C, we tested the model presented above on the same assumptions as for the EDTA system (p. 2353). From the temperature variation of  $\Delta H_2^\circ$  for Pr and Yb (representing the "x"-form and "y"-form, respectively) it is obvious that the temperature variation of  $\Delta H_H^\circ$  is smaller here than in the EDTA system. Nevertheless, the temperature variation of  $\Delta H_H^\circ$  had to be described with a polynomial of the third degree (Ref. 2, p. 2346) in order to fit the data with sufficient accuracy. The values of  $\Delta H_H^\circ$  and  $\Delta C_{PH}^\circ$  are given in Table 1. The  $\Delta C_{PH}^\circ$ -values for the diglycolate complexes are approximately ten times lower than the corresponding values obtained for the EDTA complexes, while the  $\Delta H_H^\circ$ -values are almost the same.

Using the set of parameters given in Table 1, the  $\Delta C_{P_2}^\circ$ -values were calculated from eqn. (4) as described earlier. The  $\Delta C_{P_2}^{\circ(z)}$ -values used were the  $\Delta C_{P_2}^\circ$ -values for Pr at the various temperatures.

These calculations show that the differences between the experimental and calculated  $\Delta C_{P_2}^\circ$ -values are larger for the diglycolate complexes than for the EDTA complexes. We believe that this is a result of larger experimental uncertainties in the diglycolate measurements caused by the presence of three consecutive equilibria.

B. As pointed out earlier,<sup>1</sup> the variation of  $\Delta H_1^\circ$ , the enthalpy change for the formation of the first diglycolate complex, through the rare earth series is about as large as the variation of  $\Delta H_2^\circ$ . However, no hydration equilibrium of the type discussed above seems to be present in the formation of the first complexes as no maximum for the variation of  $\Delta C_{P_1}^\circ$  with  $Z$  is obtained. This would imply that the term  $dn/dT$  in relations (4) and (7) is zero.

One possible way to explain this behaviour is to assume a gradual change of geometry in the hydration shells of the complexes. This change must result in one definite geometry for each lanthanoid. If the total geometrical change results in an enthalpy change  $\Delta H_\alpha^\circ$  (see below), then the enthalpy change for each element can be described as a certain fraction of this quantity.

The variation of  $\Delta H_1^\circ$  with  $Z$  can, in a purely formal way, be described by eqn. (3) whether a hydration equilibrium is present or not. However, the temperature dependence of the  $\Delta H^\circ$  vs.  $Z$  curves can be used to distinguish between the two possibilities. If no temperature variation in  $n$  is observed there can be no equilibrium with a non-zero enthalpy change present in the system.

The quantities  $n$  in eqn. (3) have been determined from the experimental  $\Delta H_1^\circ(Z)$  curves at the various temperatures investigated, in the same way as described earlier for the EDTA system at 20°C (p. 2354). From these calculations one can conclude, that the quantities  $n$ , for the various rare earths, are constant with temperature; *i.e.* no solvation equilibrium is present in this step. In systems where no change in hydration occurs when the temperature is changed, we will in the following use the symbol  $\alpha$  instead of  $n$ . The constant

Table 3. The quantity  $\alpha$  for the various rare earths.

	Pr	Sm	Gd	Tb	Dy	Ho	Er	Yb	Ln
$\alpha$	0	0	0.282	0.605	0.789	0.920	0.979	1.000	—

$\alpha$ -values obtained from the above calculations for each element are given in Table 3.

Eqn. (3) can now be written as

$$\Delta H_1^\circ = \Delta H_1^{\circ(o)} + \alpha \Delta H_\alpha^\circ \quad (8)$$

where  $\Delta H_1^{\circ(o)}$  is the enthalpy change for a complex formation reaction with no additional changes involved whatsoever. Derivation of eqn. (8) will give

$$\Delta C_{P1}^\circ = \Delta C_{P1}^{\circ(o)} + \alpha \Delta C_{P\alpha}^\circ \quad (9)$$

where  $\Delta C_{P\alpha}^\circ$  is obtained from the temperature variation of the corresponding enthalpy change  $\Delta H_\alpha^\circ$ . The  $\Delta H_\alpha^\circ$ -values have been determined from the experimental data as described before (p. 2353), *i.e.* the  $\Delta H_1^\circ - Z$  curve at 20°C and the temperature variation of  $\Delta H_1^\circ$  for the elements Sm and Yb. The temperature variation of  $\Delta H_\alpha^\circ$  have been described by a polynomial of the third degree (see above) and the results are given in Table 4. On the same assumptions as before (pp. 2353 and 2354), the  $\Delta C_{P1}^{\circ(o)}$ -values in relation (9) are equal for all elements in the rare earth series.

