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Kinetics and Mechanism of the Interfacial Mass Transfer of Eu(III) in the System: Bis(2-ethylhexyl)phosphoric Acid, *n*-Dodecane-NaCl, Lactic Acid, Polyaminocarboxylic Acid, Water

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Abstract

The rate laws which characterize the interfacial mass transfer of Eu^{3+} between aqueous phases containing a mixture of lactic acid and a polyaminocarboxylic acid (DTPA or HEDTA) and organic phases containing HDEHP in *n*-dodecane have been experimentally determined. The data demonstrate that in a wide range of stirring conditions the mass transfer process is entirely controlled by the rate of interfacial chemical reactions. A reaction mechanism where the four aqueous species, Eu^{3+}, Eu–lactate, Eu–polyaminocarboxylate, and the mixed complex Eu–lactate–polyaminocarboxylate, are simultaneously reacting with the interfacially adsorbed HDEHP molecules has been worked out. This mechanism fully agrees with the experimental kinetic data. The rate constants which characterize most of the rate-determining steps have been calculated. Some practical implications of the faster mass transfer kinetics obtained with HEDTA are briefly discussed in relation to tervalent actinide-lanthanide group separations.

INTRODUCTION

In a previous paper the distribution equilibria of Eu(III) between weakly acidic aqueous solutions containing either DTPA or HEDTA and lactic acid and organic solutions of bis(2-ethylhexyl)phosphoric acid, HDEHP, have been reported (*1*). The practical importance of such a system in relation to actinide-lanthanide group separations in the so-called Talspeak process has been also discussed (*1*). A major drawback to the practical exploitation of

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such a separation system has been up till now the relatively slow extraction kinetics of some lanthanides, although it was early recognized that the extraction kinetics could be accelerated by adding to the aqueous phase large concentrations of lactic acid, e.g., 1 *M* (*2*).

Few kinetics investigations, mainly qualitative in nature, have been performed with the aim to elucidate the nature of the rate-determining steps and possibly to find out a way to accelerate the kinetics (*2–4*) of Talspeak-type processes. Previous studies have utilized experimental techniques which did not permit one to control the interfacial area available for the mass transfer process and/or have employed inadequate data treatment, where the contribution of the forward and reverse extraction rates were not separated (*2–4*). Further, all previous studies have been restricted to only one polyaminocarboxylic acid, i.e., DTPA. As a consequence, only qualitative information has been obtained on the mechanisms and no suggestions have been made on possible ways to accelerate the extraction equilibria.

In the framework of an extensive research program aiming at elucidating the mass transfer rates and mechanisms of many liquid–liquid extraction processes of metal cations, we have therefore studied the mass transfer kinetics of Eu(III). Eu(III) is in fact a typically slowly extracting cation in Talspeak-type processes. Extracting organic phases consisting of HDEHP in *n*-dodecane and aqueous phases containing a mixture of the polyaminocarboxylic acids DTPA or HEDTA and lactic acid plus an inert electrolyte (NaCl) have been used to simulate Talspeak process conditions. The experimental methodology as well as the data treatment previously described (5) to obtain mechanisms from rate laws have been followed.

The study has been performed with the double aim to elucidate the mechanisms involved and possibly to improve the process conditions by accelerating the extraction equilibria and/or reducing the amount of aqueous lactic acid.

EXPERIMENTAL

Reagents. The purity of most of the reagents has been reported in Ref. *1*. All other polyaminocarboxylic and carboxylic acids used in this work were analytical grade products. All aqueous solutions have been prepared in such a way to yield a total monovalent anion concentration equal to 1 *M*, i.e., $[Cl^-] + [lactate^-] = 1\ M$, following a procedure already described (*1*).

Rate Data. The rate data have been obtained radiometrically monitoring the ^{152,154}Eu aqueous activity in a continuous way. A constant-interfacial-area stirred cell similar to that of Ref. 5 has been used. The continuous monitoring of the Eu activity has been performed through a bypass of the cell which allowed a small volume of the aqueous phase to circulate continuously through a scintillation flow cell coupled to a phototube and a chart recorder. A peristaltic pump was used to circulate the aqueous solution.

The rate experiments performed as a function of concentrations have been carried out at the constant stirring speed of 150 rpm. The same experiments were also performed at constant chemical composition and variable stirring speeds, ranging from 50 to 170 rpm. In other experiments the specific interfacial area, a_i, i.e., the ratio between the geometrical interfacial area and the volume of the aqueous phase (equal organic and aqueous volumes were used throughout), was varied by changing either the cell diameter or the volume of the phases.

