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Thermodynamic Properties of Rare Earth Complexes

XV. Enthalpy and Heat Capacity Changes for the Formation of Rare Earth EDTA Complexes from $MgEDTA^{2-}$ at 10, 20, 30 and 40°C

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The changes in enthalpy and heat capacity for the formation of La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Ho(III), and Yb(III) EDTA complexes according to the reaction

$$MgEDTA^{2-} + Ln^{3+} \rightarrow LnEDTA^{-} + Mg^{2+}$$

have been determined at 10.00, 20.00, 30.00, and 40.00°C. In addition, for La(III), Eu(III), and Tb(III), determinations have also been made at 15.00, 25.00, and 35.00°C. All data refer to an aqueous sodium perchlorate solvent with the sodium ion concentration equal to 1.00 M. The enthalpy changes at the various temperatures were obtained from direct calorimetric determinations and these data have been fitted to polynomials of the type

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

From these functions, the corresponding heat capacity changes have been obtained. The heat capacity data for the rare earth EDTA complexes indicate the presence of a hydration equilibrium of the same type as previously found for the second rare earth diglycolate complexes.

In previous communications,[1,2] we have discussed the relative merits of spectroscopic and thermodynamic methods to establish the occurrence of hydration equilibria among rare earth complexes. The spectroscopic method has been used very successfully in the study of hydration equilibria among the rare earth EDTA complexes.[3,4] However, it is quite clear that this method is useful only in systems where the absorption bands of the metal ion are changed substantially by changes in the coordination shell. Changes in the surroundings normally show only a small influence on the $f-f$ transitions, a fact which severely restricts the use of the spectroscopic method in lanthanoid systems.[2] Geier's study [3,4] of europium EDTA complexes is one case where the method has been applied with good results. It seemed worthwhile to

investigate this system also with the thermodynamic method, that is, a determination of ΔC_P° as outlined in Refs. 1 and 2, in order to compare the results of the two methods.

In the present investigation the enthalpy changes for the reaction

$$MgEDTA^{2-} + Ln^{3+} \rightarrow LnEDTA^- + Mg^{2+} \quad (1)$$

have been determined by a direct calorimetric method at 10, 20, 30, and 40°C. This method gives the same information on the occurrence of hydration equilibria among the $LnEDTA^-$-complexes as the direct determination

$$Ln^{3+} + EDTA^{4-} \rightarrow LnEDTA^- \quad (2)$$

but is experimentally much easier to use.

The investigation has included nine lanthanoids, *i.e.* La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Ho(III), and Yb(III). In order to investigate the accuracy of the $\Delta H^\circ - T$ functions normally obtained from four experimental temperatures only, determinations of the enthalpy changes have been made for La(III), Eu(III), and Tb(III) also at 15, 25, and 35°C.

The stability constants for reaction (1) are large [6] and a quantitative amount of $LnEDTA^-$ is thus formed when Ln^{3+} is added to a solution of $MgEDTA^{2-}$. All measurements refer to an aqueous perchlorate medium with 1.00 M total sodium ion concentration. All concentrations, volumes and additions in this study refer to 25°C as discussed in a preceding publication.[1]

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 by Grenthe *et al.*[7] The $Na_2MgEDTA$ used was obtained from the Siegfried Company. Standardization of the stock solutions of the salt was done by addition of known amounts of Zn^{2+}-ions in excess to the solutions, this excess being then back-titrated with a standard EDTA-solution using xylenol orange as an indicator. Sodium perchlorate was obtained from Baker ($NaClO_4.H_2O$, *p.a.*).

Calorimetric titrations. The calorimeter used has been recently described.[5] The experimental procedure was the same as before.[5,8] The calorimeter was filled with 100.054 cm^3 (V_0) of a solution S. From calibrated piston burettes, known volumes (v) of a solution T were added. The solutions S and T had the following compositions:

$$S \left\{ \begin{array}{l} C_M\ Ln(ClO_4)_3 \\ pH = 7.0 \\ 1.00\ M\ NaClO_4 \end{array} \right. \qquad T \left\{ \begin{array}{l} C_A\ Na_2MgEDTA \\ pH = 7.0 \\ (1.00\ M - 2\ C_A)\ NaClO_4 \end{array} \right.$$

All the concentrations, C_M, were about 10 mM. The concentration, C_A, of $MgEDTA^{2-}$ in solution T was 0.08317 M. The sodium ion concentration was 1.00 M in all the measurements.

