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Aminopolycarboxylates of Rare Earths. 12. Determination of Formation Rate Constants of Lanthanide(III)–ethylenediamine–tetraacetate Complexes via a Kinetic Study of the Metal–Exchange Reactions

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The kinetics of the exchange reactions between Ceedta$^-$ and Nd^{3+}, Gd^{3+}, Er^{3+} and Y^{3+} were investigated. The rate of the exchange reaction increases with increasing H$^+$concentration and increasing exchanging metal ion (Ln^{3+}) concentration, but dedecreases with increase of the Ce^{3+} concentration. The exchange can take place by proton-assisted dissociation of Ceedta$^-$ and by direct attack of Ln^{3+} on the complex. The reaction proceeding through the dissociation of the protonated complex CeHedta must be treated as a reversible one. Through computer fitting of the pseudo-first-order rate constants obtained on the basis of the rate equation, the rate constants characterizing the exchange process, and also those of the reactions between Ln^{3+} and Hedta^{3-} or H$_2$edta^{2-}, have been calculated. The necessary conditions are given for the determination of the rate constants of fast complex formation reactions from the rate data of metal-exchange reactions, obtained by conventional experimental techniques.

Introduction

The kinetics of exchange of the metal ions in the lanthanide(III)–ethylenediaminetetraacetate (Lnedta$^-$ = LnX) complexes has been investigated in detail by isotope exchange [1–4] and spectrophotometry [5–7] because of the importance of these reactions in the ion-exchange separation of the lanthanides. Hence, the main features of the mechanisms of the reactions are known. The exchange can take place by the proton-catalyzed dissociation of the complexes, and also by the direct attack of the exchanging metal on the complex. In the interval 3 < pH < 5 the dissociative path predominates and it is assumed that the relatively slow dissociation of the complexes is followed by the fast reaction of the free ligand with the exchanging metal. However, the rates of these fast formation reactions have not been investigated.

In a recent study of the kinetics of the exchange reactions between Ceedta$^-$ and Ni^{2+} or Co^{2+}, we showed [7] that the reactions of the free ligand formed by the dissociation of the complex depend on the water-exchange rates of both the outcoming and the incoming metal ions. As a result, the dissociation of Ceedta$^-$ must be regarded as a reversible reaction, and the rate constant for the formation of Niedta^{2-} or Coedta^{2-} could be calculated from the rate data obtained by the conventional spectrophotometric method [7].

The formation rates of the complexes of lanthanides are very high, and the rate constants for the formation reactions are known in only a few cases [6]. With the aims of obtaining data on the formation rates of the complexes Lnedta$^-$ and of investigating the applicabilities of the method [7] in the determination of the rate constants of fast complex formation reactions, the kinetics of the following exchange reactions have been investigated:

$$\text{Ceedta}^- + \text{Ln}^{3+} \longrightarrow \text{Lnedta}^- + \text{Ce}^{3+} \quad (1)$$

where Ln = Nd, Gd, Er or Y.

Experimental

The LnCl$_3$ stock solutions used in the experiments were prepared from Ln$_2$O$_3$ of 99.9% purity (Fluka). The concentrations were determined complexometrically with a standard edta solution, using xylenol-orange as indicator. The complex KCeedta·8H$_2$O was prepared by mixing solutions of CeCl$_3$·7H$_2$O (99.9%, Koch-Light) and K$_2$H$_2$edta and the neutralizing; the K$_2$H$_2$edta was made from recrystallized H$_4$edta (p.a., Reanal).

The experiments were carried out at 25 °C, at constant ionic strength (1 mol·dm^{-3} KCl). No buffer was used, as the pH remains practically unchanged throughout the exchange reactions. The pH measurements were made with a Radiometer pHM 84 pH-meter, using a GK 2322 C combined electrode. The H$^+$ concentrations were established from the pH values via the procedure proposed by Irving *et al.* [8]. The progress of the exchange reactions was followed

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in 40 mm quartz cells with a Beckman DB-GT spectrophotometer at 280 nm, where only the absorbance of Ceedta$^-$ is significant.

