

ION-EXCHANGE CHARACTERISTICS OF THE RADIUM-ETHYLENE-DIAMINETETRAACETATE COMPLEX*

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A study of the stability of the Ra^{2+} -ethylenediaminetetraacetate (EDTA) complex was undertaken in order to determine the most favourable conditions for the fixation of Ra^{2+} on Amberlite IR 120 from radioactive waste solutions containing ^{226}Ra together with EDTA.

The behaviour of Ra^{2+} with various complexing agents was studied thoroughly by SCHUBERT^{1,2} who used ion-exchange methods³⁻⁵. The Ra^{2+} -EDTA stability constant has, however, not been determined up to now. A knowledge of the latter would enable one to predict the behaviour of ^{226}Ra on ion exchangers at all pH values.

For technical and economic reasons the contaminated solutions must be processed in a Na^+ cycle. Since the values of almost all known stability constants⁶ refer to K^+ as counter ion, it is necessary to carry out a preliminary investigation of the EDTA dissociation constants with Na^+ as counter ion.

DISSOCIATION CONSTANTS OF THE Na^+ -EDTA COMPLEX

The titration curves of the Na^+ - and K^+ -EDTA complexes were obtained by potentiometric titration. Both curves have the same shape except in the high pH ranges. From the curves obtained the fourth dissociation constant (K_4) was calculated using the method of SCHWARZENBACH⁷ slightly modified by MARTELL AND CALVIN⁸. A value of 9.6 for $\text{p}K_4$ in 0.1 M NaCl can be deduced from the above-mentioned titration curves, whereas the literature reports a $\text{p}K_4$ value of 10.26 for EDTA in 0.1 M KCl.

Taking into account the small difference between the dissociation characteristics of Na^+ -EDTA compared with the K^+ complex, the following acidity parameter⁹, α_{H} , in NaCl solutions is obtained:

$$\begin{aligned} \alpha_{\text{H}} &= 1 + [\text{H}^+] K_4^{-1} + [\text{H}^+]^2 (K_4 K_3)^{-1} + [\text{H}^+]^3 (K_4 K_3 K_2)^{-1} + [\text{H}^+]^4 (K_4 K_3 K_2 K_1)^{-1} \\ &= 1 + [\text{H}^+] \cdot 10^{9.60} + [\text{H}^+]^2 \cdot 10^{15.82} + [\text{H}^+]^3 \cdot 10^{18.49} + [\text{H}^+]^4 \cdot 10^{20.48} \quad (1) \\ &= \frac{[\text{EDTA}]}{[\text{EDTA}^{4+}]} \end{aligned}$$

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DETERMINATION OF THE Ra^{2+} -EDTA STABILITY CONSTANT*Experimental*

A modified form of the method of SCHUBERT for the determination of the stability constants of ions²⁻⁴ was applied. Solutions with different specific activities were used, permitting the calculation of the error in the resulting curves.

The procedure consists in an equilibration of 100 ml EDTA-²²⁶Ra solution (0.01 M EDTA, 0.1 M total Na⁺ salts, containing acetate buffer and different amounts of ²²⁶Ra) with 0.25 g Amberlite IR 120 previously brought into the Na⁺ form. After continuous stirring for 10 h at 20° the solution is filtered. The residual activity of the solution is sampled and measured by direct counting in an alpha scintillation counter. Corrections are made for self-absorption; the effect of Ra emanation is avoided by flushing an air stream through the counter just before the measurement starts.

The distribution coefficient K'_d (ml/g) is calculated from the difference between the activity of the original and the equilibrated solutions. Three series of experiments were carried out at pH 5.55 ± 0.05 , pH 5.85 ± 0.05 and pH 7.5 ± 0.2 . The K'_d values obtained are related to the measurements of the K_d values of ²²⁶Ra in solutions having the same composition but free of EDTA.

$$K_d = \frac{C_0 - C_E}{C_E} \times \frac{\text{ml solution}}{\text{g exchanger}} \quad (2)$$

in which: C_0 = initial concentration of ²²⁶Ra;

C_E = equilibrium concentration of ²²⁶Ra.

