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DETERMINATION OF THE FORMATION COEFFICIENTS OF Be-EDTA COMPLEXES

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Abstract—The formation constants for four complexes of Be–EDTA with a metal to ligand ratio of 1:1 have been determined.

The experimental procedure consisted in the radiometric determinations of the Be distribution coefficients on an ion exchanger in the presence and absence of EDTA.

The formation quotients were calculated by an equation of SCHUBERT modified in order to obtain the four quotients simultaneously and to correct for the sorption of a cation complex by the exchanger.

The values obtained are critically discussed and compared with previous results listed in the literature.

UNTIL recently, estimates of the stability of Be–EDTA complexes were quite contradictory.(1a,b,c,d)

The differences among the values listed in the literature(2,3,4) suggested an attempt at a more accurate determination of these quotients.

We used SCHUBERT's method(5) for measurement of a formation quotient by means of ion exchangers and modified it in order to permit the simultaneous measurement of four formation quotients.

Discussion of the method

The following species are in equilibria in an EDTA (H_4Y) solution:

$$H_3Y^- + H^+ \rightleftharpoons H_4Y \qquad K_1 = \frac{(H_4Y)}{(H_3Y^-)(H^+)}\,; \quad \log K_1 = 1{\cdot}99^*$$

$$H_2Y^= + H^+ \rightleftharpoons H_3Y^- \qquad K_2 = \frac{(H_3Y^-)}{(H_2Y^=)(H^+)}\,; \quad \log K_2 = 2{\cdot}67^*$$

$$HY^{3-} + H^+ \rightleftharpoons H_2Y^= \qquad K_3 = \frac{(H_2Y^{2-})}{(HY^{3-})(H^+)}\,; \quad \log K_3 = 6{\cdot}22^*$$

$$Y^{4-} + H^+ \rightleftharpoons HY^{3-} \qquad K_4 = \frac{(HY^{3-})}{(Y^{4-})(H^+)}\,; \quad \log K_4 = 9{\cdot}60^*$$

* These values were measured by BAETSLÉ and BENGSCH(6) for EDTA in 0·1 M NaCl.

(1) (a) J. A. CATOGGIO, *An Direcc. Nac. Quim.* Año V, p. 89 (1952); (b) D. A. EVEREST, *The Chemistry of Beryllium*, p. 66 Elsevier, Amsterdam (1964); (c) F. J. WELCHER, *The Analytical Uses of Ethylene diamine Tetra-acetic Acid* (1st Ed) p. 300, Van Nostrand, New York (1958); (d) R. PRIBIL, *Complexes in Analytical Chemistry*, Prague: Nakl C.S.A.V. (1953).

(2) J. R. MERRILL, M. HONDA and J. R. ARNOLD, *Analy. Chem.* **32**, pp. 1420–6 (1960).

(3) L. P. ADAMOVICH and I. N. NAPADAILO, *Zh. Anal. Khim.* **16**, 158 (1961).

(4) V. V. STAROSTIN, V. I. SPTISYN and G. P. SILINA, *Russian J. Inorg. Chem.* **8**, 335 (1963).

(5) J. SCHUBERT, *J. Phys. Coll. Chem.* **52**, pp. 340–350 (1948).

(6) L. BAETSLÉ and E. BENGSCH, *J. Chromatography* **8**, 265 (1962).

We assumed that each of these species (except H_4Y) is able to complex the beryllium ion. Although the present calculation could be extended to all possible complexes that might be formed, we took in consideration only 1:1 complexes because according to SCHWARZENBACH(7) complexes with other EDTA/metal ratios would be comparatively unstable and therefore we further assumed that their formation quotients would be affected by very large errors.

SCHUBERT's method(5) leads to the following equation, which holds for complex formation between a metal M^{j+} and the ligand L^{i-}.

$$\frac{K_d{}^{\circ}}{K_d{}'} = 1 + \beta_n(L^{i-})^n \tag{1}$$

Here, $K_d{}^{\circ}$ and $K_d{}'$ are the distribution coefficients of the metal in absence and presence, respectively, of the complexing agent. The formation quotient β_n is equal to $(ML_n{}^{(j-in)+})/(M^{j+})(L^{i-})^n$ and may be calculated by means of α_i, the reaction constant for the dissociation of the complexing agent,(8) viz.