The solution T was added in portions of 2.000 cm^3 at all temperatures. The enthalpy change (not corrected for the dilution) for reaction (1) can be calculated directly for each addition. At least four additions were made for each system at each temperature. From the concentrations given above it follows that the titrations are performed at excess of metal ion.

The solutions S were prepared just before use by a potentiometric neutralisation of the slightly acid ($\approx 10^{-3}$ M $HClO_4$) stock solutions by titration with NaOH. When the calorimetric titrations are performed at a low and constant hydrogen ion concentration, enthalpy changes associated with the protonation reactions of the EDTA-ions can be neglected. The same principle has been used previously by Spedding *et al.*[9]

However, the method used in this study has one disadvantage. The formation of hydrolytic products in the rare earth perchlorate solutions cannot be avoided. The investigations by Biedermann *et al.*[10,11] on Ce^{3+} and Y^{3+} indicate, on the other hand, that the hydrolysis at pH = 7.0 and [M] = 10 mM is negligible in the first half of the rare earth series. In the second half of the series the hydrolysis is gradually increasing so that at the end at most 1.5 % of the metal ions are present as hydroxo complexes. The predominating hydrolysis products are MOH^{2+} and $M_2(OH)_2^{4+}$ which occur in approximately equal amounts in the solutions used. The concentration of the hydroxo complexes varies with the change of concentration of the free lanthanoid ions, *i.e.* with the amount of $MgEDTA^{2-}$ complex added in the titrations. The enthalpy change associated with the dissociation of the hydroxo complexes is estimated [12–14] to 10 – 12 kJ mol^{-1} for a reaction of the type

$$MOH \rightarrow M + OH \qquad (3)$$

The influence of the hydroxo complexes on the measured enthalpy changes for reaction (1) can be estimated from Biedermann's stability constants and the above value of the enthalpy change for reaction (3). The correction is at most 200 J mol^{-1} for the elements with an ionic radius close to that of yttrium (*i.e.* the elements around erbium). This is approximately 1 % of the total heat evolved at complex formation with EDTA and cannot affect the general picture.

The heats of dilution of the T-solution have been determined and were found to be small in the whole temperature range used. The heats of dilution of the rare earth perchlorate solutions have been neglected.

The thermodynamic standard state in this study is chosen as before.[2]

RESULTS

The experimental Q-values obtained from the calorimetric titrations ranged from 2.5 to 4 J. The correction for the dilution of the $Na_2MgEDTA$-solution was largest at 10°C and at most 3 % of the total heat evolved. At higher temperatures, the correction never exceeded 1 %. The enthalpy changes calculated from the corrected Q-values for the various systems are given in Table 1. The error is given as one standard deviation and is based on five determinations, except at 40°C where only four determinations have been made. The uncertainties in the experimental $\Delta H°$-values are approximately the same for all the systems at all temperatures.

The temperature dependence of the enthalpy changes for the formation of the rare earth EDTA complexes was described by the same type of functions as for the rare earth diglycolate complexes,[2] *i.e.* polynomials of the type:

$$\Delta H° = A + BT + CT^2 + DT^3 \qquad (4)$$

The constants in the equation have been based on four experimental temperatures for all systems except for La(III), Eu(III), and Tb(III). In order to check the accuracy of such a fit, a comparison has been made for these elements between the constants obtained from experimental values at four and at seven temperatures. This comparison showed that the agreement between the two sets of constants was satisfactory and hence no significant error is introduced if the temperature dependence of the enthalpy changes are based on only four experimental values. In fact, an inspection of the results obtained for, *e.g.*, Eu, will show that the temperature variation of $\Delta C_P°$ will differ *at most* by 2 J/K mol depending on which of the two sets of constants that is used.

