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Distribution Equilibria of Eu(III) in the System: Bis(2-ethylhexyl)phosphoric Acid, Organic Diluent—NaCl, Lactic Acid, Polyaminocarboxylic Acid, Water

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Abstract

The distribution equilibria of Eu^{3+} between aqueous phases containing lactic acid and *N'*-(2hydroxyethyl)ethylenediamine-*N,N,N'*-triacetic acid (HEDTA) or diethylenetriamine-*N,N,N',N',N''*-penetaacetic acid (DTPA) at constant ionic strength ($\mu = 1.0$), and *n*-dodecane solutions of HDEHP have been studied. The formation constants of the simple Eu–lactate complexes and Eu–lactate–HEDTA mixed complex were evaluated from the K_d data. The conclusion is reached that no lactic acid is coextracted into the organic phase at tracer metal concentrations. The separation factors between Eu^{3+}, Pm^{3+}, and Am^{3+} have been evaluated in the presence of HEDTA.

INTRODUCTION

The distribution equilibria of tervalent lanthanide and actinide ions between weakly acidic aqueous phases containing a mixture of polyaminocarboxylic acid and lactic acid and organic solutions of bis(2-ethylhexyl)phosphoric acid, HDEHP, have attracted the interest of previous investigators because of their practical implications (*1*–*5*). An actinide-lanthanide group separation is in fact possible using these chemical conditions, and a separation scheme based on such a system was indeed proposed by Weaver and Kappelmann using DTPA in the so-called Talspeak process (*6*).

However, because of the applied nature of these studies, few data have

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been reported where sufficiently well-defined chemical conditions were used to allow one to evaluate correctly the stoichiometry of the reactions involved and their formation constants. The difficulty of controlling the chemical conditions of such a system in terms of activities of both the aqueous and the organic species is not a trivial problem when one considers that highly concentrated lactic acid aqueous solutions and nonideal organic solutions are involved.

The present investigation has been performed in order to better identify some of the equilibria involved in Talspeak-related processes, and particularly the possible formation of mixed Eu(III)–polyaminocarboxylic–lactic acid complexes. In our study, control over the activity coefficients of the aqueous phase metal species and anions has been obtained by using a constant ionic medium. The influence that concentrated aqueous lactic acid solutions have on the hydrogen ion activity has been also carefully considered by potentiometric glass electrode measurements. The activity coefficients of the organic extractant have been reported in a previous investigation (*7*).

EXPERIMENTAL

Reagents

The radionuclides ^{241}Am, $^{152\text{-}154}$Eu, and ^{147}Pm were obtained from ANL stocks. Complexing reagents were obtained from the following sources: Lactic acid 85% (American Drug and Chemical Co.), *N*′-(2-hydroxyethyl)-ethylenediamine-*N*,*N*,*N*′-triacetic acid (HEDTA) 99% (Aldrich), diethylenetriamine-*N*,*N*,*N*′,*N*′,*N*″-pentaacetic acid (DTPA) (Aldrich). The lactic acid and HEDTA were used as obtained and the DTPA was recrystallized three times from water. *n*-Dodecane was a Phillis 66 99% pure product, and diethylbenzene was a high purity Aldrich product. HDEHP, purified by the method of Ref. *13*, was an Eastman Kodak Co. product.

Determination of the [H$^+$] Concentration

All the aqueous solutions used in this work have been prepared in such a way to yield a final total monovalent anion concentration equal to 1 *M*, i.e., $[\mathrm{Cl}^-] + [\mathrm{lactate}^-] = 1$ *M*, by mixing proper amounts of NaCl and lactic acid solutions.