With the use of the known stability constants of the complexes Lnedta$^-$ [9] the concentrations of Ceedta$^-$, Ce^{3+} and Ln^{3+} (Ln = Nd, Gd, Er or Y) were chosen so that the exchange reaction should take place practically quantitatively. Under such conditions the reactions can be regarded as pseudo-first-order ones and the rate of exchange can be given as

$$-\frac{d[\mathrm{Ceedta}]_t}{dt} = k_p[\mathrm{Ceedta}]_t \qquad (2)$$

where k_p is a pseudo-first-order rate constant and $[\mathrm{Ceedta}]_t$ is the total concentration of the complex at a given time. The constants k_p were determined from the measured absorbance values as described previously [7].

Results and Discussion

It is well known from earlier studies that the metal-exchange reactions of Lnedta$^-$ are of first order with respect to the concentration of the complex [1–5]. Thus, in the solutions investigated the concentration of Ceedta$^-$ was constant, 4×10^{-4} *M*, while the concentrations of H$^+$, Ce^{3+} and Ln^{3+} were varied. The excess of Ce^{3+} and also the Ln^{3+} concentration were high enough to guarantee the pseudo-first order for both the formation of Lnedta$^-$ and the re-formation of Ceedta$^-$.

As a practical condition, the following inequality was used: $K_{Ceedta}[Ce^{3+}]\,20 \leq K_{Lnedta}[Ln^{3+}]$ (K_{Ceedta} and K_{Lnedta} are the stability constants of the complexes). If this inequality was fulfilled, the conversion in the exchange reactions was higher than 95%.

The rate constants of the formation reactions of complexes can be determined only when the rate of the formation of Lnedta$^-$ can be slowed down by increase of the Ce^{3+} concentration. This condition is approximately fullfilled if $k_{Ce}^{-H_2O}[Ce^{3+}] > k_{Ln}^{-H_2O}[Ln^{3+}]/10$ ($k_{Ce}^{-H_2O}$ and $k_{Ln}^{-H_2O}$ are the characteristic water-exchange rate constants of Ce^{3+} and Ln^{3+}).

The pseudo-first-order rate constants, k_p, obtained at different H$^+$, Ln^{3+} and Ce^{3+} concentrations are contained in Tables I–IV.

From the tabulated data it can be seen that k_p, that is the rate of the exchange reaction, increases with the increase of the H$^+$ concentration and of the exchanging metal ion concentration. However, the increase of the Ce^{3+} concentration suppresses the rate of the reaction. Making use of the results of studies of similar reactions [1–7] we can interpret our findings on the assumption of the following reaction path:

TABLE I. k_p Values of the Reaction between Ceedta$^-$ and Nd^{3+}.

$C_{Ce^{3+}} = 0.01$ *M*					
$C_{Nd^{3+}} = 0.05$ *M*		$C_{Nd^{3+}} = 0.06$ *M*		$C_{Nd^{3+}} = 0.07$ *M*	
pH	k_p s^{-1}	pH	k_p s^{-1}	pH	k_p s^{-1}
5.019	0.040	4.895	0.057	5.303	0.040
4.895	0.047	4.874	0.059	5.070	0.052
4.771	0.058	4.771	0.070	5.031	0.055
4.661	0.072	4.587	0.10	4.950	0.061
4.335	0.15	4.153	0.29	4.862	0.070
4.228	0.20	4.060	0.38	4.799	0.078
4.079	0.30	4.045	0.39	4.707	0.092
		3.951	0.53	4.546	0.13
				4.399	0.18
$C_{Nd^{3+}} = 0.06$ *M*					
$C_{Ce^{3+}} = 0.006$ *M*		$C_{Ce^{3+}} = 0.008$ *M*		$C_{Ce^{3+}} = 0.012$ *M*	
5.540	0.033	5.844	0.026	5.601	0.026
5.525	0.034	5.664	0.028	5.542	0.027
5.142	0.053	5.439	0.033	5.405	0.030
4.830	0.091	5.221	0.041	5.258	0.033
4.766	0.10	5.102	0.048	4.773	0.062
4.518	0.18	4.956	0.059	4.554	0.093
4.251	0.35	4.739	0.087	4.226	0.20
4.050	0.63	4.645	0.11	4.153	0.25
		4.145	0.36		

