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Determination of the Formation Constants of Actinoid and Lanthanoid Lactate Complexes by Means of Electrophoresis

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Determination of the complex formation constant of actinides (Am, Cm) and lanthanides (Pm, Eu, Lu) with lactic acid was carried out by means of the electrophoretic method. "Cellogel", a gelatinized cellulose acetate was used as the supporting medium for electrophoresis at 10°C. Electrolyte solutions of various pH at an ionic strength of 1.5 were prepared from 0.5M lactic acid solution for electrophoresis at various pH values. The migration zones of α- and β-emitter were determined by α track on cellulose nitrate and autoradiographic image on X-ray film, respectively. The mobility of each nuclide at different pH was analyzed to obtain the formation constants of lactate complex of each element with reference to dissociation equilibrium. The β_1 values thus obtained were consistent with those obtained by other methods. The method was found to be especially useful for determining the complex formation constants of *trans*-uranium elements with only tracer amounts of these elements.

Electrophoresis has been used not only for the separation of various ions, but also for the study of coordination compounds or ion pairs in certain solution systems. Since it is possible to get information on the presence of the functional groups in a given solution system from the relationship[1–4] $U=aZ/\sqrt{M}$ (U: the zone mobility of the migrating substances, Z: their charge, M: the molecular weight), studies[5–10] have

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been carried out on the determination of formation constants of complex compounds. The method is suitable and effective for radioactive elements, especially *trans*-uranium elements, since their radioactivities can be easily measured by various methods including autoradiography even in tracer amounts of these elements.

Basic factors concerning electromigration mobility have been studied and the formation constants of some actinide and lanthanide element complexes with lactic acid have been estimated radiochemically, the results of which are reported in this paper.

Theoretical Consideration

In order to estimate the formation constants from electrophoretic mobility data, the following theoretical consideration can be made. Since the trivalent metal ions of lanthanide and actinide elements do not form polynuclear complexes,[11] the consecutive equilibria of mononuclear complexes ML, ML_1, $\cdots ML_N$ and the corresponding equilibrium constants are given by the following equations.

$$\left.\begin{aligned} &M^{3+} + L = ML^{2+};\ K_1 = \frac{[ML]}{[M][L]} \\ &ML^{2+} + L = ML_2{}^{+};\ K_2 = \frac{[ML_2]}{[ML][L]} \\ &ML_{N-1}^{3-(N-1)} + L = (ML_N)^{3-N};\ K_N = \frac{[ML_N]}{[ML_{N-1}][L]} \end{aligned}\right\} \quad (1)$$

In the method of Bjerrum to arrive at the values of K_N, the stability or formation constant, the underlying principle is the unambiguous relationship between the average number $\bar{n}$ of anionic ligands bound to a metal ion in an equilibrium mixture and the total anion concentration.

$\bar{n}$ can be expressed as

$$\bar{n} = \frac{[ML]+2[ML_2]+\cdots+N[ML_N]}{[M]+[ML]+[ML_2]+\cdots+[ML_N]} \quad (2)$$

The concentrations of complexes in this equation can be substituted by the expression derived from Eq. (1). Eliminating [M] in both the numerator and denominator, we have

$$\bar{n} = \frac{(K_1[L])+2(K_1K_2[L]^2)+\cdots+N(K_1K_2\cdots K_N[L]^N)}{1+(K_1[L])+(K_1K_2[L])+\cdots+(K_1K_2\cdots K_N[L]^N)} \quad (3)$$

Introducing the complex product defined by

$$\beta_n = \frac{[ML_N]}{[M][L]^n} = \prod_{i=1}^{N} K_i \quad (4)$$

Eq. (3) can be written in a more concise form:

$$\bar{n} = \frac{\sum_{n=1}^{N} n\beta_n[L]^n}{1+\sum_{n=1}^{N}\beta_n[L]^n} \quad (5)$$

If the average charge of a complex of trivalent metal ion with n of anion ligands is represented by $\bar{Z}$, the zone mobility U_c is expressed by

$$U_c = a\frac{\bar{Z}}{\sqrt{M}} = \frac{a}{\sqrt{M}}(3-\bar{n}) = U_k - a\frac{\bar{n}}{\sqrt{M}} \quad (6)$$

where the mobility of non-coordinated trivalent metal ions is given by $U_k=a\ 3/\sqrt{M}$.

