Contribution from the Institute of Inorganic and Analytical Chemistry, Kossuth - University, Debrecen, Hungary

Kinetic Study of the Isotope-Exchange Reactions of the Central Ions of the Lanthanide Ethylenediaminetetraacetate and *trans*-1,2-diaminocyclohexanetetraacetate Complexes

E. Brücher and P. Szarvas

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The kinetics of the Ce, Nd, Gd, Tb, and Lu isotope-exchange reactions have been studied in weakly acidic medium in the systems Ln^{3+}–LnEDTA and Ln^{3+}–LnDCTA. The rate equations for the exchange reactions are as follows:

$$R_{LnEDTA} = k_1[LnEDTA]_t[H^+]+k_2[LnEDTA]_t[H^+]$$

$$R_{LnDCTA} = k_1'[LnDCTA]_t[H^+]$$

The rate constants for the exchange reactions of the DCTA complexes are approximately one and a half orders of magnitude smaller than those for the corresponding EDTA complexes. The values of the rate constants decrease from Ce to Lu by approximately four orders of magnitude.

In the reactions of the DCTA complexes, the exchange rate is determined by the rate of dissociation of the monoprotonated complexes HLnDCTA, and for the EDTA complexes by the rates of dissociation of the mono- or diprotonated complexes HLnEDTA and $H_2LnEDTA^+$.

Introduction

In the ion-exchange separation of large amounts of lanthanides, in general aminopolycarboxylic acids, and most frequently ethylenediaminetetraacetic acid (H_4-EDTA or H_4Y), are used as eluent.[1-3] It has long been known that in the separation with EDTA the bands of the higher atomic number lanthanides widen considerably and overlap each other.[3-4] A similar phenomenon was also observed in the separation of the lower atomic number lanthanides with the increase of the pH of the EDTA. To explain the phenomenon it was assumed that in the solution between the resin grains the dissociation of the lanthanide-EDTA complexes proceeds comparatively slowly.[3]

Studies carried out during the last few years have shown that the isotope-exchange reactions taking place between the tripositive lanthanide ions (Ln^{3+}) and their EDTA complexes proceed comparatively slowly in neutral and weakly acidic solution.[5-11] According to these studies the isotope-exchange reactions in acidic solution occur predominantly via the hydrogen ion catalysed dissociation of the LnEDTA complexes. *Betts* and co-workers found that the rate of the exchange reactions decreases with increase of the lanthanide atomic number approximately to the extent as the stability constant of the LnEDTA complexes increases.[5]

Even more recently we have made a detailed study of the kinetics of the exchange reactions of the central ions in the LnEDTA, LnDCTA ($H_4DCTA=H_4X=$ *trans*- 1,2-diaminocyclohexanetetraacetic acid) and Ln-HEDTA ($H_3HEDTA=$N–hydroxyethylethylenediaminetriacetic acid) complexes.[10,13] A relation was found between the rate of the exchange reactions and the column height value corresponding to one theoretical plate characteristic of the efficiency of the ion-exchange column.[14]

In this publication we report the results of a kinetic study of the isotope-exchange reactions taking place in the systems Ln^{3+}–LnEDTA and Ln^{3+}–LnDCTA.

Experimental Section

The chemicals used were of p.a. quality; the lanthanide oxides were products of BDH, Fluka or Johnson-Matthey, of 99,9% purity. $LnCl_3$ solutions were prepared from Ln_2O_3 with HCl. Their concentrations were determined with solutions of EDTA (Reanal) or DCTA (FCB Feinchem), previously standardised against a Cu^{2+} solution, using xylenol orange as indicator.

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The radioactive isotopes Nd-147, Gd-153, Tb-160, and Lu-177 were prepared in n, γ reactions by the reactor irradiation of the spectrally pure oxides. The Ce-144 isotope was a carrier-free preparation obtained from the Soviet Union. The purity of the radioactive isotopes was checked by radiochemical methods. Activity measurements were made with scintillation or GM counters.

The rates of the exchange reactions were studied in 0.1 M solutions (HCl) buffered with 0.01 M sodium acetate/acetic acid.