The kinetic data have been analyzed as described in Ref. 5, i.e., in terms of pseudo-first-order rate constants (or mass transfer coefficients) of the pseudo-first-order reversible extraction reaction

$$\text{Eu(III) (aqueous)} \underset{k_{oa}}{\overset{k_{ao}}{\rightleftharpoons}} \text{Eu(III) (organic)} \qquad (1)$$

The distribution ratios necessary to perform the calculations have been taken from Ref. *1*.

All experiments have been performed at the constant temperature of 25 ± 0.2°C.

Locale and Nature of the Rate-Determining Steps

Stirring Rate Dependency. The rate of liquid–liquid extraction of a metal cation in a stirred system can be controlled by both film diffusion processes and the kinetics of the chemical reactions taking place in the system. When the mass transfer rate is independent of the rate of stirring of the two phases, a kinetic regime can be assumed, i.e., only chemical reactions are controlling the rate of mass transfer (*6*). The dependence of the aqueous to organic mass transfer coefficient on the stirring rate of the two phases is shown in Fig. 1 for aqueous phases containing DTPA (full points) and HEDTA (triangles). Extraction kinetics independent of the stirring rate are obtained in both cases at 150 rpm, indicating that the extraction rate occurs in a kinetic regime.

Specific Interfacial Area Dependency. The rate of a liquid–liquid extraction process occurring in a kinetic regime can be controlled by either a homogeneous phase or interfacial chemical reactions. In the latter case a linear dependence must exist between the mass transfer coefficient and the specific interfacial area (*6*). This kind of dependency is shown in Fig. 2. The

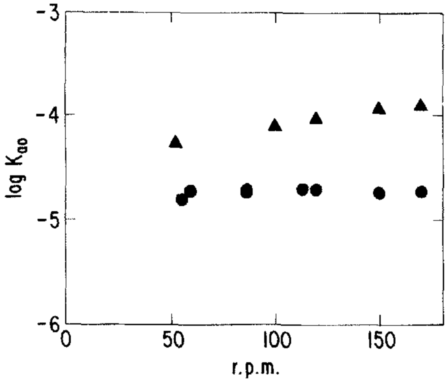

FIG. 1. Dependence of the aqueous to organic mass transfer coefficient, k_{ao}, on the stirring rate of the aqueous and organic phases, rpm. (▲) Organic phase, HDEHP 0.01 *F* *n*-dodecane; aqueous phase, HEDTA 0.05 *M*, lactic acid 0.4 *M*, $-\log [H^+] = 3.0$. (●) Organic phase, HDEHP 0.1 *F* *n*-dodecane; aqueous phase, DTPA 0.05 *M*, lactic acid 0.5 *M*, $-\log [H^+] = 3.0$.

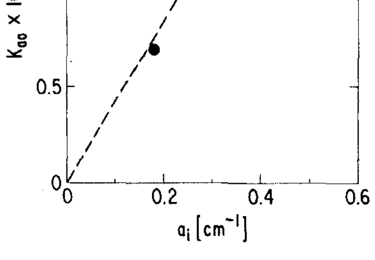

FIG. 2. Dependence of the aqueous to organic mass transfer coefficient, k_{ao}, on the specific interfacial area. a_i = interfacial area/aqueous volume. Organic phase; HDEHP 0.002 *F* *n*-dodecane. Aqueous phase: HEDTA 0.05 *M*, lactic acid 0.4 *M*, $-\log]H^+] = 3.0$.

conclusion can then be reached that the rate of extraction of Eu^{3+} into *n*-dodecane solutions of HDEHP from weakly acidic aqueous solutions containing DTPA or HEDTA and lactic acid is controlled by interfacial chemical reactions.