In order to evaluate the lactate anion concentration, the acid dissociation constant of lactic acid at $\mu = 1.0$, $K_a = 2.77 \times 10^{-4}$, from Ref. *3* has been used. The equilibrium lactate anion concentration, l, has been then calculated by the equation

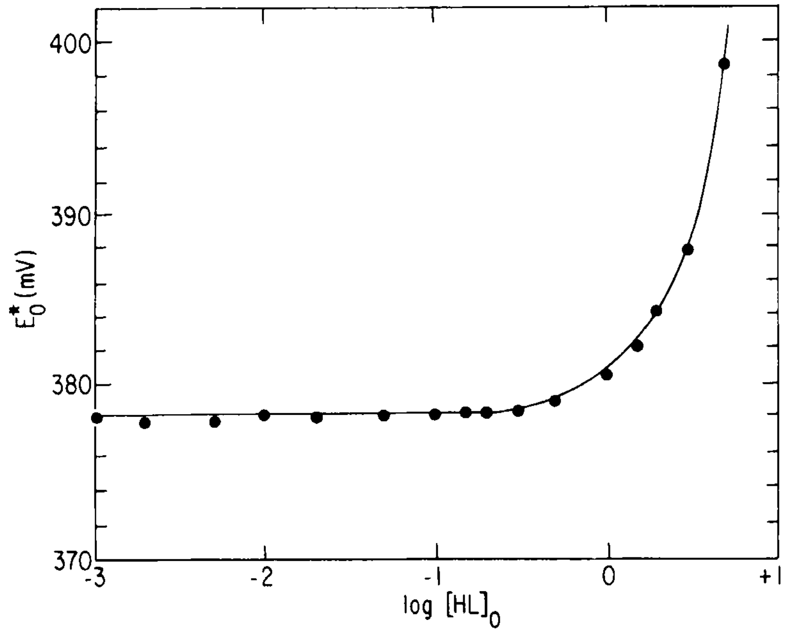

FIG. 1. Influence of total lactic acid concentration on the potentiometric determination of the hydrogen ion concentration by glass electrode. E_0^* (mV), apparent standard potential, vs log $[HL]_0$, (total lactic acid concentration) plot.

$$l = [HL]_0/(1 + [H^+]/K_a) \tag{1}$$

where $[H^+]$ is the equilibrium hydrogen ion concentration at $\mu = 1.0$ and $[HL]_0$ is the total lactic acid concentration.

The influence that the total lactic acid concentration has on the hydrogen ion activity has been evaluated potentiometrically. Solutions having an approximate constant anion concentration of 1 *M* and a total concentration of lactic acid varying between 10^{-3} and 5 *M* have been measured potentiometrically using a Sargent combination glass electrode and a Beckman Model 4500 digital pH meter. The results of these measurements are shown in Fig. 1. E_0^*, which is the apparent standard potential, has been evaluated from the equation

$$E_0^* = E - \frac{RT}{F} \ln [H^+]$$

where E is the measured emf (in mV) and $[H^+]$ is the hydrogen ion concentration, which was evaluated from Eq. (1). It can be seen that in the concentration range 10^{-3}–0.3 M, E_0^* stays constant within 0.1 mV, while for $[HL]_0 > 0.3$ M, deviations occur. Since

$$E_0^* = E_0 + E_j + (RT/F) \ln f_{H^+}$$

where E_0 = true standard potential of the cell, E_j = junction potential, f_{H^+} = activity coefficient of H^+, and the deviations can be attributed to either E_j, f_{H^+} or K_a. Regardless of which term is responsible for these deviations, the plot of Fig. 1 can be used to evaluate the apparent standard potential of the glass electrode, E_0^*, which is required to evaluate $[H^+]$ from the measured emf values. It is worth noting that if other approximate procedures were followed to evaluate $[H^+]$ (such as the usual one involving the standardization of the glass electrode against dilute buffer solutions), erroneous acidity values would have been obtained in the presence of high lactic acid concentrations.

Distribution Ratio

The distribution ratio, K_d, defined as the equilibrium ratio between the organic and aqueous metal concentrations, has been measured by scintillation and gamma counting techniques. In order to ensure the attainment of equilibrium, the aqueous and the organic phases have been mixed in a multiple vortex mixer for 7 d. All measurements have been performed at 25 ± 0.1°C.

