Aminopolycarboxylates of Rare Earths. 13. The Apparent Molal Volumes of the Lanthanide(III), Cobalt(III) and Chromium(III) Ethylenediamine Tetraacetate Complexes

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The apparent molal volumes of the complexes KLnedta (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er and Yb), KCoedta and KCredta were determined from density measurements. The apparent molal volumes of the complexes KLnedta show a non-monotonous change with increasing atomic number; there is a significant increase in the values between Nd and Gd. To explain the observed trend, a structural change is postulated to take place gradually on progressing from Gd towards La. With increasing ionic size, there is an increase in the metal–ligand bond distances and in the mobility of the functional groups, resulting in a jump in the number of coordinated water molecules by one between Gd and Nd. There is a further increase in the hydration of the central ions, connected with the gradual de-coordination of a carboxylate group. As a result of the gradual structural change there is one free carboxylate group on average in Laedta$^-$ and about four water molecules are coordinated in the inner sphere, while in the complexes of the elements heavier than Gd the ligand is hexadentate and only two water molecules are in the inner sphere. The apparent molal volumes of KCoedta and KCredta are practically equal and are higher than those of the lanthanide complexes; this has been explained by the stronger hydration and the more significant water-ordering effect of the Ln^{3+} ions coordinated in the complexes Lnedta$^-$.

The postulated structural changes correlate with the trend of the protonation constant values, as well as with the results of ^{1}H NMR studies on the complexes Lnedta$^-$.

Introduction

During the last 30 years the ethylenediaminetetraacetate (edta^{4-}) complexes of the lanthanide(III) ions (Ln^{3+}) have been studied in detail because of their importance in ion-exchange separation and the analytical chemistry of the lanthanides. In spite of these studies, the structures of the complexes Lnedta$^-$ in solution—the number of coordinated functional groups of the ligand and also the number of water molecules coordinated in the inner sphere of the metals—are not clear-cut, and the interpretations of the different indirect experimental results are often conflicting.

It is generally accepted that the coordination number (CN) of the Ln^{3+} ions in aqueous solution is higher than 6, probably 8 or 9 [1], and as a consequence the edta ligand does not occupy all the coordination sites. According to an X-ray diffraction study of the solid complexes KLnedta$(H_2O)_x$, the number of water molecules found in the first coordination sphere is 3 for the lighter and 2 for the heavier elements, while the coordination number decreases from 9 to 8 [2]. Similar conclusions were drawn from the trends of the stability constants of the mixed ligand complexes Ln(edta)X (X = iminodiacetate or nitrilotriacetate) and of the complexes Ln(edta)$_2$ [3, 4]. The heat capacity changes involved in the formation of the complexes Lnedta have been explained on the same assumption [5]. The visible spectra of the complexes Euedta$^-$ [6] and the change in the spectra with the variation of temperature [7] have been interpreted by assuming the formation and equilibrium of two isomeric complexes Euedta$^-$. Geier *et al.* assumed a decrease in the CN of the Ln^{3+} ions from 9 to 8 between Sm and Gd, with a gradual shift of the equilibrium $\text{Lnedta}(H_2O)_x \rightleftharpoons \text{Lnedta}(H_2O)_{x-1} + H_2O$ [7]. Kostromina *et al.* preferred the increase of the denticity of the ligand from 5 to 6, with the replacement of one water molecule by a carboxylate group [6]. For a long time the idea of Geier *et al.* was generally accepted, and the formation of hydration isomers for other Ln(III) aminopolycarboxylates was also observed [8]. The results of a ^{17}O NMR relaxation study of Gdedta$^-$ solutions have also been interpreted by assuming the formation of two hydration isomers [9]. However, to interpret the water proton relaxation times measured in the presence of the complexes Lnedta$^-$, Alsaadi *et al.* assumed the hexadentate nature of the edta ligand and a CN of 9 for all the lanthanides [10].

Since the views of the different authors are quite contradictory, it seemed worthwile to study the problem with the use of some other method.

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In the study and interpretation of the behaviour of the $Ln^{3+} \cdot aq$ ions in aqueous solution, the determination of the apparent molal volumes of $LnCl_3$, $Ln(NO_3)_3$ and $Ln(ClO_4)_3$ proved to be very valuable [11–13]. The apparent molal volume of an electrolyte reflects the degree of interaction between the ions and the solvent molecules [14], but apparent molal volumes are only rarely used to characterize complexes [15]. However, in the case of the high-stability complexes $Lnedta^-$, which undergo practically no dissociation between pH 3 and 11, determination of the apparent molal volumes is quite feasible.

To obtain information on the effect of substitution of a water molecule for a carboxylate group of edta, and to compare the properties of complexes of the tervalent lanthanides and transition metals, the apparent molal volumes of KCredta and KCoedta have also been determined.