Rate Laws and Proposed Mechanisms

I. Extraction Rate Law and Mechanism without Aqueous Complexing Agents

In a previous paper (5) it has been shown that in the absence of interfacial film diffusional contributions, the mass transfer rate of Eu^{3+}, between aqueous chloride solutions ($\mu = 1$) and *n*-dodecane solutions of HDEHP, can be interpreted in terms of an interfacial mechanism. According to this mechanism the aqueous Eu^{3+} cations react with the interfacially adsorbed HDEHP molecules, forming an interfacial complex intermediate which is then transferred into the organic phase by reacting with the HDEHP dimer molecules present in the organic bulk. The equations which describe this mechanism, when $-\log [H^+] > 2$, are the following:

$$M + 3(HX)_i \underset{k_{-1}}{\overset{k_1^*}{\rightleftharpoons}} (MX_3)_i + 3H \tag{2}$$

$$(MX_3)_i + 3\overline{(HX)_2} \underset{k_{-2}^*}{\overset{k_2}{\rightleftharpoons}} \overline{MX_3 \cdot 3(HX)} + 3(HX)_i \tag{3}$$

$$v_I = -\frac{d[Eu^{3+}]}{dt} = \frac{k_1 a_D^3}{a_D^3 + \dfrac{k_{-1}}{k_2} h^3} m - \frac{k_{-2} h^3}{\dfrac{k_2}{k_{-1}} a_D^3 + h^3} \overline{m} \tag{4}$$

In Eqs. (2)–(4) as well as in the equations which follow, charges have been dropped, the subscript *i* indicates interfacially adsorbed species, the bar organic species, HX is HDEDHP, a_D is the HDEHP dimer activity (*1*), h is the H^+ concentration, m is the Eu^{3+} aqueous concentration, $\overline{m}$ is the europium organic concentration, and $k_1 = k_1^*[(HX)_i]^3$, $k_{-2} = k_{-2}^*[(HX)_i]^3$ [the interfacial concentration of HDEHP is constant for HDEHP $> 10^{-4}$ *F* in *n*-dodecane (*7*)].

II. Extraction Rate Law and Mechanism in the Presence of Lactic Acid

The influence that the presence of lactate anions in the aqueous solutions has on the pseudo-first-order rate constants, k_{ao} and k_{oa}, is shown in Fig. 3. These data are fitted by the following empirical rate laws:

$$k_{ao} = \frac{A_1(1 + \beta_1 l)}{1 + \Sigma\beta_i l^i} \tag{5}$$

$$k_{oa} = A_2 + A_3 l \tag{6}$$

where A_1, A_2, and A_3 are empirical rate constants, β_i are the europium–lactate complex formation constants (*1*), and l stands for the lactate anion concentration evaluated from Eq. (1) of Ref. *1*. Rate equations in agreement with rate laws (5) and (6) can be derived by assuming that, in addition to the mechanism described in Section I, a similar mechanism occurs in the presence of lactic acid, with the 1:1 europium–lactate complex being the additional reacting species. It follows:

$$\mathrm{ML} + 3(\mathrm{HX})_i \underset{k_{-3}}{\overset{k_3^*}{\rightleftharpoons}} (\mathrm{MLX_3})_i + 3\mathrm{H} \tag{7}$$

$$(\mathrm{MLX_3})_i + 3(\overline{\mathrm{HX}})_2 \underset{k_{-4}^*}{\overset{k_4}{\rightleftharpoons}} \overline{\mathrm{MX_3 \cdot 3(HX)}} + 3(\mathrm{HX})_i + \mathrm{L} \tag{8}$$

$$v_{\mathrm{II}} = -\frac{d[\mathrm{ML}]}{dt} = \frac{k_3 a_{\mathrm{D}}^3 \beta_1 l}{a_{\mathrm{D}}^3 + \dfrac{k_{-3}}{k_4} h^3}\, m - \frac{k_{-4} h^3 l}{\dfrac{k_4}{k_{-3}} a_{\mathrm{D}}^3 + h^3}\, \overline{m} \tag{9}$$

where $k_3 = k_3^*[(\mathrm{HX})_i]^3$, $k_{-4} = k_{-4}^*[(\mathrm{HX})_i]^3$, ML is the 1:1 europium–lactate complex, and L is the lactate anion. In writing Eqs. (7) and (8) the same $[\mathrm{H}^+]$ and $[(\overline{\mathrm{HX}})_2]$ dependencies experimentally evaluated in Ref. 5 have been assumed. The overall rate law, taking into account that both Eu^{3+} and EuL^{2+} can react at the interface with HDEHP, is then obtained by summing Eqs. (4) and (9). Considering that in the aqueous phase

$$[\mathrm{Eu}]_{\mathrm{tot}} = [\mathrm{Eu}^{3+}](1 + \Sigma\beta_i l^i) \tag{10}$$