Results and discussion

The results of the three series of experiments are given in Tables I, II and III and plotted in Figs. 1a and b. On the ordinate is plotted the difference between the initial and the equilibrium activity of the solution, which is directly proportional to the activity fixed on the resin. On the abscissa the residual activity of the solution is given.

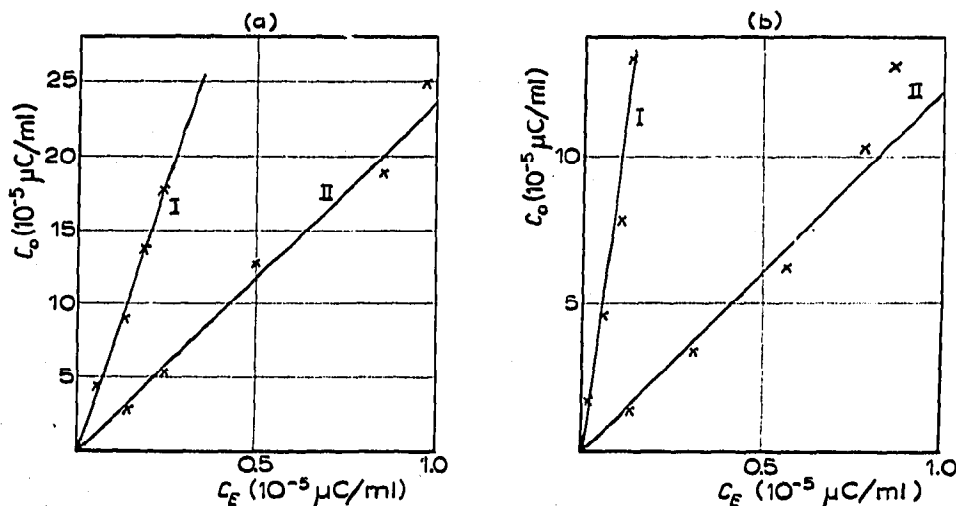


Fig. 1. Equilibrium distributions of ²²⁶Ra in solutions without EDTA (I) and with EDTA (II), at pH 5.55 (a) and pH 5.85 (b).

The K_d values may be deduced from the graphs which indicate that they are independent of the tracer concentration. However, the pH has a strong influence on the distribution of the tracer ions in presence of chelates, especially in the neutral pH range.

According to SCHUBERT⁴ the stability constant of the complex Ra^{2+} -EDTA

TABLE I
²²⁰Ra-EDTA-AMBERLITE IR 120 EQUILIBRIA AT pH 5.55 ± 0.05 *

Equilibrium without chelating agent		Equilibrium with chelating agent (0.01 M EDTA)	
C_0	C_E	C'_0	C'_E
4.36	0.059	2.97	0.142
9.05	0.128	5.52	0.245
13.80	0.190	13.1	0.502
17.90	0.245	18.90	0.855
		25.8	0.973
$K_d = 28,600$		$K'_d = 9,070$	
$\sigma = 1.84\%^{**}$		$\sigma = 10.6\%$	

* All concentrations of ²²⁰Ra are expressed in $\mu\text{C}/\text{ml} \times 10^{-5}$.

** σ = standard deviation in %.

may be calculated using the relationship between the distribution coefficients with and without chelating agent, the concentrations of the complexing agent and the acidity parameter α_H of EDTA in Na^+ solution at a given pH⁹:

$$K_{\text{Ra}^{2+} - \text{EDTA}} = \left(\frac{K_d}{K'_d} - 1 \right) \alpha_H [\text{EDTA}]^{-1} \quad (3)$$

where: K_d = distribution coefficient of ²²⁰Ra in absence of EDTA;

K'_d = distribution coefficient of ²²⁰Ra in presence of EDTA;

$$\alpha_H = 1 + \sum_{j=1}^{j=4} [\text{H}^+]^j K_{Hj} (\text{EDTA}).$$

TABLE II
²²⁰Ra-EDTA-AMBERLITE IR 120 EQUILIBRIA AT pH 5.85 *

Equilibrium without chelating agent		Equilibrium with chelating agent (0.01 M EDTA)	
C_0	C_E	C'_0	C'_E
1.64	0.021	1.49	0.130
4.56	0.055	3.62	0.309
7.86	0.108	7.71	0.570
13.40	0.140	10.98	0.788
		13.81	0.865
$K_d = 32,800$		$K'_d = 4,944$	
$\sigma = 11\%^{**}$		$\sigma = 14\%$	

* Activities are expressed in $\mu\text{C}/\text{ml} \times 10^{-5}$.