At time t = 0 the radioactive atomic species were always present in solution as the aquated Ln^{3+} ions. The anionic complexes $LnEDTA^-$ and $LnDCTA^-$ were separated from the Ln^{3+} ions on a 3 mm × 10 mm column filled with the fraction of Dowex 50X8, 2/400 mesh cation-exchange resin with a settling rate of 5-7 cm/min. At the beginning of an experiment, the shaken solution (10 ml) was forced through the column with a relatively high (20-25 drops/min, 1 drop ~0.03 ml) flow rate. When the Ln^{3+} ion concentration is less than 5×10^{-4} M, the total «free» Ln^{3+} is bonded on the resin and at the same time there is practically no exchange between the Ln^{3+} already bound and that passing through the column in complex form. At suitable times 1-2 drops of the solution dripping from the column were collected in a measuring cup and the activity measured. Since the volume of solution between the resin grains in the column is about 1 drop, the time of sampling can be determined with an error of 1-2 seconds. With this procedure it is possible to study the rates of exchange reactions with half-times greater than 30 seconds. The experimental results are well reproducible. With 3-4 parallel measurements, the exchange constants F ($F = X_t/X_\infty$, where X_t and X_∞ are the activities of the sample at time t and after establishment of the exchange equilibrium) show an average deviation of 4-6%.

The experiments were carried out at 20±0.1 °C.

Results

The rates R of the isotope-exchange reactions were calculated from the Mackay-Roginszkiy relation:[15]

$$R = -\frac{2.303}{t} \cdot \frac{ab}{a+b} \log(1-F) \qquad (1)$$

where t is the time, and a and b are the concentrations of Ln^{3+} and of the LnEDTA or LnDCTA complexes.

The rates of the exchange reactions were studied as functions of the Ln^{3+}, H^+ and complex concentrations. The experimental results are shown in Figures 1-6.

In both the Ln^{3+}–LnEDTA and Ln^{3+}–DCTA systems the rates of the exchange reactions were directly proportional to the concentration of the complexes (Figures 1 and 4) and practically independent of the Ln^{3+} ion concentration over the examined pH range (Figures 2 and 5). Figures 3 shows that the rate of exchange between Ln^{3+} and the LnEDTA complexes at higher pH values was directly proportional to the H^+ ion concentration. At lower pH values the order of reaction referring to the H^+ concentration was between 1 and 2.

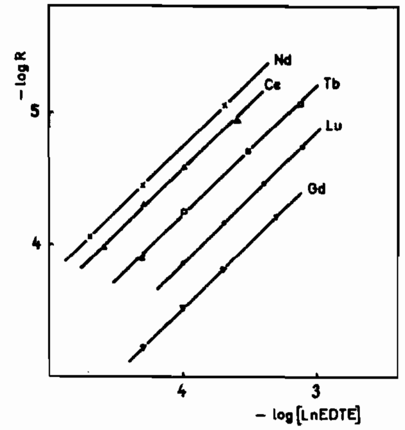

Figure 1. Dependence of the exchange rate on the LnEDTA concentration

$[Ce^{3+}] = 5 \times 10^{-5} M$, pH = 5.5
$[Nd^{3+}] = 1.5 \times 10^{-4} M$, pH = 5.83
$[Gd^{3+}] = 1 \times 10^{-4} M$, pH = 5.44
$[Tb^{3+}] = 1 \times 10^{-4} M$, pH = 5.35
$[Lu^{3+}] = 1 \times 10^{-4} M$, pH = 3.96

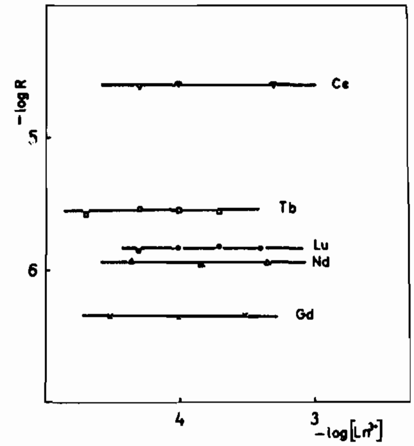

Figure 2. Dependence of the exchange rate on the Ln^{3+} ion concentration

$[CeY]_t = 1 \times 10^{-4} M$, pH = 5.62
$[NdY]_t = 2 \times 10^{-5} M$, pH = 5.83
$[GdY]_t = 1 \times 10^{-4} M$, pH = 6.12
$[TbY]_t = 1 \times 10^{-4} M$, pH = 5.73
$[LuY]_t = 2 \times 10^{-4} M$, pH = 3.96

The exchange taking place in the Ln^{3+}–LnDCTA system was directly proportional to the H^+ concentration over the entire pH range studied (Figure 6).