TABLE II. k_p Values of the Reaction between Ceedta$^-$ and Gd^{3+}.

$C_{Ce^{3+}} = 0.02$ *M*					
$C_{Gd^{3+}} = 0.02$ *M*		$C_{Gd^{3+}} = 0.03$ *M*		$C_{Gd^{3+}} = 0.04$ *M*	
pH	k_p s^{-1}	pH	k_p s^{-1}	pH	k_p s^{-1}
6.899	0.0056	5.833	0.0090	5.675	0.013
6.283	0.0058	5.724	0.0097	5.459	0.014
5.560	0.0069	5.492	0.011	5.359	0.015
4.901	0.012	4.993	0.016	5.335	0.016
3.827	0.14	4.212	0.069	4.253	0.083
3.821	0.14	4.165	0.078	4.197	0.096
3.794	0.16	4.060	0.10	3.860	0.25
3.575	0.33	3.719	0.30	3.621	0.57
3.490	0.46	3.648	0.39		
$C_{Gd^{3+}} = 0.04$ *M*					
$C_{Ce^{3+}} = 0.01$ *M*		$C_{Ce^{3+}} = 0.03$ *M*		$C_{Ce^{3+}} = 0.04$ *M*	
6.710	0.013	5.048	0.017	5.499	0.013
5.533	0.017	4.487	0.036	4.384	0.036
5.462	0.018	4.238	0.062	4.166	0.058
5.256	0.022	4.061	0.10	4.124	0.064
4.393	0.11	3.791	0.22	4.106	0.067
4.287	0.14	3.620	0.39	3.709	0.22
4.043	0.28	3.520	0.55	3.450	0.54
		3.492	0.61		

TABLE III. k_p Values of the Reaction between $Ceedta^-$ and Er^{3+}.

$C_{Ce^{3+}} = 0.024\ M$					
$C_{Er^{3+}} = 0.0244\ M$		$C_{Er^{3+}} = 0.0385\ M$		$C_{Er^{3+}} = 0.0488\ M$	
pH	$k_p\ s^{-1}$	pH	$k_p\ s^{-1}$	pH	$k_p\ s^{-1}$
5.186	0.0074	5.370	0.0095	4.768	0.022
5.032	0.0082	5.320	0.0096	4.173	0.063
4.423	0.019	5.222	0.0099	4.122	0.072
4.181	0.031	5.190	0.010	4.108	0.074
4.002	0.048	5.119	0.010	4.106	0.074
3.739	0.10	4.935	0.011	4.024	0.091
3.706	0.12	4.740	0.013	3.946	0.11
		4.192	0.028	3.873	0.14
		4.086	0.035	3.799	0.17
				3.770	0.19
				3.748	0.20
				3.710	0.23
$C_{Er^{3+}} = 0.0385\ M$					
$C_{Ce^{3+}} = 0.012\ M$		$C_{Ce^{3+}} = 0.036\ M$		$C_{Ce^{3+}} = 0.048\ M$	
5.256	0.014	5.612	0.0092	5.370	0.0095
5.227	0.014	5.530	0.0094	5.320	0.0096
4.892	0.021	5.384	0.0098	5.222	0.0099
4.782	0.025	5.184	0.011	5.190	0.010
4.615	0.034	5.162	0.011	5.119	0.010
4.052	0.13	4.805	0.014	4.935	0.011
		4.709	0.015	4.740	0.013
		4.599	0.017	4.192	0.028
		4.462	0.021	4.086	0.035

TABLE IV. k_p Values of the Reaction between $Ceedta^-$ and Y^{3+}.