** σ = standard deviation in %.

The value of the α_H parameter amounts to $6.38 \cdot 10^4$ at pH 5.55. Substituting the K_a and the K'_a values together with the appropriate α_H parameter in equation (3) one obtains:

$$K_{Ra^{2+} - EDTA} = 1.37 \pm 0.15 \cdot 10^7$$

The second series of experiments was carried out at pH 5.85 in the same circumstances as previously described. The results are given in Table II.

The stability constant calculated with these figures amounts to:

$$K_{Ra^{2+} - EDTA} = 1.1 \pm 0.2 \cdot 10^7$$

with $\alpha_H = 1.94 \cdot 10^4$ at pH 5.85 and 0.01 M EDTA.

The third series of measurements, performed at a pH value of about 7.5, gives at a first approach less accurate results (see Table III) than those performed at pH 5. The reason may be found in the fact that most buffer solutions necessary for the

TABLE III
²²⁶Ra-EDTA-AMBERLITE IR 120 EQUILIBRIA AT THE pH 7 RANGE*

Equilibrium without chelating agent			Equilibrium with chelating agent (0.01 M EDTA)			
pH	C_0	C_E	pH	C_0'	C_E'	K_d'
7.6	10.7	0.085	7.30	33.1	25.5	118
7.4	19.1	0.149	7.30	79.8	54.2	172
7.5	32.8	0.233	7.40	157.0	128.0	89
			7.60	132.0	120	40
$K_d = 52,000$		$\sigma = 4.7\%^{**}$	7.70	64.5	59.5	41

* Activity expressed in $\mu\text{C/ml} \times 10^{-5}$.

** Standard deviation in %.

stabilization of the pH, interfere with the Ra^{2+} -EDTA complexation, and therefore could not be added.

In order to standardize the K'_a values with respect to one definite pH, e.g. 7.5, the distribution coefficients obtained have to be multiplied by a correction factor which is the ratio between the α_H parameter at the actual pH and the one at pH 7.5 ($\alpha_H = 1.32 \cdot 10^2$).

The $K_{Ra^{2+} - EDTA}$ in the pH 7 range may be calculated according to equation (3):

$$K_{Ra^{2+} - EDTA} = \left(\frac{52,000}{64} - 1 \right) \times 1.32 \times 10^2 : 10^{-2} = 1.08 \pm 0.16 \cdot 10^7$$

As can be deduced from the measurement in the slightly acid and neutral solutions the Ra^{2+} -EDTA stability constant has a mean value of 1.18 ± 0.17 or a $\log K = 7.07$ ($\sigma = 0.06$). The same method was tested on ⁸⁹Sr-EDTA, $\log K = 8.77$ being obtained, whereas 8.63 is given in the literature⁶. SCHWARZENBACH⁹ mentions that above pH 3 only the 1:1 complexes of EDTA are important for alkaline earth metals ($n = 1$).

Writing the formulation of the Ra^{2+} -EDTA complex constant in a logarithmic form one gets:

$$\log \left(\frac{K_d}{K'_d} - 1 \right) = \log K_{\text{Ra}^{2+} - \text{EDTA}} + n \log \frac{[\text{EDTA}]}{\alpha_{\text{H}}} \quad (4)$$

This formula is represented on a log-log diagram by a straight line with a slope of 1:1, if $n = 1$. Using the results deduced from Tables I, II and III, one obtains on such a diagram a straight line with slope 0.97 (see Fig. 2), indicating the validity of the SCHWARZENBACH statement for the Ra^{2+} -EDTA complex and consequently for all the alkaline earth-EDTA complexes.