RESULTS AND DISCUSSION

Extraction of Eu^{3+} by HDEHP–*n*-Dodecane Solutions from Aqueous Lactic Acid Solutions

The extraction data of Eu^{3+} from aqueous solutions having a constant acidity, $\log [H^+] = -2.66$, and total lactic acid concentration varying from 10^{-4} up to 5 M by an *n*-dodecane solution of HDEHP 5×10^{-3} F, are shown in Fig. 2. By assuming that the decrease of K_d is only caused by the progressive complexation of Eu^{3+} by lactate anions and describing the Eu^{3+} extraction reaction by (*8*):

$$Eu^{3+} + 3\overline{(HX)_2} \rightleftharpoons \overline{EuX_3 \cdot 3(HX)} + 3H^+ \qquad (2)$$

where HX = HDEHP and the bar indicates organic species, the following equation is obtained for the distribution ratio:

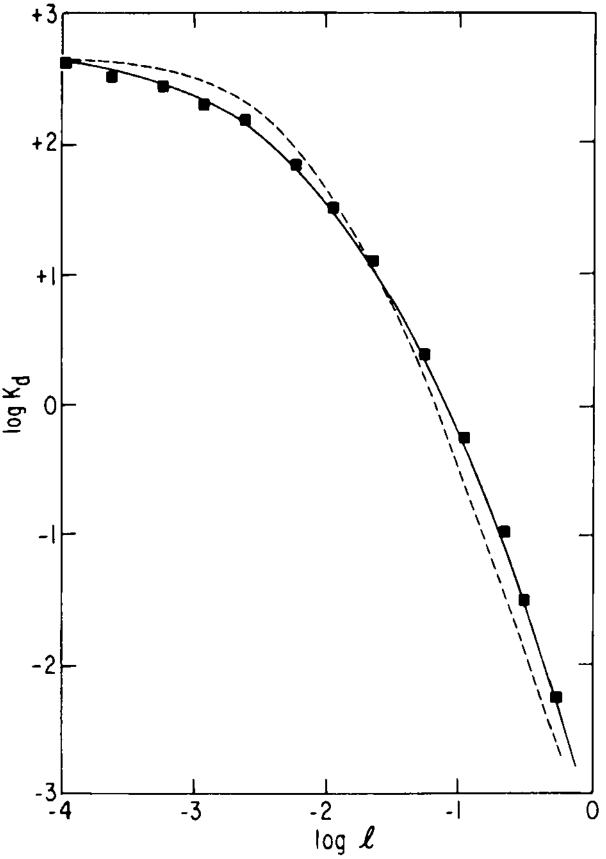

FIG. 2. Distribution ratio of Eu^{3+}, K_d, vs lactate anion concentration l, at log $[H^+] = -2.66$. Organic phase: HDEHP 5×10^{-3} *F* in *n*-dodecane. The solid and dashed lines have been calculated by Eq. (3). Solid line: β_i constants of this work. Dashed line: β_i constants of Ref. *9*.

$$K_d = K_e \frac{a_D^3}{[H^+]^3} \left(1 + \Sigma \beta_i l^i\right)^{-1} \tag{3}$$

$K_e = 300$ (*8*) is the equilibrium constant of Reaction (2), a_D is the activity of the HDEHP dimer in *n*-dodecane (*7*) and β_i are the overall formation constants of the Eu^{3+}–lactate complexes

$$\beta_i = \frac{[\text{Eu–lactate}_i]^{3-i}}{[Eu^{3+}][\text{lactate}^-]^i}$$

By inserting into Eq. (3) the β_i values of Ref. *9*, $\log \beta_1 = 2.53$, $\log \beta_2 = 4.60$, $\log \beta_3 = 5.87$ ($\mu = 2$, ClO_4^-), the dashed line of Fig. 2 is obtained. The agreement between the experimental points and the calculated line is rather good in spite of the different aqueous medium, showing that even in the presence of concentrated lactic acid solutions an inverse 3rd power dependence on [H^+] is maintained. These results indicate that no appreciable amounts of Ln-monolactate complex are coextracted into the organic phase at tracer level metal concentrations, contrary to previous findings (*3*).

