Studies of the Alkaline Earth Complexes in Various Solutions. IV. Solvent Extraction Study of Radium(II) Complexes with Some Aminocarboxylic Acids in Perchlorate Media

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Few investigations have been conducted on complex formation of radium(II) in aqueous solutions. This may be due to the fact that only tracer studies are possible in practice because of the high level radioacitivity of radium isotopes.

In the present paper, the complex formation of radium(II) with six very common aminocarboxylic acids has been studied by a liquid-liquid distribution method. Radium(II) was extracted with a mixture of thenoyltrifluoroacetone (TTA) and tributylphosphate (TBP) in carbon tetrachloride. Stability constants were determined by a graphic method from the distribution data.

Experimental

Radium-228 was imported from Radiochemical Center, Amersham, England. It was purified by a solvent extraction cycle which was reported previously.[1] The organic phases were always carbon tetrachloride containing 0.1 M TTA and 0.1 M TBP. The aqueous phase was sodium perchlorate media at ionic strength 0.1 M. No special buffer was added to the aqueous phase, but the hydrogen ion concentration was adjusted by the substitution of 0.1 M sodium hydroxide for 0.1 M sodium perchlorate. This hydroxide carried an equivalent amount of TTA from the organic phase into the aqueous phase and this dissociated TTA anion, together with a small amount of undissociated TTA,[*1] buffered the aqueous phase. The addition of a complex forming ligand was made by way of various amounts of disodium salt solution of the aminocarboxylic acid. The aqueous and organic phases were placed in stoppered glass tubes (volume 20 m*l*) and agitated mechanically for one hour. The initial volume of the two phases was 5.0 m*l*. The two phases were then centrifuged and a 2 m*l* portion was pipetted from each phase and the samples thus separated let stand for 3 days. The γ-radioactivity of the samples in which radium-228 (half-life 6.7 yr.) was in transient radioactive equilibrium with γ-radioactive actinium-228 (half-life 6.13 hr) was measured with a well-type (NaI) scintillation counter. A small portion was also taken from the aqueous phase and the hydrogen ion concentration measured potentiometrically using an aqueous solution containing 0.0100 M perchloric acid and 0.09 M sodium perchlorate as the standard of $-\log[H^+]=2.00$.

TABLE 1. DISSOCIATION CONSTANTS OF THE AMINOCARBOXYLIC ACIDS AND THE STABILITY CONSTANTS OF THE ALKALINE EARTH METAL COMPLEXES WITH THESE LIGANDS IN 0.1 M SODIUM PERCHLORATE MEDIA AT 25°C

$K = [RaL^{2-l}]/[Ra^{2+}][L^{l-}]$

Ligand*	pK_a**					log K***				
	1	2	3	4	5	Mg	Ca	Sr	Ba	Ra
CyDTA	2.51	3.60	6.20	11.78	—	10.3	12.5	10.0	8.0	8.3
DTPA	1.94	2.87	4.37	8.69	10.56	9.3	10.6	9.7	8.8	8.5
EDTA	2.07	2.75	6.24	10.34	—	8.7	10.7	8.6	7.8	7.5
EGTA	2.08	2.73	8.93	9.54	—	5.2	11.0	8.5	8.4	7.7
HEDTA	2.72	5.41	9.81	—	—	5.2	8.0	6.8	6.2	5.6

*	CyDTA	Cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetic acid
	DTPA	Diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid
	EDTA	Ethylenediamine-*N,N,N',N'*-tetraacetic acid
	EGTA	2,2'-Ethylenedioxyl bis[ethyliminodi(acetic acid)]
	HEDTA	*N'*-(2-Hydroxylethyl)ethylenediamine-*N,N,N'*-triacetic acid
	NTA	Nitrilotriacetic acid

** The acid dissociation constants were taken from Ref. 5.

*** Stability constants for radium(II) complexes are obtained from the present work. Other constants were taken from Ref. 5.