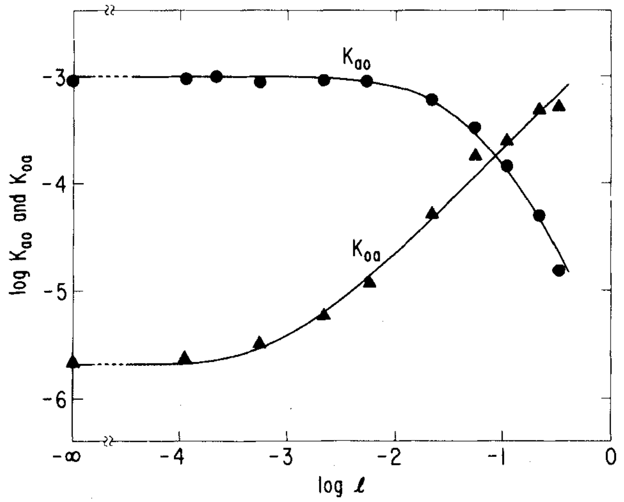

FIG. 3. Dependence of the pseudo-first-order rate constants, k_{ao} (●) and k_{oa} (▲) on the aqueous lactate concentration, l. Organic phase: HDEHP 0.005 F n-dodecane. Aqueous phase: Variable lactic acid, $-\log [H^+] = 2.66$. The solid lines have been calculated by Eqs. (11) and (12) with rate constants of Table 1 and equilibrium constants from Ref. *1*.

and assuming that Eu^{3+} and EuL^{2+} behave as identical kinetic units, i.e., setting for the Eu–lactate complex the same rate constants as for Eu^{3+}, $k_1 = k_3$, the following expressions are obtained for the pseudo-first-order rate constants

$$k_{ao} = f_1 \frac{(1 + \beta_1 l)}{(1 + \Sigma\beta_i l^i)} \tag{11}$$

$$k_{oa} = f_{-1}(k_{-2} + k_{-4} l) \tag{12}$$

where $k_1 = k_3$, $k_{-1}/k_2 = k_{-3}/k_4$ and

$$f_1 = \frac{k_1 a_D^3}{a_D^3 + \dfrac{k_{-1}}{k_2} h^3}$$

$$f_{-1} = \frac{h^3}{\dfrac{k_2}{k_{-1}} a_D^3 + h^3}$$

Equations (11) and (12) fit well the experimental data as shown by the calculated solid lines of Fig. 3. The k_{-4} constant has been evaluated by best fitting the k_{oa} data. The rate constants which have been used to calculate the solid lines of Fig. 3 by Eqs. (11) and (12) are reported in Table 1.

III. Extraction Rate Law and Mechanism in the Presence of Polyaminocarboxylic Acids (no lactic acid)

The pseudo-first-order rate constants in the presence of HEDTA and DTPA at the total constant concentration of 0.05 *M* and $[H^+] = 10^{-3}$ *M* are shown in Fig. 4. The data indicate an independence from the lactate anion concentration in the range $0\text{–}10^{-3}$ *M*. The lactate independent mass transfer coefficients can be represented by the empirical relationships

$$k_{ao} = A_4 \qquad (13)$$

$$k_{oa} = A_5 \qquad (14)$$

where A_4 and A_5 are empirical rate constants. These constants cannot be derived from rate Eq. (4), properly taking into account the H^+ and HDEHP activities as well as the decreased concentration of Eu^{3+}, caused by the presence of the polyaminocarboxylic acid. In fact, by dividing the first terms of Eq. (4) by the term $(1 + \Sigma\gamma_n[H_nY])$, representing the complexity sum (*1*), k_{ao} values about 10^3 (for DTPA) and 10^2 (for HEDTA) lower than the experimental ones are obtained. Therefore the presence of new interfacially reactive species, Eu-HEDTA and Eu-DTPA, has to be assumed. By writing for these species the same equations as for the Eu–lactate species:

$$\mathrm{MY} + 3(\mathrm{HX})_i \underset{k_{-5}}{\overset{k_5^*}{\rightleftharpoons}} (\mathrm{MYX_3})_i + 3\mathrm{H} \qquad (15)$$

$$(\mathrm{MYX_3})_i + 3\overline{(\mathrm{HX})}_2 \underset{k_{-6}^*}{\overset{k_6}{\rightleftharpoons}} \overline{\mathrm{MX_3}\cdot 3(\mathrm{HX})} + 3(\mathrm{HX})_i + \mathrm{Y} \qquad (16)$$

it follows, under the same assumptions as in Case II, that

$$v_{\mathrm{III}} = -\frac{d[\mathrm{MY}]}{dt} = f_3\gamma_0 y m - f_{-3} y \overline{m} \qquad (17)$$