$C_{Ce^{3+}} = 0.024\ M$					
$C_{Y^{3+}} = 0.0325\ M$		$C_{Y^{3+}} = 0.052\ M$		$C_{Y^{3+}} = 0.065\ M$	
pH	$k_p\ s^{-1}$	pH	$k_p\ s^{-1}$	pH	$k_p\ s^{-1}$
4.210	0.041	5.906	0.0084	4.815	0.027
3.921	0.080	5.789	0.0087	4.384	0.058
3.760	0.12	5.082	0.015	4.163	0.092
3.627	0.17	4.580	0.032	4.084	0.11
3.528	0.22	4.473	0.039	4.061	0.12
3.274	0.46	4.472	0.039	4.055	0.12
		4.470	0.039	4.003	0.13
		4.120	0.081	3.994	0.13
		3.945	0.12	3.953	0.15
				3.770	0.23
$C_{Y^{3+}} = 0.052\ M$					
$C_{Ce^{3+}} = 0.012\ M$		$C_{Ce^{3+}} = 0.036\ M$		$C_{Ce^{3+}} = 0.048\ M$	
6.321	0.0078	5.660	0.0090	5.577	0.0092
5.777	0.0093	5.607	0.0092	5.200	0.012
5.736	0.0095	4.609	0.027	5.065	0.014
5.719	0.0096	4.430	0.038	5.011	0.015
5.540	0.011	4.275	0.051	4.512	0.031
4.752	0.029	4.202	0.060	4.501	0.031
4.701	0.032	4.189	0.061	4.255	0.050
4.181	0.095	3.864	0.13	4.224	0.053
4.009	0.14	3.862	0.13	4.107	0.068
		3.843	0.13	3.865	0.12

$$\text{Ceedta}^- + \text{H}^+ \overset{K^H}{\rightleftharpoons} \text{CeHedta} \qquad (3)$$

There is always a protonation equilibrium in these solutions. The rates of protonation and deprotonation of the complexes are very high. The protonated complex formed can dissociate; this process (rate constant k_{CeHX}) is relatively slow:

$$\begin{array}{l} \text{CeHedta} \underset{k_{H_iX}^{Ce}}{\overset{k_{CeHX}}{\rightleftharpoons}} \text{Ce}^{3+} + \text{Hedta}^{3-} \\ \qquad\qquad\qquad\qquad\quad \Big\Updownarrow \text{iH} \\ \qquad\qquad\qquad\qquad\quad \text{H}_i\text{edta}^{4-i} \end{array} \qquad (4)$$

The free ligands take part in a fast protonation equilibrium. The value of i depends on the H^+ concentration; in the pH interval studied i may be 1, 2 or 3. The species $H_i$edta react rapidly with the exchanging metal ion Ln^{3+}:

$$\text{H}_i\text{edta}^{4-i} + \text{Ln}^{3+} \xrightarrow{k_{H_iX}^{Ln}} \text{Lnedta}^- + \text{iH}^+ \qquad (5)$$

The fall in k_p with the increase of the Ce^{3+} concentration indicates the possible re-formation of $Ceedta^-$, that is the reaction is reversible. However, if $K_{LnX} \gg K_{CeX}$ and/or $C_{Ln} \gg C_{Ce}$, reaction (5) is practically irreversible.

The progress of the exchange reaction (1) thus depends on both the rate of formation of $Lnedta^-$ and the rate of re-formation of $Ceedta^-$. The rates of these processes are determined by the characteristic water-exchange rates and by the concentrations of Ce^{3+} and Ln^{3+}.