Table 1. The enthalpy changes $\Delta H°$ with their corresponding standard deviations for the various rare earth EDTA complexes at 10, 15, 20, 25, 30, 35, and 40°C.

Metal ion	$-\Delta H_{283}°$ / kJ mol^{-1}	$-\Delta H_{288}°$ / kJ mol^{-1}	$-\Delta H_{293}°$ / kJ mol^{-1}	$-\Delta H_{298}°$ / kJ mol^{-1}	$-\Delta H_{303}°$ / kJ mol^{-1}	$-\Delta H_{308}°$ / kJ mol^{-1}	$-\Delta H_{313}°$ / kJ mol^{-1}
La	22.113±0.045	21.512±0.061	21.004±0.023	20.579±0.059	20.111±0.050	19.614±0.034	18.989±0.060
Pr	22.825±0.026		21.886±0.065		21.182±0.052		20.351±0.052
Nd	24.391±0.050		23.304±0.095		22.560±0.037		21.672±0.097
Sm	25.334±0.070		23.946±0.041		22.716±0.061		21.354±0.020
Eu	23.270±0.040	22.540±0.103	21.881±0.039	21.242±0.050	20.651±0.012	20.014±0.039	19.369±0.021
Gd	20.323±0.025		19.133±0.010		18.181±0.029		17.067±0.029
Tb	16.658±0.052	16.489±0.079	16.385±0.034	16.275±0.027	16.177±0.017	15.933±0.032	15.649±0.019
Ho	16.834±0.045		16.928±0.017		17.052±0.009		16.798±0.017
Yb	19.976±0.092		20.003±0.031		20.206±0.016		20.140±0.044

Table 2. The enthalpy changes and heat capacity changes at 25°C calculated from the eqns. (4) for the various rare earths.

Metal ion	$-\Delta H_{298}^{\circ}$ / kJ mol^{-1}	ΔC_{p298}° / J K^{-1} mol^{-1}
La	20.567	87.5
Pr	21.528	68.9
Nd	22.920	72.4
Sm	23.330	121.8
Eu	21.251	122.8
Gd	18.651	93.5
Tb	16.284	21.5
Ho	17.012	−14.1
Yb	20.110	−22.2

The enthalpy and heat capacity changes at 25.0°C obtained from the functions of type (4) for the various rare earths are given in Table 2. The ΔH°-values at 25°C in this study are not in agreement with those reported by Spedding *et al.*[9] for the corresponding reaction (1). However, this is not unexpected because of differences in both ionic strength and ionic medium.

The variation through the rare earth series of the heat capacity change ΔC_p° at 25.0°C for reaction (1) is shown in Fig. 1. The ΔC_p°-values pass through

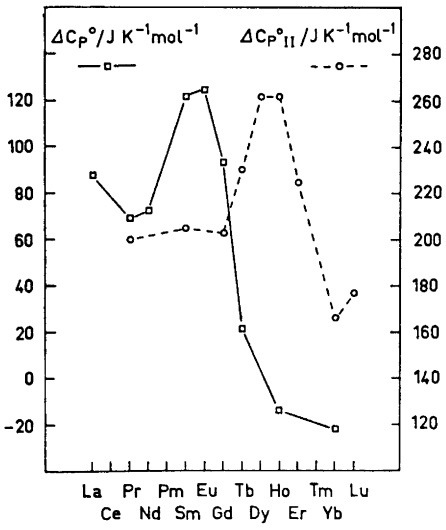

Fig. 1. The heat capacity changes at 25° for the reactions $Ln(ClO_4)_3 + Na_2MgEDTA \rightarrow NaLnEDTA + NaClO_4 + Mg(ClO_4)_2$ (□) and $Ln(ClO_4)_3 + 2Na_2(diglyc) \rightarrow NaLn(diglyc)_2 + 3NaClO_4$ (○).

a maximum at europium. The appearance of a maximum is a strong indication for the presence of a hydration equilibrium for the LnEDTA complexes. The conclusion from this investigation is in agreement with that drawn by Geier [3] on the basis of his spectroscopic investigation of the europium-EDTA system.

Thus, both the thermodynamic and spectroscopic methods give in this case compatible results.