TABLE 1

Interfacial Rate Constants k_i (cm·s^{-1})

Forward reactions		Reverse reactions	
k_1 Eu^{3+}	$(1.00 \pm 0.05) \times 10^{-3}$	k_{-1}/k_2 $(MX_3)_i$	$(1.33 \pm 0.1) \times 10^{-2}$
k_3 Eu–lactate^{2+}	$(1.00 \pm 0.05) \times 10^{-3}$	k_{-2} EuX_3 3(HX)	$(2.3 \pm 0.1) \times 10^{-4}$
k_5 Eu–HEDTA	$(2.2 \pm 0.2) \times 10^{-5}$	k_{-4} EuX_3 3(HX) + lactate	0.25 ± 0.01
k_5 Eu–DTPA	$(2.0 \pm 0.2) \times 10^{-6}$	$\frac{k_{-6}k_{-5}}{k_6}$ EuX_3 3(HX) + HEDTA	$(2.0 \pm 0.2) \times 10^{8}$
k_7 Eu–HEDTA–lactate	$(1.4 \pm 0.1) \times 10^{-4}$	$\frac{k_{-6}k_{-5}}{k_6}$ EuX_3 3(HX) + DTPA	$(1.7 \pm 0.3) \times 10^{14}$
$k_7\ \eta_1$ Eu–DTPA–lactate	$(2.5 \pm 0.3) \times 10^{18}$	$\frac{k_{-7}k_{-8}}{k_8}$ EuX_3 3(HX) + HEDTA + lactate	$(1.9 \pm 0.2) \times 10^{10}$
$k_9\ \eta_2$ Eu–HEDTA–lactate$_2$		$\frac{k_{-7}k_{-8}}{k_8}$ EuX_3 3(HX) + DTPA + lactate	$(8 \pm 0.5) \times 10^{15}$
$k_9\ \eta_2$ Eu–DTPA–lactate$_2$	$(1.2 \pm 0.1) \times 10^{3}$	$\frac{k_{-9}k_{-10}}{k_9}$ EuX_3 3(HX) + HEDTA + 2 lactate	0.11 ± 0.02
		$\frac{k_{-9}k_{-10}}{k_9}$ EuX_3 3(HX) + DTPA + 2 lactate	3.5 ± 0.3

where

$$f_3 = \frac{k_5 a_D^3}{a_D^3 + \frac{k_{-5}}{k_6} h^3}, \qquad f_{-3} = \frac{k_{-6} h^3}{\frac{k_6}{k_{-5}} a_D^3 + h^3}$$

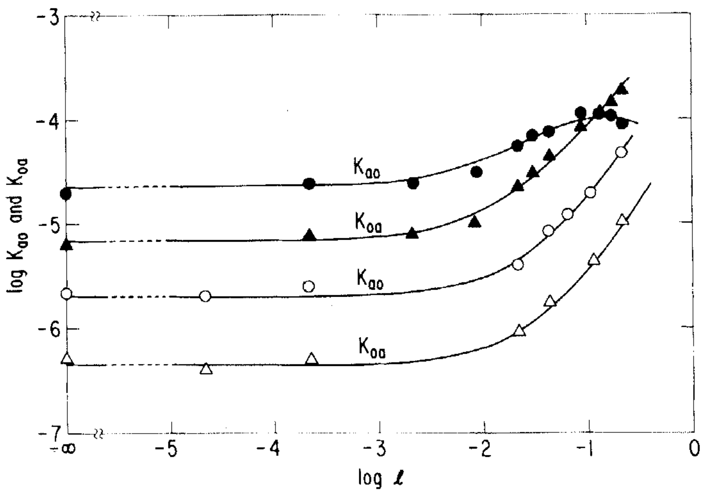

FIG. 4. Pseudo-first-order rate constants k_{ao} and k_{oa} vs aqueous lactate concentration in the aqueous phase, *l*. (●) k_{ao}, (▲) k_{oa}, organic phase, HDEHP 0.01 *F* *n*-dodecane; aqueous phase, HEDTA 0.05 *M*, $-\log[H^+] = 3.0$. (○) k_{ao}, (△) k_{oa}, organic phase, HDEHP 0.1 *F* *n*-dodecane; aqueous phase, DTPA 0.05 *M*, $-\log[H^+] = 3.0$. The solid lines have been calculated by Eqs. (23) and (24) with rate constants of Table 1 and the complex formation constants of Ref. *1*.