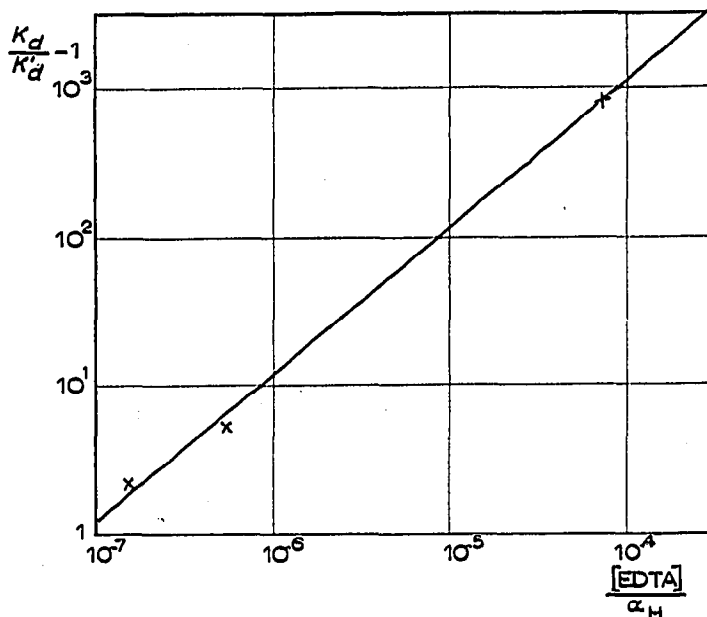


Fig. 2. Graphical representation of the experimental values related to equation (4).

The accuracy of the determinations is influenced by the presence of Na^+ ions in all the series of experiments and of acetate ions in the first series only (pH 5.55 and 5.85).

A quantitative estimation of the interference of the Na^+ ions on the availability of the free complexing agent may be made on the following basis. Both stability constants are given by the expressions:

$$K_{\text{Na}^+ - \text{EDTA}} = \frac{[\text{Na}^+ - \text{EDTA}]^{3-\alpha_{\text{H}}}}{[\text{Na}^+][\text{EDTA}]} \quad \text{and} \quad K_{\text{Ra}^{2+} - \text{EDTA}} = \frac{[\text{Ra}^{2+} - \text{EDTA}]\alpha_{\text{H}}}{[\text{Ra}^{2+}][\text{EDTA}]}$$

Introducing the experimental values one obtains:

$$[\text{Na}^+ - \text{EDTA}]^{3-} = 10^{1.66} \times 10^{-1} \times \frac{[\text{EDTA}]}{\alpha_{\text{H}}} \quad \text{and} \quad [\text{Ra}^{2+} - \text{EDTA}]^{2-} = 10^{7.07} \times 10^{-10} \times \frac{[\text{EDTA}]}{\alpha_{\text{H}}}$$

from which it follows that:

$$\frac{[\text{Na}^+ - \text{EDTA}]^{3-}}{[\text{Ra}^{2+} - \text{EDTA}]^{2-}} = 3.9 \times 10^3$$

The error would be important if a large part of the $[\text{EDTA}]^{4-}$ were bound by the Na^+ ions; however, this occurs in alkaline solutions only. At pH 5.5 the error amounts to $0.76 \cdot 10^{-2}\%$ and at pH 7.5 to 3.45 %; both errors are negligible with respect to the fluctuations in the K_a and K'_a measurements. The presence of acetate ions as buffer at pH 5.5 causes a systematic error which could be calculated along the same lines as

TABLE IV
 K'_a VALUES STANDARDIZED TO pH = 7.5 USING EQUATION (3)

pH	$\alpha_H \times 10^{-2}$	Conversion factor to pH 7.5	Actual K'_a	Standardized K'_a at pH 7.5	Mean K'_a at pH 7.5
7.30	2.17	0.608	118	72; 105	
7.40	1.69	0.78	89	69	
7.60	1.04	1.27	40.6	51	64*
7.70	0.82	1.65	41.5	66	$\sigma = 13\%$

* Excluding the K'_a value of 105.

described for Na^+ if the stability constant for Ra^{2+} acetate were known. The latter has not yet been determined, therefore we took the corresponding value of the Ba^{2+} acetate complex ($\log K = 0.40$) as probable figure¹⁰. Taking into account the Ba^{2+} acetate stability constant, one obtains a maximum error of 5 % which is again tolerable.