Equation (3) and the experimental data of Fig. 2 have then been used to evaluate the β_i values in the NaCl + lactate medium. The following values have been obtained: $\log \beta_1 = 2.95$, $\log \beta_2 = 4.40$, $\log \beta_3 = 5.47$, in reasonable agreement with the constants of Ref. *9*. To further demonstrate the validity of Eq. (3), experiments have been performed where both the acidity of the aqueous phase and the extractant concentration were varied. The results are plotted in Fig. 3(A) as a function of the total aqueous lactic acid concentration. The same data have been plotted in Fig. 3(B) in the normalized form $\log y$ versus $\log [H^+]$, where $y = K_d(1 + \Sigma\beta_i l^i)\, a_D^{-1}$, using the β_i values of this work and the a_D values of Ref. *7*. Since it follows from

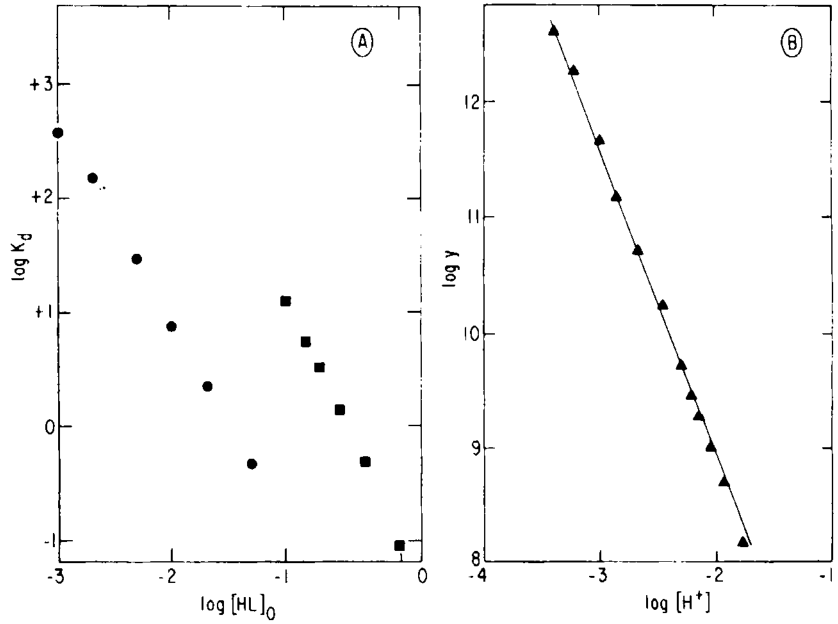

FIG. 3. (A) Distribution ratio of Eu^{3+}, K_d, vs total lactic acid concentration, $[HL]_0$, at variable acidity. (●) 1×10^{-3} *F* HDEHP, (■) 5×10^{-3} *F* HDEHP in *n*-dodecane. (B) Normalized plot, log y vs log [H^+], of the same data. The slope of the solid line is −3.

Eq. (3) that $y = K_d/[H^+]^3$, the -3 slope of the straight line, fitting the date of Fig. 3(B), further indicates the absence of lactate coextraction into the organic phase.

Extraction of Eu^{3+} by HDEHP-*n*-Dodecane Solutions from Aqueous Solutions Containing Both Lactic Acid and a Polyaminocarboxylic Acid

The extraction data of Eu^{3+} from aqueous solutions having a constant acidity, $[H^+] = 1 \times 10^{-3}$ *M*, a constant polyaminocarboxylic acid concentration of 0.05 *M* and variable lactic acid concentration by *n*-dodecane solutions of HDEHP are shown in Fig. 4. The data refer to the two polyaminocarboxylic acids, DTPA and HEDTA. The results of Fig. 4 can be again interpreted by the extraction equilibrium (2) providing the further complexation between Eu^{3+} and the polyaminocarboxylic acid, as well as the possible formation of mixed Eu(III)–lactate–polyaminocarboxylate complexes, are properly taken into account. By defining the complex