Substituting $\bar{n}$ of Eq. (5) into Eq. (6), we get

$$\begin{aligned} U_c &= U_k - \frac{a}{\sqrt{M}}\cdot\frac{\sum_{n=1}^{N} n\beta_n[L]^n}{1+\sum_{n=1}^{N}\beta_n[L]^n} \\ &= \frac{U_k+\sum_{n=1}^{N}\left(U_k - a\frac{n}{\sqrt{M}}\right)\beta_n[L]^n}{1+\sum_{n=1}^{N}\beta_n[L]^n} \\ &= \frac{U_k+\sum_{n=1}^{N}U_n\beta_n[L]^n}{1+\sum_{n=1}^{N}\beta_n[L]^n} \end{aligned} \quad (7)$$

where U_n is the mobility of a complex of trivalent metal ion coordinated with n univalent anion ligands (n: integer) and can be represented by the following equation from the relation $U_k=a\ 3/\sqrt{M}$.

$$U_n = a\frac{(3-n)}{\sqrt{M}} = a\frac{3}{\sqrt{M}} - a\frac{n}{\sqrt{M}} = U_k - \frac{n}{\sqrt{M}} \quad (8)$$

In Eq. (7), the values of U_k, U_n, and β_n are constant under the same experimental conditions, whereas U_c varies with [L].

To determine β_n from U_c and U_n, mobility U_c should be obtained for different organic ligand concentrations. As the functional groups of the organic acid accept or donate protons, the dissociation constant of the equilibrium ($H_nL \rightleftarrows H_{n-1}L+H^+$) is determined by the pH value. The ligand concentration $[H_{n-1}L]$ is then obtained as a function of the pH values. Thus solutions with different ligand concentrations can be prepared from those with identical concentrations of the organic acid by changing pH value. The relationship between the dissociation degree α of univalent organic acid and pH value is given by

$$\alpha = \frac{1}{1+10^{-(\mathrm{pH}-\mathrm{pK})}} \quad (9)$$

where pK is $-\log K_d$, K_d being the dissociation constant of the organic acid. The ligand concentration can be determined by multiplying the dissociation degree by the normality of the organic acid. The formation constant β_n can then be determined from the relationship between the experimental mobility U_c and the defined pH value.

In Eq. (7), $\sum_{n=2}^{N}\beta_n[L]^n$ can be neglected at low ligand concentrations because it is much smaller than $\beta_1[L]$. Thus, at low ligand concentrations, β_1 can be calculated by

$$U_c = \frac{U_k+U_1\beta_1[L]}{1+\beta_1[L]} \quad (10)$$

from which we get

$$\beta_1 = \frac{U_k-U_c}{U_c-U_1}\cdot\frac{1}{[L]} \quad (11)$$

Therefore

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[11] K. Buchtela, "Isotopenpraxis" 3, Jahrgang. Heft 12 (1967).

$$\log \frac{U_k - U_c}{U_c - U_1} = \log \beta_1 - p[\mathrm{L}] \tag{12}$$

Thus the plot of $\log (U_k - U_c)/(U_c - U_1)$ *vs.* $p[\mathrm{L}]$ should give a straight line with slope 1. The intercept of this line with the abscissa is $\log \beta_1$.

The β_2 value can be calculated from the following equations.