The newly determined Ra^{2+} -EDTA stability constant fits in quite well with those of the other alkaline earth metals⁷.

DETERMINATION OF THE MOST FAVORABLE CONDITIONS FOR THE FIXATION OF ^{226}Ra ON AMBERLITE IR 120 FROM EDTA-CONTAINING SOLUTIONS

The chemical conditions required for the decontamination of EDTA solutions containing ^{226}Ra may be derived from the investigation of the stability constant of the chelate complex. The factors that influence the distribution of the Ra^{2+} among Ra^{2+} , Ra^{2+} -EDTA and Ra^{2+} resinate, are the K_a and the K'_a values, the pH and the concentration of EDTA^{4-} .

The amount of free Ra^{2+} in equilibrium with its complexed form Ra^{2+} -EDTA is given by the following expression:

$$[\text{Ra}^{2+}] = \frac{[\text{Ra}^{2+} - \text{EDTA}] \alpha_H}{K_{\text{Ra}^{2+} - \text{EDTA}} [\text{EDTA}]} \quad (5)$$

When the former solution is brought into contact with ion-exchange resins the total amount of ^{226}Ra in the system is distributed as follows:

$$^{226}\text{Ra}_{\text{Total}} = \text{Ra}^{2+}_{\text{Resinate}} + \text{Ra}^{2+}_{\text{Free}} + \text{Ra}^{2+}\text{-EDTA}$$

The main purpose of the present study consists in the calculation of the amount of ^{226}Ra which remains in the solution after being brought into contact with the ion-exchange resin.

The residual ^{226}Ra in the solution may be derived from the following formulas:

$$\begin{aligned} \text{Ra}_{\text{Total}} &= \text{Ra}^{2+}_{\text{Free}} + \text{Ra}^{2+}_{\text{Free}} \frac{K_{\text{Ra}^{2+} - \text{EDTA}}[\text{EDTA}]}{\alpha_{\text{H}}} + \text{Ra}^{2+}_{\text{Free}} \frac{K_d}{A} \\ &= \text{Ra}^{2+}_{\text{Free}} \left(1 + X + \frac{K_d}{A} \right) \end{aligned} \quad (6)$$

where: A = a constant factor (ml solution/g resin);

$$X = K_{\text{Ra}^{2+} - \text{EDTA}} [\text{EDTA}] [\alpha_{\text{H}}]^{-1}.$$

The distribution coefficient K'_d of Ra on the resin in presence of EDTA is given by the equation:

$$K'_d = \frac{\text{Ra}_{\text{Total}} - \text{Ra}^{2+}_{\text{Free}} - \text{Ra}^{2+}_{\text{Free}} X}{\text{Ra}^{2+}_{\text{Free}} + \text{Ra}^{2+}_{\text{Free}} X} \cdot A$$

which may be rearranged as follows:

$$\text{Ra}_{\text{Total}} = \text{Ra}^{2+}_{\text{Free}} \left(\frac{K'_d}{A} + 1 \right) (1 + X) \quad (7)$$

Equating (6) and (7) one obtains finally:

$$K'_d = \frac{K_d}{1 + X} \quad (8)$$

The values are given in Table V, calculated for the following experimental conditions: $[\text{EDTA}] = 10^{-2} M$; $\text{pH} = 3$ to 9 ; $A = 400$.

TABLE V
CALCULATED VALUES OF α_{H} , X AND K_d/K'_d AS FUNCTIONS OF THE pH

pH	α_{H}	$X = 10^{5.07} (\alpha_{\text{H}})^{-1}$	K_d/K'_d	Experimental K_d/K'_d
3	$9.92 \cdot 10^9$	$1.17 \cdot 10^{-5}$	1	1
3.5	$7.64 \cdot 10^8$	$1.51 \cdot 10^{-4}$	1.000015	
4	$6.90 \cdot 10^7$	$1.66 \cdot 10^{-3}$	1.00166	
4.5	$6.82 \cdot 10^7$	$1.69 \cdot 10^{-2}$	1.0169	
5	$7.03 \cdot 10^5$	$1.64 \cdot 10^{-1}$	1.164	
5.5	$7.87 \cdot 10^4$	$1.468 \cdot 10$	2.468	
5.55	$6.52 \cdot 10^4$	1.78	2.78	3.15
5.85	$1.94 \cdot 10^4$	6.0	7.0	6.6
6	$1.06 \cdot 10^4$	10.9	11.9	
6.5	$1.92 \cdot 10^3$	60	61	
7	$4.66 \cdot 10^2$	247	248	
7.5	$1.32 \cdot 10^2$	$8.79 \cdot 10^2$	880	840
8	$4.16 \cdot 10^1$	$2.79 \cdot 10^3$	2791	
8.5	$1.375 \cdot 10^1$	$8.47 \cdot 10^3$	8471	
9	5.015	$23.10 \cdot 10^3$	23101	