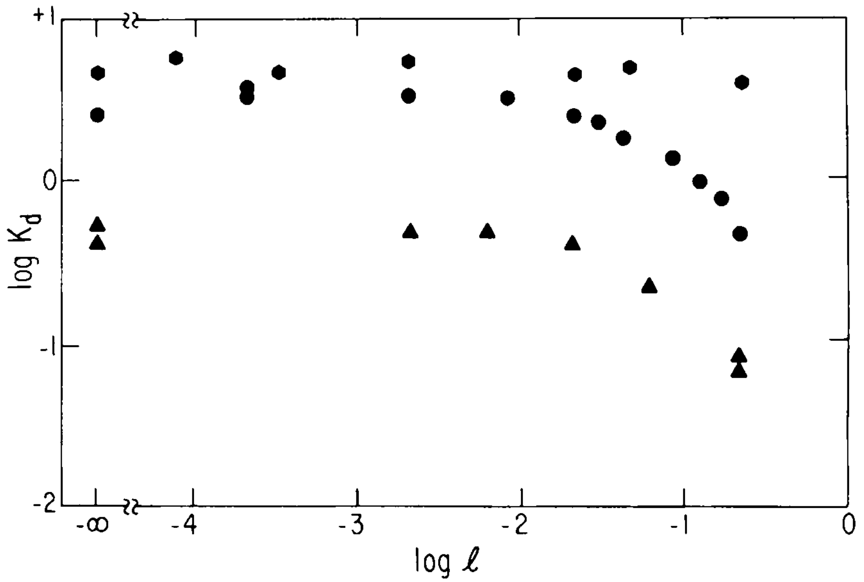

FIG. 4. Distribution ratio of Eu^{3+}, K_d, vs lactate anion concentration, *l*, in the presence of polyaminocarboxylic acids. (●) organic phase 0.1 *F* HDEHP *n*-dodecane, aqueous phase DTPA 0.05 *M*, $[H^+] = 10^{-3}$ *M*. (●) Organic phase 0.01 *F* HDEHP *n*-dodecane, aqueous phase 0.05 *M* HEDTA, $[H^+] = 10^{-3}$ *M*. (▲) Organic phase 0.005 *F* HDEHP *n*-dodecane, aqueous phase 0.05 *M* HEDTA, $[H^+] = 10^{-3}$ *M*.

formation of Eu^{3+} with the differently protonated forms of the polyaminocarboxylic acid, H_nY, according to the equations:

$$Eu^{3+} + H_nY^{n-z} \rightleftharpoons EuH_nY^{3+n-z} \qquad (4)$$

with $n = 0, 1, 2, 3, 4, 5$ for DTPA ($z = -5$) and $n = 0, 1, 2, 3$ for HEDTA ($z = -3$)

$$\gamma_n = \frac{[EuH_nY^{3+n-z}]}{[Eu^{3+}][H_nY^{n-z}]} \qquad (5)$$

and limiting the mixed complex formation reactions only to the ones involving one unprotonated polyaminocarboxylate anion:

$$Eu^{3+} + Y^{-z} + j \text{ lactate}^{-} \rightleftharpoons \text{Eu–Y–lactate}^{3-j-z} \qquad (6)$$

$$\eta_j = \frac{[\text{Eu–Y–lactate}_j^{3-j-z}]}{[Eu^{3+}][Y^{-z}][\text{lactate}^{-}]^j} \qquad (7)$$

Equation (3) becomes

$$K_d = K_e \frac{a_D^3}{[H^+]^3} \left(1 + \Sigma\, \beta_i l^i + \Sigma\, \gamma_n [H_nY] + y\, \Sigma\, \eta_j l_j\right) \qquad (8)$$

where y stands for the concentration of Y^{-z}. The independence of K_d from l for DTPA (Fig. 4), due to the very strong complexing power of DTPA for Eu^{3+}, does not allow one to evaluate the mixed complex. A value of 2.3×10^6 for the term $\Sigma\, \gamma_n[H_nY]$ is instead obtained for DTPA at $[H^+] = 1 \times 10^{-3}$ M. Neglecting the contribution of the protonated forms and using a value of $[Y^{-5}] = 1.8 \times 10^{-16}$, calculated from literature values of the acid dissociation constants of DTPA (*10*), we obtain $\log \gamma_0 = 22.11$, in good agreement with the previously reported value of $\log \gamma_0 = 22.39$ of Ref. *10*. In the case of HEDTA the drop of K_d, occurring when the lactate anion concentration increases, allows one to calculate both γ_0 and η_j. Following the same kind of reasoning as for DTPA from the data where no lactate anion dependence is shown, a value of $\log \gamma_0 = 14.59$ is evaluated for HEDTA when $[Y^{-3}]$ is calculated from the data of Ref. *11*. This constant can be compared with the literature value of $\log \gamma_0 = 15.45$ from Ref. *10*. Once the term $\Sigma\, \gamma_n[H_nY]$ is known, Eq. (8) can be used to evaluate the formation constants of mixed complexes after rearranging it in the form