In principle, the exchange can also take place by the slow spontaneous dissociation of $Ceedta^-$ (rate constant k_{CeX}), followed by the fast formation of $Lnedta^-$, but the contribution of this reaction path is in general negligible [1–5]. The exchange reactions involving direct attack of the exchanging metal on the complex through the formation of a binuclear intermediate may play an important role at lower H^+ concentrations. Such reactions are the following:

$$\text{Ceedta}^- + \text{Ln}^{3+} \xrightarrow{k_{CeX}^{Ln}} \text{Lnedta}^- + \text{Ce}^{3+} \qquad (6)$$

$$\text{CeHedta} + \text{Ln}^{3+} \xrightarrow{k_{CeHX}^{Ln}} \text{Lnedta}^- + \text{Ce}^{3+} + \text{H}^+ \qquad (7)$$

If all the possible reaction paths (4)–(7) are taken into account, the rate equation of exchange reaction (1) can be given as

$$-\frac{d[CeX]_t}{dt} = k_{CeX}{}^{Ln}[CeX][Ln^{3+}] + k_{CeHX}{}^{Ln}[CeHX][Ln^{3+}] + k_{CeHX}[CeHX] - \sum_i k_{H_iX}{}^{Ce}[H_iX][Ce^{3+}] \quad (8)$$

The concentration of the free ligands $H_iedta^{(4-i)^-}$ varies as

$$\frac{d[H_iX]}{dt} = k_{CeHX}[CeHX] - \sum_i k_{H_iX}{}^{Ce}[H_iX][Ce^{3+}] + k_{H_iX}{}^{Ln}[H_iX][Ln^{3+}] \quad (9)$$

With regard to the large excess of Ce^{3+} and Ln^{3+} and the high stability constants of the complexes, it can be assumed that the concentration of the free ligand H_iX is very small and approximately constant, so that $d[H_iX]/dt \approx 0$. With this assumption, from (8) and (9) we obtain the following rate equation:

$$-\frac{d[CeX]_t}{dt} = k_{CeX}{}^{Ln}[CeX][Ln^{3+}] + k_{CeHX}{}^{Ln}[CeHX][Ln^{3+}] + \sum_i k_{H_iX}{}^{Ln}[H_iX][Ln^{3+}] \quad (10)$$

where $[CeX]_t = [CeX] + [CeHX]$.

If the concentrations of the species $H_iedta^{(4-i)^-}$ are expressed in terms of the protonation constants of the ligand [9] and the stability constant of $Ceedta^-$, (2) and (10) yield the following equation:

$$k_p = \frac{(k_{CeX}{}^{Ln} + k_{CeHX}{}^{Ln}K_{CeHX}[H^+] + \sum_i k_{H_iX}{}^{Ln}\beta_i[H^+]^i(K_{CeX}[Ce^{3+}])^{-1})[Ln^{3+}]}{1 + K_{CeHX}[H^+]} \quad (11)$$

TABLE V. The Rate Constants of the Formation Reactions of the $Lnedta^-$ Complexes and the $k_{CeX}{}^{Ln}$ Values.

$k\ M^{-1}\ s^{-1}$	Nd^{3+}	Gd^{3+}	Er^{3+}	Y^{3+}
$10^{-8}\ k_{HX}{}^{Ln}$	2.7 ± 0.2	3.0 ± 0.2	1.8 ± 0.1	0.9 ± 0.1
$10^{-6}\ k_{H_2X}{}^{Ln}$	1.1 ± 0.1	1.1 ± 0.1	0.54 ± 0.04	0.18 ± 0.01
$k_{CeX}{}^{Ln}$	0.35 ± 0.04	0.28 ± 0.03	0.22 ± 0.02	0.14 ± 0.02