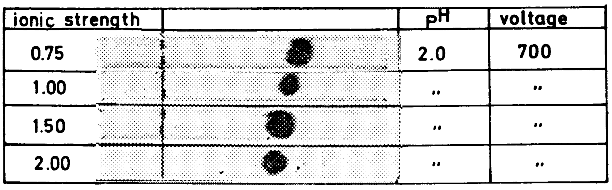
$$U_c = \frac{U_k + U_1\beta_1[\mathrm{L}] + U_2\beta_2[\mathrm{L}]^2}{1 + \beta_1[\mathrm{L}] + \beta_2[\mathrm{L}]^2} \tag{13}$$

$$\beta_1 = \frac{\beta_1[\mathrm{L}](U_1 - U_c) + (U_k - U_c)}{[\mathrm{L}]^2(U_c - U_2)} \tag{14}$$

Experimental

Materials and Apparatus. The supporting medium is "Cellogel," the gelatinized cellulose acetate provided from Chemetron-Milano, Italy. It was found by preliminary electrophoretic studies[12] of ^{147}Pm and ^{177}Lu on various supporting materials, that, except for "Cellogel," metal ions were liable to be adsorbed on filter papers usually used for electrophoresis. The "Cellogel" strips preserved in 40% methanol solution were rinsed and stored in distilled water for a few days to remove methanol.

Electrophoresis was carried out by mean of the apparatus provided by Mamino Industry Co. The supporting medium was placed in carbon tetrachloride bath cooled by circulating water of constant temperature (10±0.1°C) in order to avoid heat caused by electric current. The background electrolyte solution was 0.5M lactic acid and its ionic strength was adjusted to 1.5 with potassium chloride, since mobility is affected by ionic strength (Fig. 1) through the change of either resistance or complex formation constants.



ionic strength	pH	voltage
0.75	2.0	700
1.00	"	"
1.50	"	"
2.00	"	"

Fig. 1. Autoradiograms of promethium at different ionic strength.

The radioisotopes used were ^{147}Pm, ^{152}Eu, ^{177}Lu, ^{241}Am, and ^{242}Cm. ^{152}Eu and ^{177}Lu having high specific activity were prepared by neutron irradiation of europium and lutetium target in KUR reactor. ^{242}Cm was obtained in carrier-free state after the radiochemical separation of neutron irradiated ^{241}Am target.[13]

The reagents used were all extra pure ones supplied from Wako Pure Chem Ind. Ltd. The stock solutions (1—3N HCl solution) of radioactive nuclides were evaporated to dryness dissolved into electrolyte solutions of various pH and allowed to stand for one day.

The electrolyte solutions were prepared as follows. Lactic acid solution (about 1N) was prepared and its concentration was determined by titration with 0.1N sodium hydroxide. Solutions of NaOH(2N) and HClO$_4$(2N) were prepared and each was mixed with 1N lactic acid in the volume ratio 1:1. This gave two solutions; 0.5M lactic acid—1N NaOH, 0.5M lactic acid—1N HClO$_4$. They were mixed together in various ratios to obtain solution of desired pH.

Procedure. The "Cellogel" strips were dipped at first in the solutions of the background electrolyte (pH 3, 7, and 10) and then in the solutions with various pH used for migration. The excess electrolyte on the "Cellogel" strips was removed with filter paper and then about 1—2 *μl* of the radioactive sample solution was placed at the starting point marked on the strip. The diameter of the sample spot was about 3 mm. After the "Cellogel" strip had been placed in the migration chamber, a constant voltage was applied between the two electrodes.

After the migration, the "Cellogel" strip was dried in air and fixed to a thick paper. The migration zones of the β-emitter were determined by autoradiograph with X-ray films (Fuji medical X-ray Film), and that of α-emitters by the α-track method[14] with a cellulose nitrate film. The cellulose nitrate film was etched with a 6N sodium hydroxide solution at 60°C for 10 minutes to reveal the α tracks, and was then observed with a microscope.