[*1] The distribution constant of TTA between carbon tetrachloride containing 0.1 N TBP and 0.1 N sodium perchlorate is 27,[2] and the acid dissociation constant of TTA in this aqueous phase is 8×10^{-7}.[3]

1) T. Sekine, Y. Koike and M. Sakairi, *J. Nucl. Technolog.*, **4**, 308 (1967).

2) Y. Hasegawa and T. Sekine, unpublished data.

3) J. Stary, "The Solvent Extraction of Metal Chelates," Pergamon Press, Oxford (1964).

Results

The distribution ratio of radium(II) was calculated as follows:

$$D = \frac{[\mathrm{Ra(II)}]_{\mathrm{org,total}}}{[\mathrm{Ra(II)}]_{\mathrm{total}}} = \frac{\gamma\text{-count-rate per m}l\text{ org. phase}}{\gamma\text{-count-rate per m}l\text{ aq. phase}}$$

Figure 1 gives the $\log D$ *vs.* $-\log[\mathrm{H}^+]$ plot when the aqueous phase was 0.1 M sodium perchlorate containing no ligand. The following extraction constant was obtained from these data;

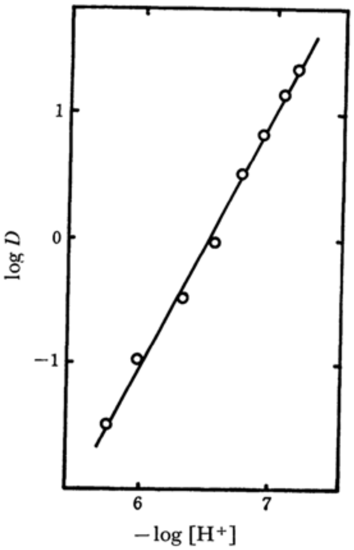

Fig. 1. $-\log[\mathrm{H}^+]$ dependence of radium(II) extraction from 0.1 M $\mathrm{NaClO_4}$ at 25°C.
Organic phase: carbon tetrachloride containing 0.1 M TTA and 0.1 M TBP.
The solid line is $\log D = -2\log[\mathrm{H}^+] - 12.94$

$$K_{ex_0} = D_0[\mathrm{H}^+]^2[\mathrm{HA}]_{\mathrm{org}}^{-2} = 10^{-10.92} \quad ([\mathrm{TBP}]_{\mathrm{org}} = 0.1\ \mathrm{M}) \tag{1}$$

here D_0 denotes $[\mathrm{RaA_2}]_{\mathrm{org}}/[\mathrm{Ra}^{2+}]$ and HA denotes TTA.

The stability constant of the first complex is defined as;

$$K = [\mathrm{RaL}^{2-l}]/[\mathrm{Ra}^{2+}][\mathrm{L}^{l-}] \tag{2}$$

When the aqueous phase contains only the first metal complex, the following equation may be written;

$$D = [\mathrm{RaA_2}]_{\mathrm{org}}/([\mathrm{Ra}^{2+}] + [\mathrm{RaL}^{2-l}]) \tag{3}$$

From Eqs. (2) and (3), the following extraction constant may be obtained;

$$K_{ex} = D[\mathrm{H}^+]^2[\mathrm{HA}]_{\mathrm{org}}^{-2} = \frac{D_0[\mathrm{H}^+]^2[\mathrm{HA}]_{\mathrm{org}}^{-2}}{1 + K[\mathrm{L}^{l-}]} \tag{4}$$

Then from Eqs. (1) and (4), the following equation is obtained;

$$K_{ex}/K_{ex_0} = (1 + K[\mathrm{L}^{l-}])^{-1} \tag{5}$$

Further details on the statistical treatment have already been given in Paper I of this series.[4]