Experimental

For the preparation of the complexes KLnedta, Ln_2O_3 of 99.9% purity (Fluka) and recrystallized H_4edta (Reanal) were used. The Ln_2O_3 was dissolved in HCl and the concentration of the $LnCl_3$ solution was determined complexometrically, using xylenol orange as indicator. The KLnedta solution obtained with the use of equivalent amounts of $LnCl_3$ and K_4-edta was left to evaporate slowly. The obtained crystals of $KLnedta \cdot (H_2O)_x$ were recrystallized from water, and the solid compound was used to prepare the KLnedta stock solution (pH ≈ 5.5–6). The concentration of the solution was determined gravimetrically. The lanthanides were precipitated as oxalates and, after ignition, were weighed as oxides. Both the analysis and the dilution of the stock solutions for the density measurements were carried out by weighing.

For the preparation of the complexes $H[Credta(H_2O)]$ and KCoedta established methods were used [15, 16]. The elemental compositions found for the complexes (C, H, N) agreed with those calculated from the formulae. KCoedta and KCredta stock solutions were made by weighing the solid complexes. For the preparation of KCredta, the pH of the solution was adjusted to 5.5 by the use of KOH.

Density measurements were carried out at 25 ± 0.01 °C with a Hereaus-Paar DMA 02C digital instrument. From the densities (d) of the solutions, the apparent molal volumes (Φ_v) were calculated using the formula:

$$\Phi_v = \frac{1000}{cd_o}(d_o - d) + \frac{M_2}{d}$$

where c is the molar concentration, d_o is the density of water (at 25.00 °C 0.99707 g/cm^3) and M_2 is the molecular weight of the complex.

The concentration interval of the measurements was limited by the sensitivity of the instrument (~0.01 *M*) and by the low solubility of the complexes KLnedta (0.1–0.2 *M*).

Results and Discussion

The apparent molal volumes calculated from the solution densities are shown in Figs. 1–3. It can be seen that Φ_v exhibits a linear dependence on $\sqrt{c}$, that is the Masson equation [14] can be applied;

$$\Phi_v = \Phi_v^o + S_v\sqrt{c}$$

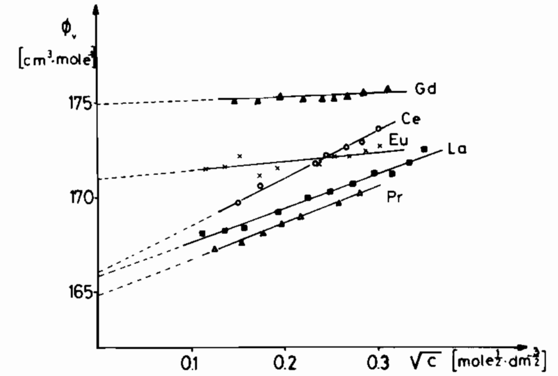

Fig. 1. The apparent molal volumes of the complexes KLnedta.

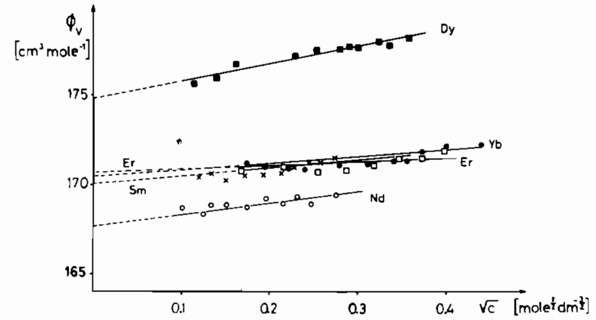

Fig. 2. The apparent molal volumes of the complexes KLnedta.

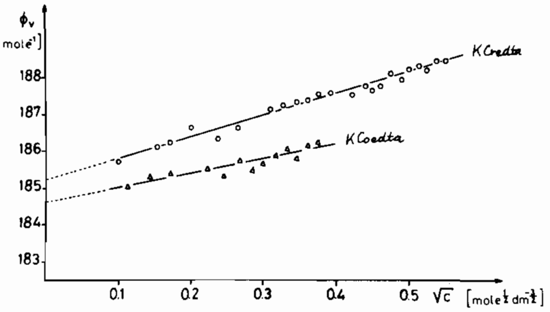

Fig. 3. The apparent molal volumes of the complexes KCoedta and KCredta.

where S_v is the slope of the straight line, and Φ_v° is the apparent molal volume extrapolated to zero concentration. For calculation of the S_v and Φ_v° values, the least squares method was used. The results are listed in Table I.

TABLE I. The Apparent Molal Volumes and S_v Values of the Complexes[a].