On the basis of the above, the apparent kinetic equations for the exchange reactions are as follows:

$$R_{LnY} = k_1[LnY]_t[H^+] + k_2[LnY]_t[H^+]^2 \qquad (2)$$

$$R_{LnX} = k_1'[LnX]_t[H^+] \qquad (3)$$

where $[LnY]_t$ and $[LnX]_t$ are the analytical concentrations of the LnEDTA and LnDCTA complexes.

The calculated values of the apparent rate constants k_1, k_2, and k_1' are given in Table I. Included in this Table are the literature rate constants for the Ce, Lu,

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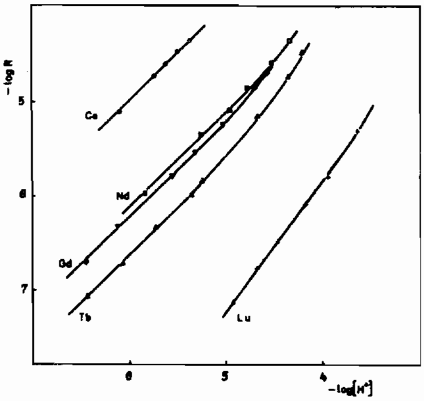

Figure 3. Dependence of the exchange rate on the H⁺ ion concentration

$[CeY]_t = 1\times10^{-4}\,M$, $[LuY]_t = 2\times10^{-4}\,M$,
$[NdY]_t = 2\times10^{-5}\,M$, $[Ce^{3+}] = 5\times10^{-5}\,M$
$[GdY]_t = [Gd^{3+}] = 1\times10^{-4}\,M$ $[Nd^{3+}] = 1.5\times10^{-4}\,M$
$[TbY]_t = [Tb^{3+}] = 1\times10^{-4}\,M$ $[Lu^{3+}] = 1\times10^{-4}\,M$

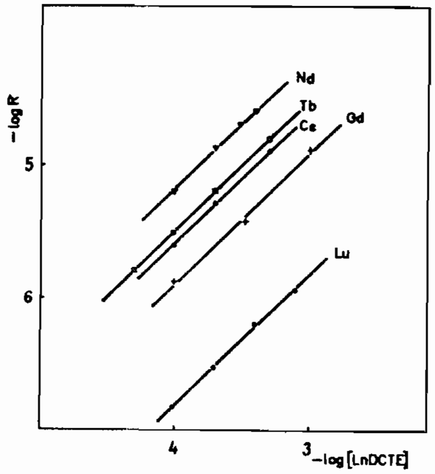

Figure 4. Dependence of the exchange rate on the LnDCTA concentration

$[Ce^{3+}] = 5\times10^{-5}\,M$, pH = 5.24
$[Nd^{3+}] = 1\times10^{-4}\,M$, pH = 4.35
$[Gd^{3+}] = 1\times10^{-4}\,M$, pH = 4.12
$[Tb^{3+}] = 1\times10^{-4}\,M$, pH = 3.05
$[Lu^{3+}] = 1\times10^{-4}\,M$, pH = 2.62

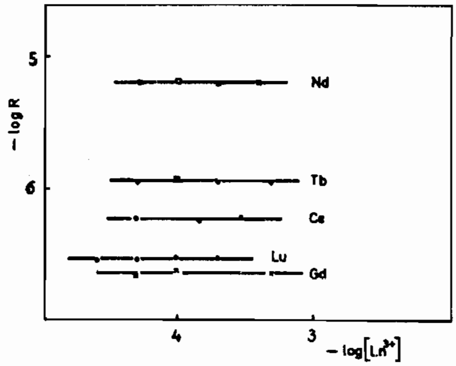

Figure 5. Dependence of the exchange rate on the Ln³⁺ concentration

$[CeX]_t = 1\times10^{-4}\,M$, pH = 4.90
$[NdX]_t = 2\times10^{-4}\,M$, pH = 4.62
$[GdX]_t = 2\times10^{-4}\,M$, pH = 3.90
$[TbX]_t = 1\times10^{-4}\,M$, pH = 3.53
$[LuX]_t = 2\times10^{-4}\,M$, pH = 2.52