The ligand concentration was calculated using

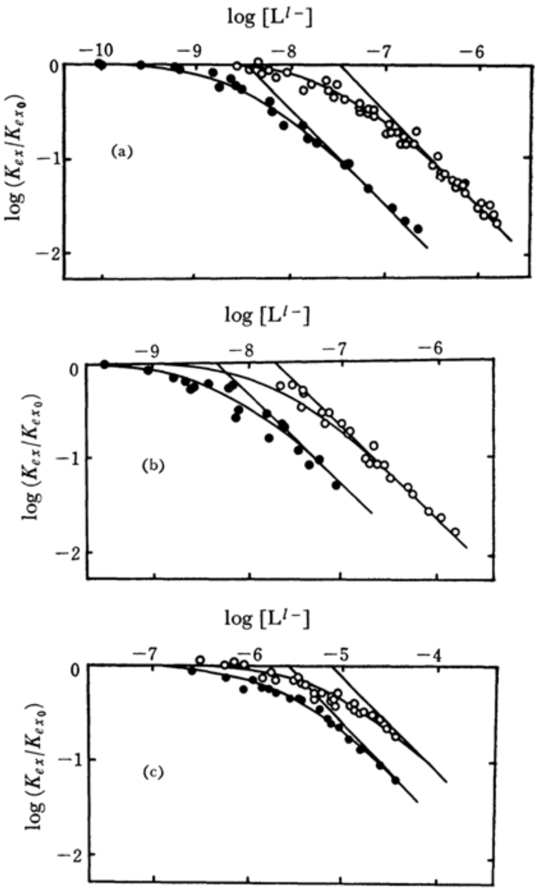

Fig. 2. $\log(K_{ex}/K_{ex_0})$ *vs.* $\log[\mathrm{L}^{l-}]$ plot.
Organic phase: carbon tetrachloride containing 0.1 M TTA and 0.1 M TBP.
Aqueous phase: 0.1 M $\mathrm{Na(ClO_4)}$
The ligand and the curves drawn in the figures are as follows:
(a) Open circles:
EDTA, $Y = -\log(1 + 10^{7.5}[\mathrm{L}^{4-}])$
Closed circles:
DTPA, $Y = -\log(1 + 10^{8.5}[\mathrm{L}^{5-}])$
(b) Open circles:
EGTA, $Y = -\log(1 + 10^{7.7}[\mathrm{L}^{4-}])$
Closed circles:
CyDTA, $Y = -\log(1 + 10^{8.3}[\mathrm{L}^{4-}])$
(c) Open circles:
NTA, $Y = -\log(1 + 10^{5.1}[\mathrm{L}^{3-}])$
Closed circles:
HEDTA, $Y = -\log(1 + 10^{5.6}[\mathrm{L}^{3-}])$

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[4] T. Sekine, M. Sakairi and Y. Hasegawa, This Bulletin, **39**, 2141 (1966).

the acid dissociation constants⁵⁾ given in Table 1. These acid dissociation constants previously reported were calculated from pH measurements. On the other hand, in the present work, the stoichiometric hydrogen ion concentration was always measured and thus the activity coefficient of hydrogen ion, 0.86,⁶⁾ was used to convert $-\log[H^+]$ into pH.

Figures 2a to 2c show the log (K_{ex}/K_{ex0}) *vs.* $\log[L^{l-}]$ plot. The stability constants were determined by a curve-fitting method.⁴⁾ Data analysis was carried out assuming no formation of complexes containing protons. This assumption seems reasonable because no remarkable deviation of the points, which might be caused by the formation of such complexes, is observed in the figures containing experimental data obtained at various different hydrogen ion concentrations ($6<-\log[H^+]<7$).

The present measurement for the EDTA complex ($\log K=7.5$) is very close to a previous measurement ($\log K=7.4$).⁷⁾ No data seems to have been reported on radium(II) complexes with other ligands.

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5) A. Ringbom, "Complexation in Analytical Chemistry", John Wiley and Sons Inc., New York (1963).

6) B. E. Conway, "Electro Chemical Data," page 102, Elsevier (1952).

7) F. Nelson, R. A. Day and K. A. Kraus, *J. Inorg. Nucl. Chem.*, **15**, 140 (1960).