Table 4.  $\Delta H_\alpha^\circ$  and  $\Delta C_{P\alpha}^\circ$  according to eqns. (8) and (9) for the formation of the first rare earth diglycolate complexes at 5, 20, 25, 35, and 50°C.

$T$ K	$\Delta H_\alpha^\circ$ J mol <sup>-1</sup>	$\Delta C_{P\alpha}^\circ$ J K <sup>-1</sup> mol <sup>-1</sup>
278	14770	21
293	14690	-26
298	14542	-33
308	14180	-37
323	13770	-12

The heat capacity changes calculated using eqn. (9) (and with  $\Delta C_P^{\circ(o)}$  equal to  $\Delta C_{P1}^\circ$  for Sm) show satisfactory agreement with the experimental quantities. The values at 25°C are given in Table 5. By addition of the calculated heat capacity changes for the first two consecutive steps, the over-all heat capacity changes,  $\Delta C_{P\text{II}}^\circ$ , are obtained which also are given in Table 5 at 25°C. The variation of  $\Delta C_{P\text{II}}^{\circ \text{calc}}$  with  $Z$  at 25°C has been plotted in Fig. 2 in comparison with the experimental curve. In our opinion, the agreement is satisfactory except for Dy for which we believe the experimental values are in error.

Table 5. The experimental and calculated heat capacity changes at 25°C for the reactions:

1.  $\text{Ln}^{3+} + \text{A}^{2-} \rightarrow \text{LnA}^+$
2.  $\text{Ln}^{3+} + 2\text{A}^{2-} \rightarrow \text{LnA}_2^-$

Metal ion	$\frac{\Delta C_{\text{PI}}^{\circ} \text{ exp}}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta C_{\text{PI}}^{\circ} \text{ calc}}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta C_{\text{PII}}^{\circ} \text{ exp}}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta C_{\text{PII}}^{\circ} \text{ calc}}{\text{J K}^{-1} \text{ mol}^{-1}}$
Pr	132	138	201	207
Sm	138	138	205	207
Gd	140	131	203	200
Tb	121	118	230	209
Dy	127	112	262	223
Ho	113	108	262	248
Er	113	106	225	242
Yb	117	105	166	171
Ln	117	—	177	—

We have now seen that the model can be applied to two different types of systems. In both cases the results are in fair agreement with the experimental data. In order to decide whether hydration equilibria or some other effects (*e.g.* geometrical changes) cause the typical variation of  $\Delta H^{\circ}$  with  $Z$ , the following quantities have to be determined.

1. The variation of  $\Delta H^{\circ}$  with  $Z$  at one temperature.
2. The temperature variation of  $\Delta H^{\circ}$  for one element at the beginning and one at the end of the rare earth series. (Representing  $n = 0$  and  $n = 1$  or  $\alpha = 0$  and  $\alpha = 1$ , respectively.)
3.  $\Delta H^{\circ}$  at two temperatures for an element in that part of the rare earth series where the change in  $\Delta H^{\circ}$  with  $Z$  is largest. From the last determination, information is obtained as to whether  $n$  (or  $\alpha$ ) is constant with temperature or not.

*The temperature variation of  $\Delta C_{\text{P}}^{\circ}$  for the rare earth EDTA complexes.* In the previous investigation of the rare earth diglycolate system,<sup>1</sup> we found that the  $\Delta C_{\text{P}_2}^{\circ}$ -values for the various lanthanoid complexes varied with temperature and had in all cases minima around 30°C. From the model then presented, one would expect a positive contribution to  $\Delta C_{\text{P}}^{\circ}$  for a hydration equilibrium. Such a contribution should be detectable experimentally in the temperature variation of  $\Delta C_{\text{P}}^{\circ}$  if the experimental data are accurate enough. One of the aims of EDTA investigation<sup>2</sup> was to establish whether such an effect is detectable or not.

The experimental  $\Delta C_{\text{P}}^{\circ}(T)$  curves from the EDTA measurements<sup>2</sup> indicate contribution to the temperature variation of  $\Delta C_{\text{P}}^{\circ}$  from the presence of hydration equilibria. The curve for the elements Sm and Eu, for which we have the largest contribution according to eqn. (4), seem to be less curved than those for the other elements (see Fig. 3).

Using the praseodymium system as a reference as before, we can now compare the quantities  $d\Delta C_{\text{P}}^{\circ}/dT - d\Delta C_{\text{P}}^{\circ(z)}/dT$  determined from the experiments, with the corresponding quantities calculated from the model.