$$\alpha_i = (LH_n)/(L^{i-})$$

The adaptation of Equation (1) to the simultaneous determination of four formation quotients for which $n = 1$, gives:

$$\frac{K_d{}^{\circ}}{K_d{}'} = \frac{1 + \beta_4(Y^{4-}) + \beta_3(HY^{3-}) + \beta_2(H_2Y^{2-}) + \beta_1(H_3Y^{-})}{1 + \dfrac{(BeH_3Y^{+})_R}{(Be^{2+})_R}} \tag{2*}$$

The adapted equation involves a positively charged complex (BeH_3Y^+). Since the value of the ratio $(BeH_3Y^+)_R/(Be^{2+})_R$ is not known, and as it should be proportional to the H_3Y^- concentration, which is responsible for the cation complex formation, we took this ratio as equal to a constant k times (H_3Y^-).

$$\beta_4 = \frac{(BeY^{2-})}{(Be^{2+})(Y^{4-})} \qquad \beta_3 = \frac{(BeHY^{-})}{(Be^{2+})(HY^{3-})}$$

$$\beta_2 = \frac{(BeH_2Y)}{(Be^{2+})(H_2Y^{2-})} \qquad \beta_1 = \frac{(BeH_3Y^{+})}{(Be^{2+})(H_3Y^{-})}$$

$$(Y^{4-}) = \frac{(EDTA)}{\alpha_4} = (EDTA)\left[(H^+)^4K_4K_3K_2K_1 + (H^+)^3K_4K_3K_2 + (H^+)^2K_4K_3 + (H^+)K_4 + 1\right]^{-1}$$

$$(HY^{3-}) = \frac{(EDTA)}{\alpha_3} = (EDTA)\left[(H^+)^3K_3K_2K_1 + (H^+)^2K_3K_2 + (H^+)K_3 + \frac{1}{(H^+)K_4} + 1\right]^{-1}$$

$$(H_2Y^{2-}) = \frac{(EDTA)}{\alpha_2} = (EDTA)\left[(H^+)^2K_2K_1 + (H^+)K_2 + \frac{1}{(H^+)K_3} + \frac{1}{(H^+)^2K_3K_4} + 1\right]^{-1}$$

$$(H_3Y^{-}) = \frac{(EDTA)}{\alpha_1} = (EDTA)\left[(H^+)K_1 + \frac{1}{(H^+)K_2} + \frac{1}{(H^+)^2K_2K_3} + \frac{1}{(H^+)^3K_2K_3K_4} + 1\right]^{-1}$$

(EDTA): total concentration of EDTA
K_4, K_3, K_2, K_1: association constants (see above).

(7) G. SCHWARZENBACH, *Complexometric Titrations*, p. 9, Methuen, London (1960).

(8) A. RINGBOM, *Complexation in Analytical Chemistry* (1st Ed.), p. 38, Interscience, New York (1963).

With this hypothesis, the calculation of β_4, β_3, β_2, β_1, and k is limited to solving a system of five equations obtained from Equation (2) for different experimental conditions.

In order to get these four equations, the corresponding values of K_d°/K_d' may be obtained by varying the total EDTA concentration or the hydrogen ion concentration. As at low pH values the EDTA solubility is quite low, approximately 10^{-3} M, we preferred to work at constant EDTA concentration and vary the pH. The ratio (EDTA)/(Be^{2+}) was made equal to 100 in all experiments.

In order to prevent the formation of products resulting from beryllium hydrolysis,⁽⁹⁾ the concentration of ^9Be carrier was kept below 10^{-5} M and the selected pHs were not higher than 5·5. These conditions are in agreement with Equation (2), in which no hydrolysis concentration term has been considered.

Our preference for using ^7Be solutions with carrier was due to the considerable adsorption of beryllium at very low concentrations on glassware.

EXPERIMENTAL

Reagents

(a) $BeSO_4$, used as carrier, was obtained by crystallizing four times to 50 per cent yield the reaction product of commercial grade BeO and H_2SO_4 and drying the crystals by heating at 400°C to constant weight.

(b) ^7Be carrier free solution, used as Cl_2Be in hydrochloric acid solution (Specific activity = 40 μc/ml.

(c) NaCl reagent grade.

(d) EDTA Merck reagent grade.

(e) Dowex 50 × 8 (100 mesh) resin in sodium form (49% moisture)

(f) NaOH 0·100 M

(g) HCl 0·100 M

Method

The following solutions were prepared from the reagents:

(I) Be: 10^{-5}M; NaCl 0·1 M; ^7Be: 3500 c/min ml
(II) Same as I, but also 10^{-3} M EDTA.