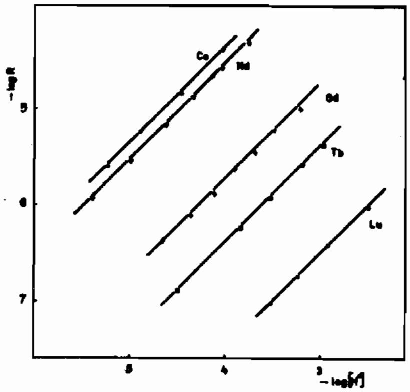

Figure 6. Dependence of the exchange rate on the H⁺ ion concentration

$[CeX]_t = 1\times10^{-4}\,M$, $[Ce^{3+}] = 5\times10^{-5}\,M$
$[NdX]_t = 2\times10^{-4}\,M$, $[Nd^{3+}] = 1\times10^{-4}\,M$
$[GdX]_t = 2\times10^{-4}\,M$, $[Gd^{3+}] = 1\times10^{-4}\,M$
$[TbX]_t = [Tb^{3+}] = 1\times10^{-4}\,M$ $[Lu^{3+}] = 1\times10^{-4}\,M$
$[LuX]_t = 5\times10^{-4}\,M$,

and Nd exchange reactions; our calculated constants agree quite well with these.

As shown by the results obtained for the Lu exchange, using the rate constants reported in Table I the calculated reaction rate values R′ agree well with the experimentally determined values R (Table II).

(The discussion of the R″ values will occur later).

Discussion

From the results shown in Figures 1-6, the isotope-exchange reactions between the Ln^{3+} ions and the LnEDTA or LnDCTA complexes take place by a dissociation mechanism. The dissociation of the complexes is catalysed by H^+ ions. The relatively slow dissociation is followed by a fast reaction between the Ln^{3+} ions and the free ligand.

This result agrees essentially with the reported results[5-11] relating to the exchange reactions of the central ions of the LnEDTA complexes. In the studies of the exchange reactions between Dy, Yb,[5] and Lu[9] and their EDTA complexes, it was found that at higher pH values the reaction rate increases to a small extent with the increase of the free Ln^{3+} ion concentration but this effect is not significant. In the studies of the La, Nd,[5] Ce[8] and Ho[7] exchange reactions, as in our work no dependence was observed of the reaction rate on the Ln^{3+} concentration.

The catalytic effect of H^+ ions on the dissociation of the complexes may be explained by assuming that the dissociation takes place via the protonation of the complexes and the rate-determining step is the formation of the protonated complexes or their dissociation. This proposal may be reasoned on the basis of rate equation (2) in the following manner. Taking into consideration the equations defining the stability constants of the protonated complexes

$$K_1 = [HLnY]/[LnY^-][H^+]$$

$$K_2 = [H_2LnY^+]/[HLnY][H^+]$$

and the experimental conditions existing at the applied

Table I. Apparent rate constants of the exchange reactions [a]

	k_1 l.mole^{-1}. sec^{-1}		k_2 l^2.mol^{-2}. sec^{-1}	k_1' l.mol^{-1}. sec^{-1}	
Ce	1.57×10^3 [8]	$(1.8 \pm0.19)\times10^3$	—	65 [8]	75 ± 7
Nd	1.08×10^3 [b] [5]	$(6.6 \pm0.35)\times10^2$	—		23 ± 0.6
Gd		87 ± 4	$(2.2\pm0.28)\times10^6$		1.5 ± 0.16
Tb		31 ± 2	$(9.5\pm0.7)\times10^5$		0.64 ± 0.05
Lu	0.23 [c] [9]	0.52 ± 0.06	$(5.4\pm0.6)\times10^3$		$(1.0 \pm0.11)\times10^{-2}$

[a] While this paper was in preparation, G. A. Nyssen and D. W. Margerum published a report (*Inorg. Chem.*, 9, 1814 (1970)) on the dissociation kinetics of LnDCTA complexes. Their results are in agreement with the k_1' values reported in this Table. [b] At 25.9 C°. [c] At 25 °C.