$$Z = \frac{K_d[H^+]^3}{K_e a_D^3} - \left(1 + \Sigma\, \beta_i l^i + \Sigma\, \gamma_n [H_nY]\right) = y\, \Sigma\, \eta_j l^j \qquad (9)$$

The Z versus l data for HEDTA are shown in Fig. 5. The points fall on a straight line up to a lactate anion concentration of 0.17 M, indicating the formation of the mixed Eu–Y–lactate complex. The formation constant of the mixed complex, evaluated from the slope of the straight line, is $\eta_l = 4.8 \times 10^{16}$ when a value of $y = 2.73 \times 10^{-12}$ is used. This value is obtained by dividing the experimental value $\Sigma\, \gamma_n[H_nY]$ by γ_0 of Ref. *10*. The sharp upward deviation of the points at $l = 0.22\ M$ ($[HL]_0 = 1\ M$) indicates that a further mixed complex, Eu–Y–lactate$_2$, is also formed. However, the few experimental points available do not make the evaluation of its formation constant reliable. The evaluated η_l constant can be compared to literature values for mixed complex formation constants referring to the equilibrium

$$\text{In(EDTA)} + \text{acetate} \overset{K_{MA}}{\rightleftharpoons} \text{In (EDTA) acetate} \qquad (10)$$

Transforming η_l into K_{MA}, dividing it by γ_0 of Ref. *10*, we obtain a value of 17 which compares the 0.19 (Pr), 0.10 (Gd) and 0.40 (Yb) (*12*). The larger free energy variation involved in the formation of the lactate–HEDTA complex is not unexpected considering that Eu(HEDTA) offers less steric

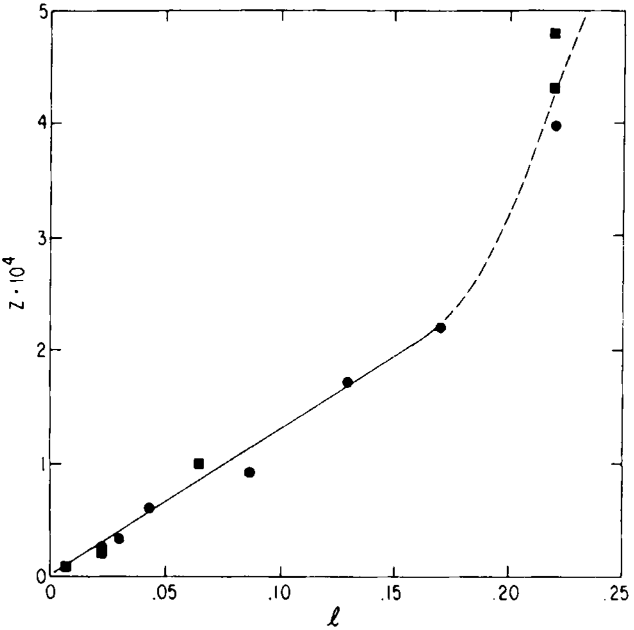

FIG. 5. Z vs l, lactate anion concentration, plot. (●) 0.01 F HDEHP, (■) 0.005 F HDEHP in n-dodecane. Aqueous phase 0.05 M HEDTA, $[H^+] = 10^{-3}\ M$.

hinderance to the attacking carboxylic acid and the stronger coordination power of lactic acid over acetic acid.

The identification of mixed complexes is of particular importance for the interpretation of the lactate-catalyzed dissociation rate of lanthanide and actinide polyaminocarboxylates. In fact, as will be discussed in another paper, mixed complexes play a very important role in the accelerated dissociation mechanism of the inert metal–polyaminocarboxylates.