where K_{CeHX} is the protonation constant of $Ceedta^-$ ($K_{CeHX} = 54$ [10]). The rate constants k_{CeX}, $k_{CeHX}{}^{Ln}$, $k_{HX}{}^{Ln}$ and $k_{H_2X}{}^{Ln}$ were calculated by computer-fitting (on the basis of (11)) of the pseudo-first-order rate constants k_p obtained at different H^+, Ln^{3+} and Ce^{3+} concentrations; the linear least squares method was used. Consideration of the protonation constants of edta ($\lg K_{HX} = 10.26$, $\lg K_{H_2X} = 6.16$ and $\lg K_{H_3X} = 2.67$ [9]) and of the interval in question permitted the assumption in the calculations that the value of i may be 1 and 2, and with this assumption the fitting was appropriate. The species H_3edta^- can be present in low concentration but its reaction with Ln^{3+} must be much slower than the corresponding reactions of $Hedta^{3-}$ and H_2edta^{2-}. The rate constants obtained are listed in Table 5. The contribution of the reaction taking place by the direct attack of Ln^{3+} on CeHedta has some importance only in the reaction with Y^{3+}($k_{CeHX}{}^{Y} = 200$ M^{-1} s^{-1}). In the other cases, the assumption of this reaction path led to a poorer fitting.

The rate constants obtained for the reaction between Ln^{3+} and the monoprotonated ligand $Hedta^{3-}$ are of the same order of magnitude as those obtained for other ligands, such as murexide [11], anthranilate [12] or oxalate [13] (the differences in the temperature of the experiment must be taken into account). The rates of formation of complexes from aqua metal ions and monodentate ligands are in general controlled by the rate of water loss from the inner sphere of the metal (Eigen mechanism [6]). However, in the reactions of multidentate ligands the rate of formation of the chelate ring may often be the rate-determining step. If the complex is formed by an Eigen mechanism, then the second-order formation rate constant can be expressed as the product of the water-exchange rate constant of the metal ion and the outer sphere association constant K_{os} of the ion ($(Ln(OH_2)_z{}^{3+}Hedta^{3-})$): $k_{HX}{}^{Ln} = k_{Ln}{}^{-H_2O}K_{os}$. The water-exchange rate constants of $Ln^{3+}\cdot aq$ are uncertain, but their order of magnitude is about 10^8 [6]. A more accurate value is known for $Gd^{3+}\cdot aq$: $k_{Gd}{}^{-H_2O} = 10.6 \times 10^8\ s^{-1}$ [14]. We found that $k_{HX}{}^{Gd} = 3 \times 10^8\ M^{-1}\ s^{-1}$ (Table 5), and hence $K_{os} = 0.28\ M^{-1}$. For the interaction of 3+ and 3− ions the predicted K_{os} value is much higher, about 100 M^{-1} [15]. Comparison of the calculated and the predicted values of K_{os} suggests that the formation rate constants obtained are too low for the rate of water exchange from the first coordination sphere to be rate-controlling. It seems more probable that the rate-controlling step in the reaction between $Ln^{3+}\cdot aq$ and $Hedta^{3-}$ is the ring closure.

The first step in the coordination of $Hedta^{3-}$ is presumably the formation of a metal-carboxylate oxygen bond, followed by the slower, rate-controlling coordination of the other carboxylate and the nitrogen atom of the non-protonated iminodiacetate fragment of $Hedta^{3-}$.

The rates of the reactions between $Ln^{3+}\cdot aq$ and H_2edta^{2-} are much lower; the rate constants $k_{H_2X}^{Ln}$ are 2–3 orders of magnitude smaller than k_{HX}^{Ln} (Table V).

The lower reaction rate must be connected with the structure of H_2edta^{2-} where both nitrogen atoms are protonated. It has been observed previously that the reactions of protonated multidentate ligands are slowed down by the presence of more protons [6]. In such cases it is assumed that the rate-determining step of the reaction is proton transfer (or deprotonation), involving the formation of a kinetically active species. In the reaction of H_2edta^{2-} there is also probably a slower, rate-controlling proton transfer step, making possible the coordination of a deprotonated iminodiacetate group of the ligand.

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