Table II. Values of the half-times and the rates of the LuEDTA exchange reactions

$[H^+]\times10^5$	$[LuEDTA]\times10^4$	$[Lu^{3+}]\times10^4$	$t_{1/2}$ min	$R\times10^7$ mol.l^{-1}. min^{-1}	$R'\times10^7$ mol.l^{-1}. min^{-1}	$R''\times10^7$ mol.l^{-1}. min^{-1}
23.4	2.0	1.0	9.25	50.0	50.08	50.0
11.0	2.0	1.0	31	14.5	14.7	14.6
6.76	2.0	1.0	61	7.35	7.18	7.34
3.47	2.0	1.0	137	3.19	2.98	2.94
2.09	2.0	1.0	280	1.64	1.59	1.57
1.20	2.0	1.0	610	0.73	0.83	0.82
11.0	1.0	1.0	47	7.36	7.35	7.30
11.0	4.0	1.0	18.5	30.0	29.4	29.2
11.0	8.0	1.0	12	51.3	58.8	58.4
11.0	2.0	0.5	20	13.9	14.7	14.6
11.0	2.0	2.0	45.5	15.4	14.7	14.6
11.0	2.0	4.0	58	15.9	14.7	14.6

pH value

$$[LnY^-] \gg [HLnY] \qquad [LnY]_t \approx [LnY^-]$$

rate equation (2) may be written in the form

$$R_{LnY} \approx \frac{k_1}{K_1}[HLnY] + \frac{k_2}{K_1K_2}[H_2LnY^+] \tag{4}$$

That is to say, the reaction rate is indirectly proportional to the concentration of the protonated complexes.

The dissociation of the complexes on protonation may happen according to the following two different reaction schemes:

$$LnY^- \overset{H^+}{\rightleftharpoons} HLnY \overset{H^+}{\rightleftharpoons} H_2LnY^+ \rightleftharpoons H_2Y^{2-} + Ln^{3+} \tag{5}$$

$$\begin{tikzcd}
LnY^- \arrow[r, shift left, "H^+"] & HLnY \arrow[l, shift left] \arrow[r, shift left, "H^+"] \arrow[d, shift right] & H_2LnY^+ \arrow[l, shift left] \arrow[r, shift left] & H_2Y^{2-} + Ln^{3+} \arrow[l, shift left] \\
 & HY^{3-} + Ln^{3+} \arrow[u, shift right] & &
\end{tikzcd} \tag{6}$$

The possibility of the formation of the triprotonated and tetraprotonated complexes was disregarded as in the pH range applied the order relating to H^+ ions is always less than two.

According to the findings in the determination of the stability constants of the monoprotonated HLnY complexes by pH-potentiometric method,[11,16] the first step in the reaction schemes (5) and (6) ($LnY + H^+ \rightarrow HLnY$) takes place practically instantaneously. Thus in the case of the existence of the reaction scheme (5), the order of the reaction referring to the H^+ ion concentration would be 2, as both the rate of the formation and the dissociation of the diprotonated complexes H_2LnY^+ is directly proportional to the second power of the H^+ ion concentration.

The found order of reaction 1 or smaller than 2 can be interpreted by the reaction scheme (6), when the rate determining steps are the dissociation of the monoprotonatd and diprotonated complexes:

$$HLnY \longrightarrow Ln^{3+} + HY^{3-} \tag{7}$$

$$H_2LnY^+ \longrightarrow Ln^{3+} + H_2LnY^{2-} \tag{8}$$

Considering the rate-determining role of the dissociations of the mono- and diprotonated complexes, the rate equation for the exchange reaction taking place in the Ln^{3+}–LnEDTA system is the following:

$$R_{LnY} = k_{HLnY}[HLnY] + k_{H_2LY}[H_2LnY^+] \tag{9}$$

where k_{HLnY} and k_{H_2LnY} are first order rate constants.

Expressing the concentrations of the protonated complexes in terms of the stability constants K_1 and K_2, and using the further relation

$$[LnY]_t = [LnY^-] + [HLnY] + [H_2LnY^+] \tag{10}$$

equation (9) may be re-written

$$R_{LnY} = [LnY]_t \frac{k_{HLnY}k_1[H^+] + k_{H_2LnY}K_1K_2[H^+]^2}{1 + K_1[H^+] + K_1K_2[H^+]^2} \tag{11}$$

The rate constants and the stability constants of the protonated complexes may be calculated using equation (11). The values calculated from the rates of the Gd, Tb and Lu exchange reactions (Fig. 3) are shown in Table III. (Calculations were performed with an ODRA 1013 digital computer).

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(16) R. S. Kolat and J. E. Powell, *Inorg. Chem.*, *1*, 485 (1962).