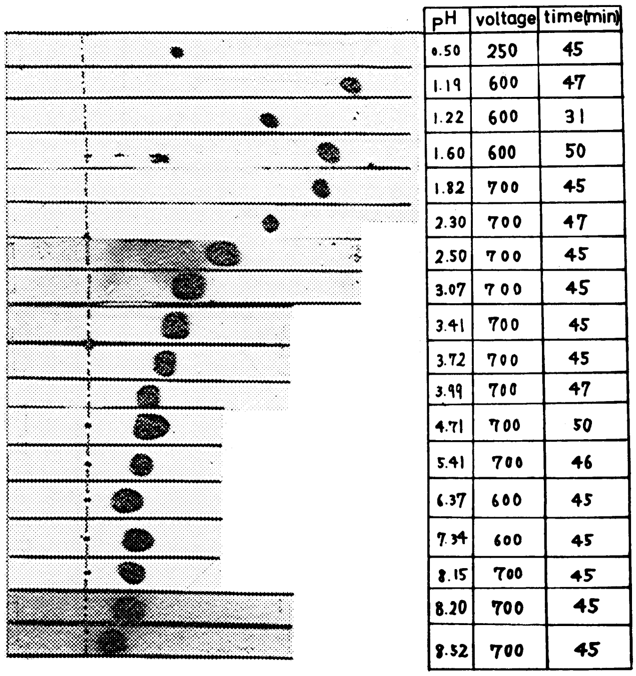
Results and Discussion

The autoradiogram of ^{147}Pm and the α-track electrophoregram of ^{241}Am are shown in Figs. 2 and 3, respectively.

The relationship between the mobility of ^{147}Pm and the pH value of the electrolyte solution (lactic acid) is shown in Fig. 4. The mobility decreases remarkably with increasing pH in the pH range 0—4, and is almost independent of the pH in the range 5—8. The mobility also decreases above pH 8.

The dissociation of lactic acid at different pH values is shown in Fig. 5 according to the data pK=3.6 for lactic acid by means of Eq. (9). It can be seen that the ligand concentration changes remarkably in the pH region 2—5, and is almost constant above pH 6.

The first drop in mobility in the pH range 0—4 (Fig. 4) depends on the decrease of the average charge



pH	voltage	time(min)
0.50	250	45
1.19	600	47
1.22	600	31
1.60	600	50
1.82	700	45
2.30	700	47
2.50	700	45
3.07	700	45
3.41	700	45
3.72	700	45
3.99	700	47
4.71	700	50
5.41	700	46
6.37	600	45
7.34	600	45
8.15	700	45
8.20	700	45
8.52	700	45

Fig. 2. Autoradiograms of promethium at different pH value.

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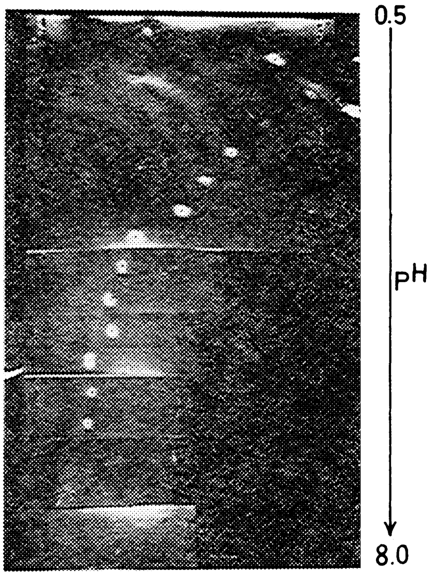

Fig. 3. Cellulose nitrate α-track after the migration of Am in different pH value (voltage and migration times are indicated in Fig. 2).