	Φ_v° (cm^3 mol^{-1})	S_v ($cm^{9/2}$ $mol^{-3/2}$ $10^{3/2}$)
La	166.2	16.10
Ce	166.1	24.60
Pr	164.8	19.15
Nd	167.7	6.40
Sm	170.1	3.84
Eu	170.9	2.73
Gd	175.1	1.24
Dy	174.8	9.39
Er	170.8	0.24
Yb	170.5	2.02
Co	184.6	3.81
Cr	185.2	5.71

[a]The average reproducibility of the Φ_v° values is about ±1 cm^3 mol^{-1}.

The constants S_v are different for the various lanthanides. This indicates that the Φ_v° values obtained are not equal to the partial molal volumes ($\bar{V}^\circ$) of the complexes, because the measurements were carried out at $c > 0.01$ *M*. However, the difference between the Φ_v° and $\bar{V}^\circ$ values is in general not too high for 1:1 electrolytes [14].

The Φ_v and Φ_v° values for the complexes KLnedta change with the increase of the atomic number of the lanthanides, but this change is not a monotonous one. In Fig. 4 the Φ_v° values for the complexes KLnedta and for $LnCl_3$ are plotted together. It can be seen that the trends of the Φ_v° values with increasing atomic number are similar.

The Φ_v° values of the ions are made up of several contributions, such as the intrinsic volume of the ions, the decrease in volume of the water molecules coordinated in the inner sphere (due to the high electrostatic field of the ion), and the change in structure of the solvent. As the contribution of the K^+ ions to the Φ_v° values is constant, the variations observed in the Φ_v° values (Fig. 4) are due to the differences in the complexes $Lnedta^-$. It is very probable that the intrinsic volume of the complexes decreases slightly with the decrease in the ionic size, and the other factors play the predominant role in the non-monotonous change in the Φ_v° values.

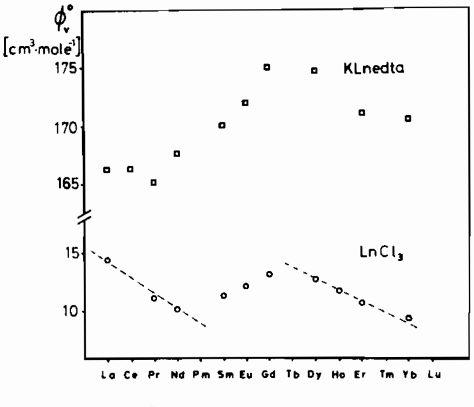

Fig. 4. The Φ_v° values of the complexes KLnedta and of $LnCl_3$ [11].

The trends in the Φ_v° values for the $Ln^{3+}\cdot aq$ ions (Fig. 4, where the contribution of the Cl^- ions is also constant) have been interpreted by Spedding *et al.* on the assumption of CNs of 9 and 8 for the lighter and the heavier elements respectively, while for Sm, Eu and Gd the formation of aqua complexes with CNs of 9 and 8 has been assumed [11–13]. The non-monotonous change of the Φ_v° values for the complexes $Lnedta^-$ also indicates a structural change between Nd and Gd, which results in a large volume increase of about 10 cm^3 mol^{-1}. The interpretation of this change is not easy without knowledge of the structures of the complexes in solution, but the results of certain other investigations can be used to give an explanation which does not contradict the experimental data.

The interpretation of the change in the Φ_v° values is not possible with only the assumption made by Geier *et al.* [7], because the de-coordination of a water molecule could not cause such a large change as that experienced. The substitution of a water molecule for a carboxylate group, as assumed by Kostromina *et al.* [6], at first seems to be a more likely conception. According to Spiro *et al.*, the formation of the Ce(III) propionate complex from propionate and Ce^{3+} ions, which likewise takes place by the displacement of a water molecule by a carboxylate group, is connected with a large volume increase of 23.6 cm^3 mol^{-1} [15]. With the use of this result, the increase in the Φ_v° values could be interpreted. Nevertheless, it is obvious that the properties of propionate and Ce^{3+} ions are far from those of the complexes $Lnedta^-$; the Φ_v° values for KCoedta and KCredta (Table I), which are practically equal, show the explanation to be erroneous.

The structures of the inert complexes $Coedta^-$ and $Credta^-$ are different. In $Credta^-$ one of the carboxylates is free and there is a water molecule in the inner sphere, while in $Coedta^-$ the ligand is hexadentate and occupies all the coordination sites [16, 17]. With regard to this difference in their structures (which are the same as those assumed by Kostromina *et al.* [6] for the $Euedta^-$ isomers), the agreement of the Φ_v° values is unexpected (we expected a higher value for $Coedta^-$). The practical agreement of the Φ_v° values is probably caused by outer sphere effects, which are of the same importance in determining the

Φ_V° values as is the volume decrease resulting from the coordination in the inner sphere [15]. The water molecules are probably more ordered around Coedta$^-$ than around Credta$^-$, because the presence of the free acetate group can disturb the structuring of the water.