Y stands for the polyaminocarboxylic acid anion of charge $-z$, $y = [Y^{-z}]$, and γ_0 is the Eu^{3+}–Y^{-z} complex formation constant. The new rate constants describing Steps (15) and (16) are reported in Table 1. They have been evaluated from the lactate-independent experimental data of Fig. 4 using the mass transfer coefficient equations which are easily derived by summing Rates (17) and (4).

IV. Extraction Rate Law and Mechanism in the Presence of Polyaminocarboxylic Acid and Lactic Acid

The data of Fig. 4 show an increase of the pseudo-first-order rate constants when the lactic acid concentration varies between 10^{-2} and 1 *M*. This lactate acceleration effect cannot be explained by summing rates v_I, v_{II}, and v_{III}, substituting for the H^+ and HDEHP activities, and deriving the mass transfer coefficients by considering that in this case the total aqueous europium concentration has been lowered by a factor $(1 + \Sigma\beta_i l^i + \Sigma\gamma_n[H_nY] + y\Sigma\eta_j l^j)$. (The new complexity sum also includes here the formation of Eu–polyaminocarboxylate–lactate mixed complexes through the term $y\Sigma\eta_j l^j$, which has been described by Eqs. 6 and 7 of Ref. *1*.) In fact, the lactate-dependent rate terms of Eqs. (11) and (12) are too small to compete with the polyaminocarboxylate-dependent rate terms of Eq. (17). However, the rate data of Fig. 4 are easily explained if one considers the mixed complexes, which are present in the solution (*1*), as the interfacially reactive species which cause the lactate-dependent increase of the pseudo-first-order rate constants. Under the same assumption as for Cases II and III, the following reaction steps and rate equation can be derived for the interfacial reactions of the EuYL and $EuYL_2$ mixed complexes:

$$\mathrm{MYL} + 3(\mathrm{HX})_i \underset{k_{-7}}{\overset{k_7^*}{\rightleftharpoons}} (\mathrm{MYLX_3})_i + 3\mathrm{H} \tag{18}$$

$$(\mathrm{MYLX_3})_i + 3(\overline{\mathrm{HX}})_2 \underset{k_{-8}^*}{\overset{k_8}{\rightleftharpoons}} \overline{\mathrm{MX_3}\cdot 3(\mathrm{HX})} + 3(\mathrm{HX})_i + \mathrm{Y} + \mathrm{L} \tag{19}$$

$$\mathrm{MYL_2} + 3(\mathrm{HX})_i \underset{k_{-9}}{\overset{k_9^*}{\rightleftharpoons}} (\mathrm{MYL_2X_3})_i + 3\mathrm{H} \tag{20}$$

$$(\mathrm{MYL_2X_3})_i + 3(\overline{\mathrm{HX}})_2 \underset{k_{-10}^*}{\overset{k_{10}}{\rightleftharpoons}} \overline{\mathrm{MX_3}\cdot 3(\mathrm{HX})} + 3(\mathrm{HX})_i + \mathrm{Y} + 2\mathrm{L} \tag{21}$$

$$\begin{aligned} v_{\mathrm{IV}} &= -\left(\frac{d[\mathrm{MYL}]}{dt} + \frac{d[\mathrm{MYL_2}]}{dt}\right) \\ &= (f_4\eta_1 yl + f_5\eta_2 yl^2)m - (f_{-4}yl + f_{-5}yl^2)\overline{m} \end{aligned} \tag{22}$$

where

$$f_4 = \frac{k_7 a_{\mathrm{D}}^3}{a_{\mathrm{D}}^3 + \dfrac{k_{-7}}{k_8} h^3}, \qquad f_5 = \frac{k_9 a_{\mathrm{D}}^3}{a_{\mathrm{D}}^3 + \dfrac{k_{-9}}{k_{10}} h^3}$$

$$f_{-4} = \frac{k_{-8} h^3}{\dfrac{k_8}{k_7} a_{\mathrm{D}}^3 + h^3}, \qquad f_{-5} = \frac{k_{-10} h^3}{\dfrac{k_{10}}{k_{-9}} a_{\mathrm{D}}^3 + h^3}$$