It is worth noticing that the drop in K_d, shown by the HEDTA data of Fig. 4, is entirely attributable to the formation of mixed complexes. In fact, also in the case of HEDTA the term $\Sigma\ \beta_i l^i$ is always negligible with respect to the term $\Sigma\ \gamma_n[H_nY]$. The lower parallel shifting of the K_d values, caused by the formation of mixed complexes, is also shown in Fig. 6, where the distribution

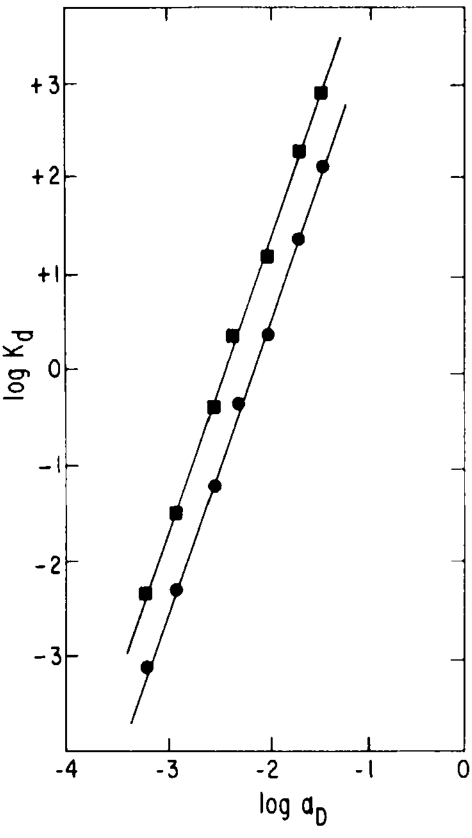

FIG. 6. Distribution ratio of Eu^{3+}, K_d, vs HDEHP dimer activity in *n*-dodecane, a_D. Aqueous phase: 0.05 M HEDTA, $[H^+] = 10^{-3}$ M. (●) $[HL]_0 = 1.0$ M. (■) no lactic acid. The straight lines have a +3 slope.

ratios of Eu^{3+}, obtained at constant acidity, $[H^+] = 10^{-3}$ *M* and $[HEDTA] = 0.05$ *M* and at 0 and 1 *M* lactic acid concentrations, have been plotted as a function of the HDEHP dimer activity. It has to be mentioned that, at zero lactic acid concentration, the extraction equilibria are established extremely slowly, in agreement with previous findings in the presence of DTPA (*1*, *5*).

Separation Factor between Eu^{3+} and Am^{3+} with HEDTA

The separation factor, α, between Eu^{3+} and Am^{3+} has been evaluated from the spacings of the straight lines of Fig. 7, where the distribution ratios