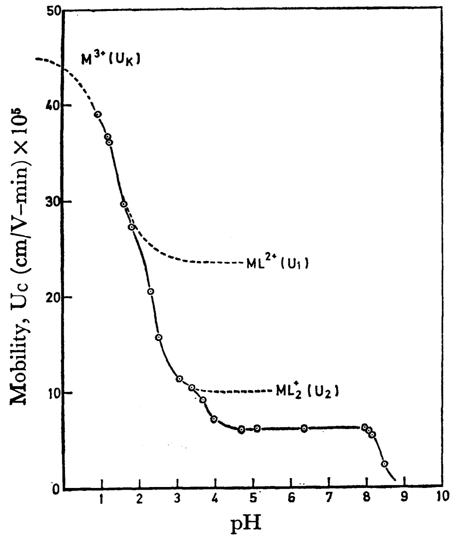

Fig. 4. Mobility — pH curve of ^{147}Pm.

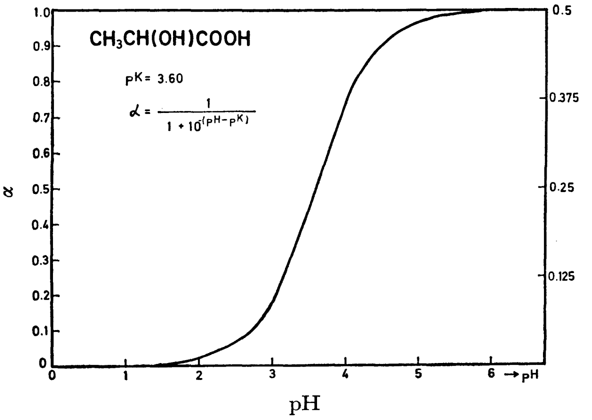

Fig. 5. Dependence of lactic acid dissociation on pH.

of the complex due to the increase of the number of anionic ligands coordinated to promethium. The constancy of mobility in the pH range 5—8 can be understood to be due to the constancy of ligand concentration of lactic acid in this pH region. The decrease of mobility above pH 8 might be due to the formation of complexes with both hydroxy and lactate ions as ligands, since the concentration of hydroxy ion is rather high. This, together with the existence of a plateau at the pH range 4—8 suggests that the effect of hydroxy ion is negligible over the pH range 0—4.

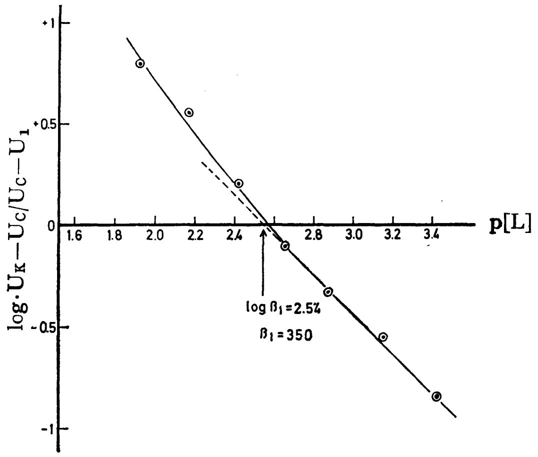

Fig. 6. The analysis for β_1 value from electrophoretic data of promethium in the lactate solution.

By estimating the value of U_k and U_1 from the mobility-pH curves (Fig. 4), we obtain the graphical plot of Eq. (12) for promethium (Fig. 6). The slope of this straight line is 1 in the range of large p[L] value, *i.e.*, of small [L] values due to small values of pH. However, in the range of small p[L] value, the gradient