The overall rate expression, capable of explaining the data of Figs. 3 and 4, as well as those of Ref. 5, is then obtained by summing v_{I}, v_{II}, v_{III}, and v_{IV}. Expressing the quantity m as a function of the total aqueous europium concentration and complexity sum, considering that at $-\log [\mathrm{H}^+] = 3.0$ it is

$$a_{\mathrm{D}}^3 \gg \frac{k_{-i}}{k_i + 1} h^3 \qquad (i = 5, 7, 9)$$

and

$$a_{\mathrm{D}}^3 \frac{k_i}{k_{-(i-1)}} \gg h^3 \qquad (i = 2, 6, 8, 10)$$

the following equations are derived for the pseudo-first-order rate constants

$$k_{\mathrm{ao}} = \frac{[k_1(1 + \beta_1 l) + k_5\gamma_0 y + k_7\eta_1 y l + k_9\eta_2 y l^2]}{(1 + \Sigma\beta_i l^i + \Sigma\gamma_n[\mathrm{H}_n\mathrm{Y}] + y\Sigma\eta_j l^j)} \tag{23}$$

$$k_{\mathrm{oa}} = \frac{h^3}{a_{\mathrm{D}}^3}\left[\frac{k_{-1}}{k_2}(k_{-2} + k_{-4}l) + \frac{k_{-5}k_{-6}}{k_6} y + \frac{k_{-7}k_{-8}}{k_8} yl + \frac{k_{-9}k_{-10}}{k_{10}} yl^2\right] \tag{24}$$

The rate constants, which describe the reactivity of the mixed complexes, have been determined by best fitting the experimental data of Fig. 4 with Eqs. (23) and (24). Their numerical values are reported in Table 1. The solid curves of Fig. 4 have been calculated by Eqs. (23) and (24) using the rate constants of Table 1. Finally, Fig. 5 shows how the pseudo-first-order rate constants vary with the HDEHP dimer activity a_{D}. The kind of dependence of both k_{ao} and k_{oa} on a_{D} is of the same type as that previously demonstrated in the absence of both lactic acid and polyaminocarboxylic acid (*5*). This result gives further support to the adequacy of the formulated reaction steps and f_i functions to represent the rate data.

DISCUSSION

The results obtained in this investigation can be explained by assuming that the mechanism which controls the interfacial dissociation of the Eu–

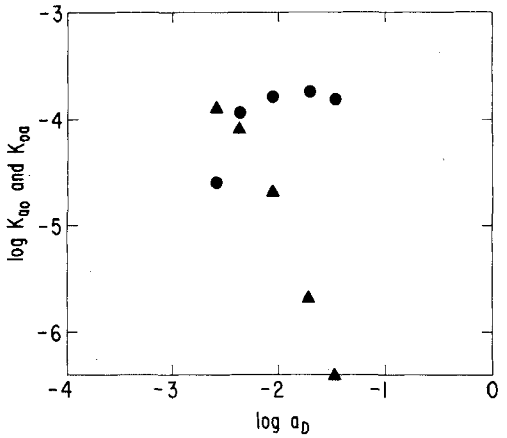

FIG. 5. Dependence of the pseudo-first-order rate constants k_{ao} (●) and k_{oa} (▲) vs dimer activity of HDEHP in *n*-dodecane, log a_D. Aqueous phase: HEDTA 0.05 *M*, lactic acid 0.4 *M*, $-\log [H^+] = 3.0$.

polyaminocarboxylate species is of the same type as that previously proposed for the homogeneous dissociation of polyaminocarboxylates (*8*). Although the influence that the proton activity has on the rate constants has not been studied here because of the impossibility of separating the several and tightly intercorrelated effects (HDEHP extraction dependency, aqueous anion concentration, etc.), it is reasonable to assume that also in this case the main step leading to the dissociation of the metal polyaminocarboxylate is a fast protonation equilibrium followed by the rate determining dissociation of the protonated species (*8*). The accelerating effect caused by the presence of the lactate anions can also be explained on the same line as that produced by acetate ions on the rate of isotopic exchange of various lanthanide–polyaminocarboxylate complexes (*8*). Considering that the lanthanide–polyaminocarboxylate complex has a structure where the chelating ligand is relegated to only one hemisphere of the metal cation, the other hemisphere being occupied by coordination water molecules (*10*), the possibility exists for lactate anions to substitute these water molecules, forming a mixed complex. The formation of this mixed complex has been indeed proved in the HEDTA case (*1*) which behaves as a pentadentate ligand. In the case of the octadentate ligand, DTPA, the formation of the mixed complex should be less favored because of the larger crowding of the coordinating groups around the Eu ion. No thermodynamic evidence of its existence has been in fact obtained. The formation of the mixed complex should then result in a labilization of the polyaminocarboxylate complex with respect to the