Table III. Stability constants and rate constants for the dissociation of protonated EDTA complexes

	K_1[16]	K_1	K_2	$k_{HLnY} \times 10^2$ sec^{-1}	$k_{H_2LnY} \times 10^{-3}$ sec^{-1}
Gd	500	480	0.2	16.3	25
Tb	400	350	0.17	9.0	18.3
Lu	320	300	0.12	0.16	0.18

The data of Kolat and Powell [16] for the stability constants of the monoprotonated complexes are also given in the Table. The stability constants K_2 of the very low stability diprotonated $H_2LnEDTA$ complexes are also given in the Table. The stability constants K_2 of the very low stability diprotonated H_2Ln-EDTA complexes were not determined earlier.

The good agreement of our calculated K_1 values and those obtained by the pH-potentiometric method [16] points to the correctness of our assumption concerning the rate-determining role of the dissociation of the protonated complexes. The rate values R″ calculated from rate equation (11) with the constants shown in Table III agree well with the experimentally obtained R values for the Lu exchange rate.

The rate of the exchange reactions of the DCTA complexes is directly proportional to the first power of the H^+ concentration even in relatively acidic medium (Fig. 6). Thus the Ln^{3+} exchange rate in the Ln^{3+}–LnDCTA system is determined by the rate of dissociation to Ln^{3+} ions and ligand of the monoprotonated HLnDCTA complexes. The rates of the dissociation of the DCTA complexes are lower than those of the EDTA complexes, as may be seen in Fig. 7.

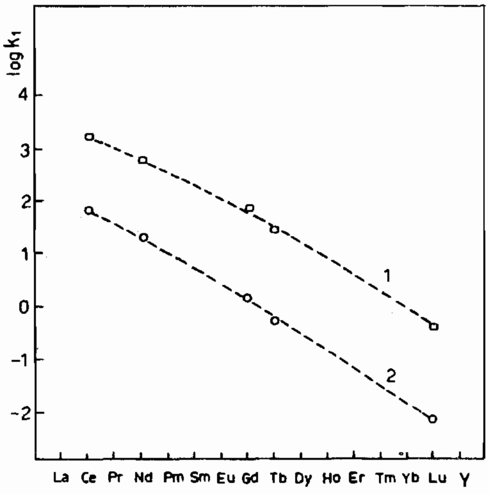

Figure 7. The rate constants k_1: 1, LnEDTA; 2, LnDCTA.

According to this Figure, the rates of the exchange reactions decrease considerably with the increase in atomic number of the lanthanides, by approximately four orders of magnitude from Ce to Lu. At the same time it is known that the stability constants of the Lu complexes are greater than those of the Ce complexes by approximately four orders of magnitude. The following relation exists in general between the rate constants k_1 and the stability constants of the complexes:

$$\frac{k_{1Ln_I}}{k_{1Ln_{II}}} \approx \frac{K_{Ln_{II}}}{K_{Ln_I}} \qquad (12)$$

where Ln_I and Ln_{II} are different lanthanide elements. Such a relation between quantities characteristic of the kinetic and thermodynamic behaviour of the complexes is the result of the very similar chemical properties of the lanthanides.

The structures of EDTA and DCTA are similar, but in spite of this their lanthanide complexes differ significantly in kinetic behaviour according to rate equations (2) and (3). The effect of the dissociation of the diprotonated complexes does not appear in the exchange reactions of the DCTA complexes. This may be interpeted to mean that the diprotonated complexes $H_2LnDCTA^+$ either do not form or are kinetically extremely labile. Clearly there must be a structural reason for this. The presence of the cyclohexane ring decreases the free rotation of the carbon between the two N atoms, stiffens the complex, and hinders the free movement of the iminodiacetate groups. There is no such restricting factor in the EDTA complexes and one of the iminodiacetate groups of the ligand can be directed away from the Ln^{3+} ion without the decomposition of the complex. On the basis of the above, the difference in kinetic behaviour of the DCTA and EDTA complexes may be explained by assuming that in the diprotonated complexes $H_2LnEDTA^+$ only one of the iminodiacetate groups is bonded to the metal ion while the two protons are bonded to the other iminodiacetate group. Because of the presence of the cyclohexane ring, relatively stable complexes $H_2LnDCTA^+$ of similar structur either do not form or are kinetically very labile and their dissociation occurs practically instantaneously; thus they have no effect on the rate of the exchange reactions.

In the pH range studied the rates of dissociation of the nonprotonated complexes $LnEDTA^-$ and $LnDCTA^-$ are practically zero whereas the dissociation of the protonated complexes proceeds relatively quickly. From this it may be concluded that a significant change takes place in the structures of the complexes on protonation.

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