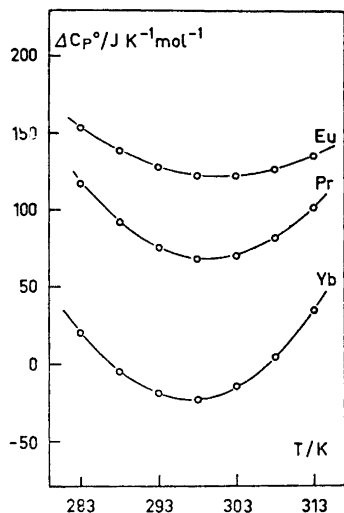


Fig. 3. The temperature variation of  $\Delta C_P^\circ$  for the formation of some rare earth EDTA complexes.

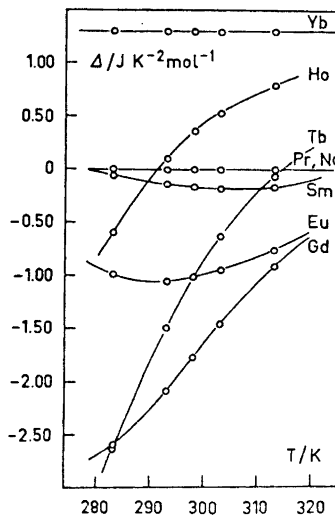


Fig. 4. The variation of  $\Delta$  with temperature for the formation of the rare earth EDTA complexes in the range 10–40°C.

The difference  $d\Delta C_P^\circ/dT - d\Delta C_P^{\circ(x)}/dT$ , is denoted  $\Delta$ . From (7) we obtain by derivation

$$\frac{d^2n}{dT^2} = \frac{\Delta C_{PH}^\circ n(1-n)T + \Delta H_H^\circ dn/dT(1-2n)T - 2\Delta H_H^\circ n(1-n)}{RT^3} \quad (10)$$

which together with the data in Tables 1 and 2 makes the determination of the right hand side in (5) possible. The calculations are made on the same assumptions as before (p. 2353). In Fig. 4 the variation of  $\Delta$  with temperature is shown for the various elements.

The slopes obtained from Fig. 4 for the various rare earths can be compared with the experimental results. With praseodymium as a reference (with only the "x"-form present) we obtain from relation (4) in Ref. 2 by derivation

$$\frac{d(\Delta_{\text{exp}})}{dT^2} = 6D_{Ln} - 6D_{Pr} = 6(D_{Ln} - D_{Pr}) \quad (11)$$

Such calculations confirm the *qualitative* description given by the model above. The only exception is Yb. The constant value of  $\Delta$  with temperature in Fig. 4 for this element is due to the use of a second degree polynomial for the description of the temperature variation of  $\Delta H_H^\circ$ . If instead a third degree polynomial is used to describe  $\Delta H_H^\circ$  vs.  $T$ , the slope of  $\Delta$  vs.  $T$  for Yb will be positive (as given by (11)), while the qualitative picture for the rest of the elements will be unchanged.

Whichever of the polynomials above is used for the description of the temperature variation of  $\Delta H_H^\circ$ , the quantitative agreement between the slopes of  $\Delta$  in Fig. 4 and those obtained from (11) is not particularly good. This is

of course not unexpected as the quantities discussed are very sensitive towards experimental errors.

*Conclusions.* 1. The observed non-monotonic variation of  $\Delta H^\circ$  with  $Z$  can be due to either solvation equilibria or discrete changes in geometry. One can distinguish between these two possibilities by the determination of the variation of  $\Delta C_p^\circ$  with  $Z$ .

2. Both the above situations can be described by the use of the model presented.

3. The success or failure in the agreement between the model and the experimental data is very much dependent on the accuracy with which the temperature derivatives of  $\Delta H^\circ$  and  $\Delta H_H^\circ$  (or  $\Delta H_\alpha^\circ$ ) can be determined.

4. As  $\Delta G_H^\circ$  varies through the rare earth series, one or both of the quantities  $\Delta H_H^\circ$  and  $\Delta S_H^\circ$  must also be varying. In the model presented above  $\Delta H_H^\circ$  has been assumed to be constant, *i.e.* the variation in  $\Delta G_H^\circ$  is entirely due to a variation in  $\Delta S_H^\circ$ . Alternatively  $\Delta S_H^\circ$  can be assumed to be a constant (see Ref. 3) with a variation in  $\Delta H_H^\circ$  through the rare earth series as a result. We prefer the first description as it makes a *direct* comparison possible between the predictions of the model and the *experimental* data.

5. As seen above the assumption of a constant  $\Delta H_H^\circ$ -value throughout the rare earth series at each temperature need not necessarily be quite correct. However, the fair agreement between the model and the experimental data indicates that a possible variation of  $\Delta H_H^\circ$  with  $Z$  must be small.

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