TABLE 2[a]

Influence of Various Carboxylic Acids on the Eu^{3+} Mass Transfer Coefficient k_{ao}

Carboxylic acid	Conc (M)	K_d	k_{ao} (cm/s)	$\log \frac{k_{ao}}{[R{-}COO^-]}$	$\log \beta_1$
None	—	3.1	2.3×10^{-5}	—	—
Lactic	0.1	2.4	5.6×10^{-5}	−2.59	2.95
Glycolic	0.1	2.7	5.2×10^{-5}	−2.56	2.93
2-Methyl-lactic	0.1	2.5	4.9×10^{-5}	−2.49	2.69
Mandelic	0.1	2.6	6.1×10^{-5}	−2.82	2.25
Maleic	0.05	3.9	2.3×10^{-5}	−3.32	3.83
Fumaric	0.05	3.8	2.6×10^{-5}	−3.04	2.86

[a] *Organic phase*: HDEHP 0.01 F n-dodecane. *Aqueous phase*: HEDTA 0.05 M, $\log[H^+] = -3.0, \mu = 1.0$. $[R{-}COO^-]$ has been computed from the pk_a values of Ref. *11*. β_1 = complex formation constant between Eu^{3+} and the carboxylate anion from Ref. *11*.

HDEHP attack. This labilization is probably the result of the reduced effective charge on the metal cation which weakens the metal-nitrogen bonds. This catalytic effect is not restricted to lactic acid. In fact, as the data of Table 2, as well as those of Refs. *3* and *4*, show, all hydroxy-carboxylic acids exhibit a similar tendency. This finding is in agreement with the literature which reports the stronger tendency to form mixed complexes exhibited by secondary ligand containing hydroxyl groups bonded to aliphatic chains (*9*). As far as the influence of the nature of the polyaminocarboxylic acid on the mass transfer coefficients is concerned, the data of Table 3 indicate a good inverse correlation with the formation constants of the europium complex. This is an expected result since more weakly complexing aminocarboxylic

TABLE 3[a]

Influence of Various Polyaminocarboxylic Acids on the Eu^3 Mass Transfer Coefficient k_{ao}

Polyaminocarboxylic acid	Conc (M)	K_d	k_{ao} (cm/s)	$\log \gamma$
HEDTA	0.005	6.5×10^2	4.6×10^{-4}	15.45
EDTA	0.005	4.9×10^2	3.3×10^{-4}	17.32
PDTA	0.005	2.9×10^2	3.2×10^{-4}	18.26
DTPA	0.005	2.0×10	6.3×10^{-5}	22.39

[a] *Organic phase*: HDEHP 0.01 F n-dodecane. *Aqueous phase*: Lactic acid 0.5 M, $\log[H^+] = -3.0$, $\mu = 1.0$. $[R{-}COO^-]$ has been computed from the pk_a values of Ref. *11*. β_1 = complex formation constant between Eu^{3+} and the polyaminocarboxylate anion from Ref. *11*.

TABLE 4

Comparison between Some Mass Transfer Coefficients of Eu^{3+}, k_{ao}, in the presence of HEDTA and DTPA

Polyaminocarboxylic acid	Lactic acid	k_{ao} (cm/s)
DTPA 0.05 *M*	1 *M*	4.7×10^{-5}
HEDTA 0.05 *M*	0.4 *M*	1.1×10^{-4}
DTPA 0.05 *M*	1 *M*	4.7×10^{-5}
HEDTA 0.05 *M*	0.1 *M*	5.6×10^{-5}

acids should be more easily labilized by lactic acid. More weakly complexing polyaminocarboxylic acids also show a decreased selectivity in complexation between lanthanides and actinides.

Finally, some practical suggestions can be obtained from the comparison of the mass transfer coefficients reported in Table 4. A larger mass transfer coefficient by a factor of 2 can be obtained with HEDTA than with DTPA at less than half the lactic acid concentration. Alternatively, the largest value of the mass transfer coefficient obtainable with DTPA at a lactic acid concentration of 1 *M* is obtained with HEDTA when the lactic acid concentration is 10 times smaller. Since, as shown in Ref. *1*, good separation factors between Am(III) and Eu(III) are also obtained with HEDTA, this polyaminocarboxylic acid could be a possible alternative to DTPA in actinide–lanthanide separation processes of the Talspeak type.

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