To interpret the Φ_V° values in the complexes of the elements between Tb and Lu, we assume the hexadentate nature of the edta and the coordination of two water molecules in the inner sphere, in agreement with conclusions from other studies [2–7]. The Φ_V° values decrease with increasing atomic number, because both the size and the lability of the complexes are lower for the smaller ions, resulting in a more ordered water-structure around the complex.

The change in the Φ_V° values between Gd and La can be explained by assuming a significant increase in the hydration of the complexes on progressing from Gd towards La. It is probable that both types of structural changes, *i.e.* those postulated by Kostromina *et al.* [6] and Geier *et al.* [7], are involved in these complexes. As a consequence of the increasing ionic sizes, in the middle of the series (between Gd and Nd) the CN of the Ln^{3+} ions increases by one [11–13] with the coordination of a further water molecule. In parallel with this, the metal–ligand bond distances and the lability of the complexes gradually increase from Gd towards La.

The metal–ligand bonds, and particularly the metal–carboxylate oxygen bonds, are formed and broken increasingly faster for the elements of larger size [21, 22]. The decrease in the average life-time of the bonds results in a gradual increase in the average number of free carboxylates, which is about one for Laedta$^-$. The site of the free carboxylate is occupied by a water molecule, and as a result the number of water molecules coordinated in the inner sphere gradually increases, reaching a value of about four for Laedta$^-$.

The gradual increase in the number of water molecules coordinated in the inner sphere leads to a decrease in the apparent molal volumes of the complexes. However, besides this effect there is probably another important contribution to the observed large change in the Φ_V° values, namely the increasing ordering of the water molecules towards La, caused by the Ln^{3+} ions. It is known from the results of X-ray diffraction studies that the ligand edta occupies only one hemisphere around the larger Ln^{3+} ions. With the increase of the atomic number the ligand surrounds the metal ions more tightly, allowing fewer sites for the water molecules in the inner sphere [2]. This presumably also holds for the complexes in solution, where the functional groups are more labile. As a consequence of the gradual structural change, the Ln^{3+} ions exhibit an increasing ordering effect on the solvent water in the direction of La. The 'structure-making' effect of the tervalent metal ions is also very significant beyond the first coordination sphere [15] and the Ln^{3+} ions in the complexes Lnedta$^-$ can display such an effect more strongly, the less they are surrounded by the ligand.

The assumption regarding the gradual change in the structure and the increasing hydration of the complexes towards La appears to be justified by the protonation constant values (K_{LnX}^H) and by the results of ^{1}H NMR studies on the complexes.

The protonation constants (K_{LnX}^H) of the complexes Lnedta$^-$ [18] decrease very significantly with increasing atomic number. The following values were obtained in the presence of a Ln^{3+} ion excess, applied in order to decrease the error caused by the dissociation of the complexes at lower pH [19] (1 *M* KCl, 25 °C):

La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
100	54	42	35	31	27	20	8	5	3

The protonation constants of the heavier elements are too low to be determined by pH-metry.

It is known that the values of the protonation constant of the complexes formed with aminopolycarboxylate ligands depend primarily on the number of free functional groups, if the charges are equal [20]. The protonation of Coedta$^-$, where all the functional groups are coordinated, is negligible [17, 20]. However, for Credta$^-$, which has a free acetate group, $K_{CrX}^H = 89$ [20]. The protonation constant of Laedta$^-$, $K_{LaX}^H = 100$, is relatively close to this value, indicating the presence of a free carboxylate (this is an average number, because the metal–ligand bonds are labile in Laedta$^-$). The significant decrease in the protonation constants with increasing atomic number shows the ever greater hindrance of the protonation; this is presumably a consequence of the decrease in the average number of free carboxylates.

The results of ^{1}H NMR studies on the complexes, the singlet nature of the signal of the acetate methylene protons in the case of Laedta$^-$, and the appearance of an AB quartet signal for these protons in the complexes of the heavier elements, have all been interpreted in terms of the decrease in the lability of the metal–ligand bonds from La towards Lu [21, 22].

The apparent molal volumes of the complexes KLnedta are 10–20 cm^3 mol^{-1} lower than those of KCoedta and KCredta. This difference can be explained by the presence of more water molecules in the inner sphere of the Ln^{3+} ions in the complexes Lnedta$^-$, and by the higher 'structure-making' effect of the Ln^{3+} ions, which are surrounded only in part by the edta ligand.

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