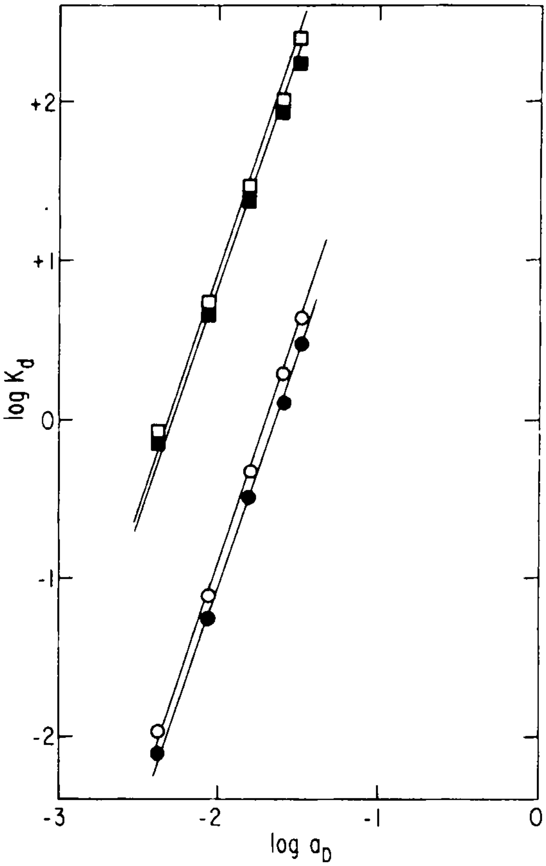

FIG. 7. Distribution ratio of Eu^{3+} and Am^{3+}, K_d, vs HDEHP dimer activity in *n*-dodecane, a_D. Squares: Eu^{3+}; (□) $[HL]_0 = 0.4$ *M*, (■) $[HL]_0 = 0.1$ *M*. Circles: Am^{3+}; (○) $[HL]_0 = 0.4$ *M*, (●) $[HL]_0$ 0.1 *M*. 0.05 *M* HEDTA, $[H = 10^{-3}$ M. The straight lines have a + slope.

of the two metals have been plotted as a function of the dimer activity of HDEHP in *n*-dodecane at two different total lactic acid concentrations. Both lines refer to the constant acidity $[H^+] = 1 \times 10^{-3}$ *M*. Since in all cases parallel straight lines of slope +3 are obtained, it follows that the separation factor is independent of the extractant concentration. An average separation factor $\alpha(Eu/Am) = 67$, nearly independent of the lactic acid concentration, in the range $0.1\ M \leq [HL]_0 \leq 0.4\ M$, can therefore be evaluated.

Figure 8 shows how the distribution ratio of Eu^{3+}, Pm^{3+}, and Am^{3+} is affected by changing the organic diluent from *n*-dodecane to diethylbenzene.

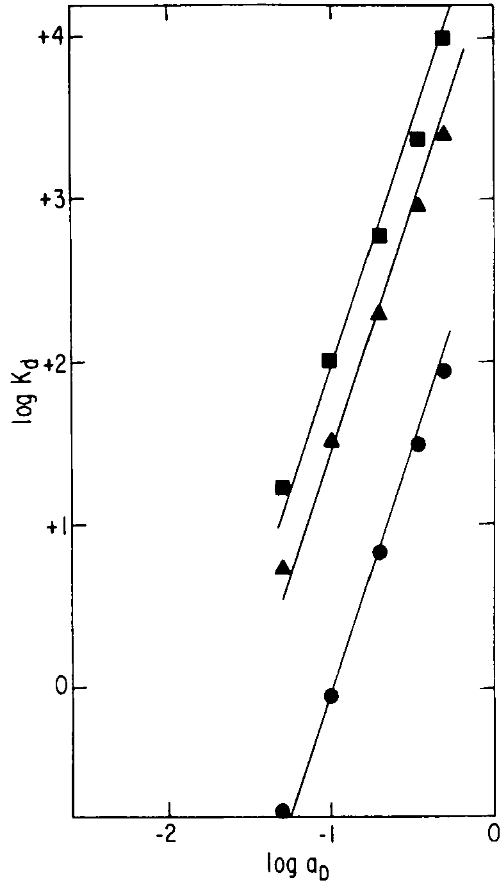

FIG. 8. Distribution ratios of Eu^{3+} (■), Pm^{3+} (▲), and Am^{3+} (●), K_d, vs HDEHP dimer concentration in diethylbenzene, a_D. Aqueous phase: $[HL]_0 = 0.1\ M$, $[H^+] = 10^{-3}\ M$, 0.05 *M* HEDTA. The straight lines have a +3 slope.

In this case the dimer activity of HDEHP has been set equal to half its formal concentration because of the ideal behavior of the extractant in aromatic diluents (*7*). The separation factors are α(Eu/Am) = 93 and α(Pm/Am) = 29. The total lactic acid concentration is 0.1 *M*. Very similar values had been reported for an organic phase 0.2 *F* HDEHP–DIPB and an aqueous phase 1 *M* lactic acid, DTPA 0.05 *M*, pH = 3.0 (*1*). Further, as expected, the distribution ratios drop about two orders of magnitudes. This fact allows one to use more concentrated HDEHP solutions for the lanthanide extractions, still keeping the distribution ratios at practical values to perform separations.

As will be described in another paper, aqueous phases containing HEDTA and lactic acid show extraction kinetics faster than those measured for DTPA–lactic acid solutions. Thus HEDTA appears as a promising alternative for lanthanide–actinide separation processes of the Talspeak type.

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