For comparison, also the variation of the over-all heat capacity change $\Delta C_P^\circ{}_{II}$ for the diglycolate system is shown in Fig. 1. This heat capacity change corresponds to the reaction

$$Ln^{3+} + 2A^{2-} \rightarrow LnA_2^+ \quad (5)$$

The reason for the comparison between $\Delta C_P^\circ{}_{II}$ for the diglycolate system and ΔC_P° for the EDTA system is, that the geometries of the coordination shells of both complexes are expected to be similar. Both ligands in the second diglycolate complex are expected to occupy positions in the same half of the coordination sphere which results in a geometry similar to that found by Hoard *et al.*[16] in the rare earth EDTA complexes.

DISCUSSION

In a recent study, we have determined the partial molal heat capacities for various rare earth perchlorates.[15] The $\bar{C}_P^\circ$-values are very near constant through the rare earth series, from which we conclude that there are no hydration equilibria for the hydrated rare earth ions. This conclusion is in agreement with the results of previous investigations.[3,17,18] The most important result of this is that the variations of ΔC_P° with Z for complex formation reactions between the rare earth ions and ligands always will reflect the changes of the partial molal heat capacity of the complex formed.

An exception from the near constancy in $\bar{C}_P^\circ$ was found for $La(ClO_4)_3$ for which the $\bar{C}_P^\circ$-value was lower than for the other rare earths. The difference is 29 ± 6 J K^{-1} mol^{-1} which is in good agreement with the difference between the ΔC_P°-values for Pr and La found in this study. The high value of ΔC_P° for the formation of the LaEDTA complex has thus nothing to do with the hydration equilibrium discussed here, but is a reflection of the different properties of lanthanum as compared with the other rare earths. For this reason, lanthanum will be excluded from further discussion here.

The variations of $\Delta C_P^\circ{}_{II}$ and $\Delta C_P^\circ{}_{EDTA}$ with Z in Fig. 1 are very similar; *e.g.* the height of the maximum is about the same in both cases. The most obvious difference between the two systems is that the maxima occur in different parts of the rare earth series, for the EDTA complexes at Eu and for the second diglycolate complexes at Dy-Ho. (It must be pointed out once more that for the formation of the first diglycolate complexes, no hydration equilibria seem to be involved.[2]) The element for which the two differently hydrated complexes have the same free energy obviously varies with the geometry of the ligand, *e.g.* from Pr – Nd in the 1,3-diaminopropane-*N*,*N*,*N*′,*N*′-tetraacetate complexes [18] ("TMTA") *via* Eu in the EDTA complexes to Dy – Ho in the second oxydiacetate complexes.

In a recent spectroscopic investigation on lanthanoid EDTA-complexes Ternovaya and Kostromina [19] found two "isomeric forms" of europium-EDTA complexes in solution. According to their interpretation of the ex-

perimental data these two forms are: $EuEDTA(H_2O)_x$ (five-coordinated EDTA) and $EuEDTA(H_2O)_{x-1}$ (six-coordinated EDTA). Furthermore, the five-coordinated and six-coordinated forms should be the dominating species at the beginning and at the end of the rare earth series, respectively, with a region of equilibrium in between.

The Russian authors have based their interpretation on a comparison of spectra of solid lanthanoid EDTA-complexes with the corresponding spectra in solution. A necessary assumption is that there is a change in the number of bonded carboxylate groups in the solid NaLnEDTA-complexes between La and Lu. No X-ray data are supplied to corroborate this assumption. On the other hand, Hoard *et al.*[16] have made structure determinations of $KLaEDTA.8H_2O$ and $KTbEDTA.8H_2O$ and found no evidence of a change in the number of coordinated carboxylate groups.

The Russian interpretation is certainly in agreement with our thermodynamic data but, in view of the available X-ray data, we prefer our own. A change in the number of coordinated carboxylate groups might be acceptable in the EDTA-system in which the ligand has many binding sites. However, for the diglycolate complexes, for which we have found the same thermodynamic behaviour as for the EDTA-complexes, it is hard to understand how such a change of the coordination number vis-à-vis the ligand could be explained.

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