The determination of the stability constant with an accuracy of two decimals on a logarithmic scale is precise enough for the reverse calculation of the K'_a values, as can be deduced from a comparison between the experimental K_a/K'_a ratio and that calculated in this way.

The figures in the 4th column of the table indicate that the Ra^{2+} ions remain free in solution up to pH 4, after which a very sharp rise of the ratio K_a/K'_a occurs (pH 4 to 9, see Fig. 3). Above pH 9 practically all Ra^{2+} ions are present in complexed form.

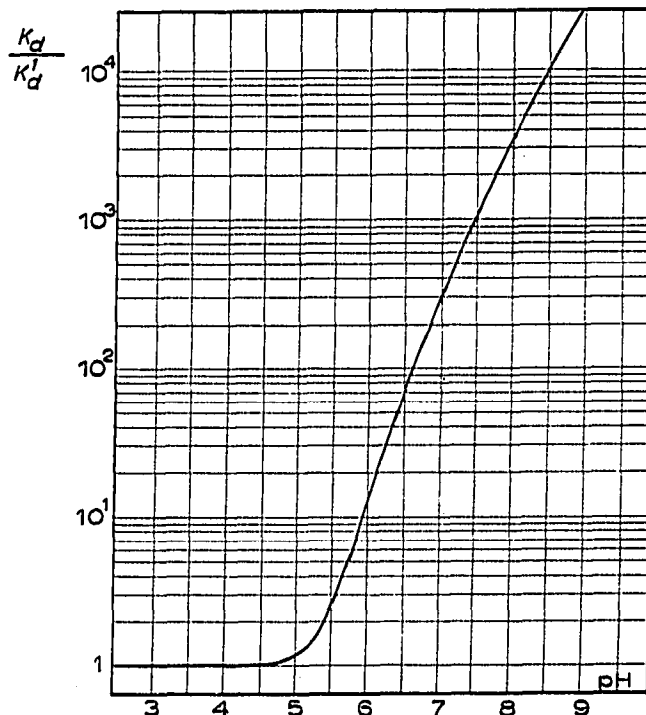


Fig. 3. The conversion factor K_a/K'_a as a function of the pH.

In order to fix the Ra^{2+} ions on the resin it is necessary to acidify the feed solution to pH 4.5 at which acidity the resin still retains its maximum exchange capacity and the EDTA does not precipitate. The volume of contaminated solution which may be purified by the Amberlite IR 120 column follows directly from the K'_a value at that pH.

After saturation of the resin the fixed Ra^{2+} may be eluted quantitatively by a very small volume of EDTA solution at pH 10 as the K'_a value drops to almost zero in alkaline solution.

A small fraction of the effluent of the feed solution would, after neutralisation to pH 10, be sufficient for that purpose. The whole cycle of decontamination of the solution and regeneration of the ion-exchange column can thus be effected without any special reagent. Based on this principle, analogue cases may be solved, for example, ^{89}Sr and rare earths in EDTA solution provided that the stability constants of their chelate complexes are not too high.

SUMMARY

The stability constant of $^{226}\text{Ra-EDTA}$ was determined using the method of SCHUBERT in a modified form.

The constant was found to be such that $\log K = 7.07 \pm 0.06$. The influence of the Na^+ and acetate ions in the solutions was taken into account by applying appropriate corrections. An equation was developed giving the relationship between the distribution coefficients in free and complexed solutions. The formulas provide the basic data for the design of a decontamination assembly for ^{226}Ra in EDTA solutions with ion-exchange columns.

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