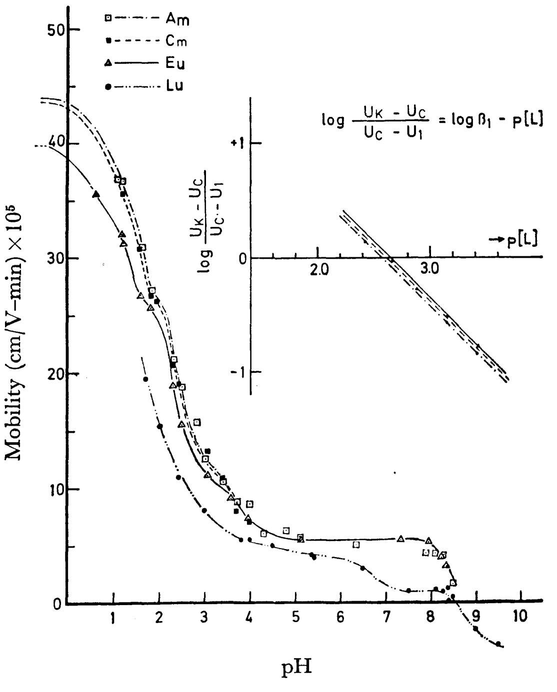

Fig. 7. Mobility — pH curves of Eu, Lu, Am, and Cm lactates and the analysis for β_1 values.

is slightly larger than 1. The reason might be that $\beta_2[\mathrm{L}]^2$ is not negligible any more in this case, because of the formation of $\mathrm{PmL_2}$ complexes. As shown in Fig. 6, the value for β_1 should be read from the intercept at the point $p[\mathrm{L}]=2.54$, giving the value 350.

The mobility-pH curves for Eu, Lu, Am, and Cm are shown in Fig. 7. They are similar to those for promethium and can be analyzed in the same manner as before.

At any pH, the smaller the mobility, the larger the tendency of complex formation. Therefore, it is shown qualitatively that the formation constants increase in the order Am<Cm<Eu<Lu.

The difference in the formation constants of Am and Cm is very small. The maximum number of coordinated lactate ions may be estimated to be about 2.4 for Lu, but about 2.5 for Eu, Am, and Cm under the conditions employed.

The plots of log $(U_k-U_c)/(U_c-U_1)$ *vs.* $p[\mathrm{L}]$ are also shown (upper right, Fig. 7). The gradients are approximately 1 for all these elements. The curve for Lu is not given since no data are available for the low pH range.

The logarithms of β_1, β_2, and β_3 values are summarized in Table 1 with the previous data. The stability constants β_1 of the lactate complexes of the rare earth elements have been found to decrease with increasing ionic strength.[15,16] The β_1 values we obtained agree fairly well with those obtained by the different methods if the effect of ionic strength on β_1 values is considered. Each log β_1 value we obtained may include an error of about 1% (absolute value) as in other works.[8,9] However, under the same conditions, a comparison of log β_1 can be made more strictly for Am, Cm, and Eu (Fig. 7). The β_2 values determined are slightly samller than those previously reported, though a larger error (about 10% of log β_2 value) may be included in the estimation of β_2.

TABLE 1. LOGARITHMS OF STABILITY CONSTANTS OF Pm, Eu, Am, AND Cm LACTATES

Element	Method	Temp. (C°)	Ionic strengh	log β_1	log β_2	log β_3	Ref.
Pm	(a)	10	1.5	2.54	4.24		this work
Eu	(b)	25	2.0	2.53	4.60		(15)
	(a)	10	1.5	2.62	4.22		this work
Am	(c)	20	0.5			5.71	(17)
	(d)	20	0.5			5.73	(17)
	(d)	—	0.5	2.77	4.64		(18)
	(a)	10	1.5	2.57	4.21		this work
Cm	(c)	20	0.5			5.76	(17)
	(d)	20	0.5			5.78	(17)
	(d)	—	0.5	2.79	4.55		(18)
	(a)	10	1.5	2.59	4.29		this work

Method: (a) electrophoresis, (b) potentiometric titration,
(c) distribution measurement, (d) ion exchange.

The electrophoretic method requires only small amounts of samples to determine stability constants. Since the difference in β_1 values of each element becomes small at high ionic strength, it is recommended that separation of elements should be carried out at low ionic strength, as the separation factor of two elements is proportional to the ratio of their stability constants.

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