Seventy-five ml portions of solutions I and II were equilibrated by shaking at room temperature, ~20°C, with 750 mg of moist resin.

The pH values were adjusted with NaOH 0·100 M or HCl 0·100 M. Volume changes due to these additions, being less than 1 per cent were neglected. After reaching pH constancy, shaking continued for 48 hours in order to assure equilibrium.

The activity of the samples before and after equilibration with the resin was measured in a well counter (2-ml aliquots)

The distribution coefficients (K_d) were calculated using the following equation:

$$K_d = \frac{A_0 - A_E}{A_E} \cdot \frac{\text{ml of solution}}{\text{g of dry resin}}$$

in which

A_0 = initial activity of ^7Be in solution
A_E = equilibrium activity of ^7Be in solution

RESULTS

Sets of values K_d° and K_d' at different pH values were obtained and are shown in Fig. 1. K_d° and K_d' values were interpolated in Graph 1 for every 0·2 pH units and

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(9) L. G. Sillen, *Quart. Rev.* **13**, 155 (1959).

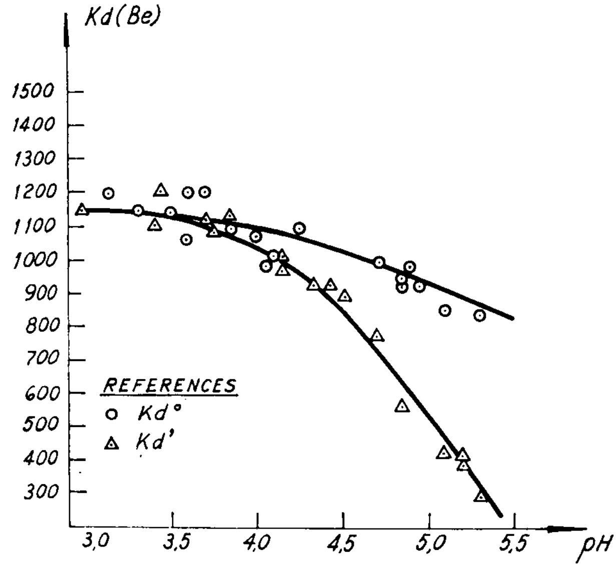

FIG. 1.—Beryllium distribution in the absence ($K_d°$) and presence (K_d') of EDTA.

values corresponding to the higher pH zone, in which the accuracy is higher, were selected. The selected values of $K_d°$ and K_d' were used, together with calculated values of (Y^{4-}), (HY^{3-}), (H_2Y^{2-}) and (H_3Y^-), to establish five equations similar to (2).

The system of five equations was solved with the help of the Mercury-Ferranti computer of the Instituto de Cálculo of the Universidad Nacional de Buenos Aires with the following results:

$$\log \beta_4 = 8{\cdot}4$$
$$\log \beta_3 = 3{\cdot}7$$
$$\log \beta_2 = 2{\cdot}1$$
$$\log \beta_1 = 2{\cdot}7$$

With the values of β_4, β_3, β_2 and β_1, the following ratios were calculated and plotted versus pH in Fig. 2 in order to illustrate the relative complexing ability of each ligand:

$$R_4 = \frac{(BeY^{2-})}{(Be^{2+})} \qquad R_3 = \frac{(BeHY^-)}{(Be^{2+})}$$

$$R_2 = \frac{(BeH_2Y)}{(Be^{2+})} \qquad R_1 = \frac{(BeH_3Y^+)}{(Be^{2+})}$$

DISCUSSION OF THE RESULTS

MERRILL *et al.*(2) using cation exchange resin at pH = 5·5 in 0·1 M Na Cl and ^{7}Be tracer, obtained, without giving information about the mathematical treatment used, $\log \beta_4 = 9{\cdot}8$ and $\beta_3 = 3{\cdot}8$. ADAMOVICH and NAPADAILO,(3) using also cation exchange resin at a lower pH ($\simeq$2) and 0·05 M NaCl ionic strength with ^{7}Be solution with 10^{-2} M carrier, obtained $\log \beta_4 \simeq 17$ and $\log \beta_3 = 8{\cdot}8$. Although at pH $\simeq$ 2 the hydrolysis products are negligible, it should be noted that these experimental conditions are unfavorable for studying the complexing of Be^{2+} by Y^{4-} and HY^{3-} ions,

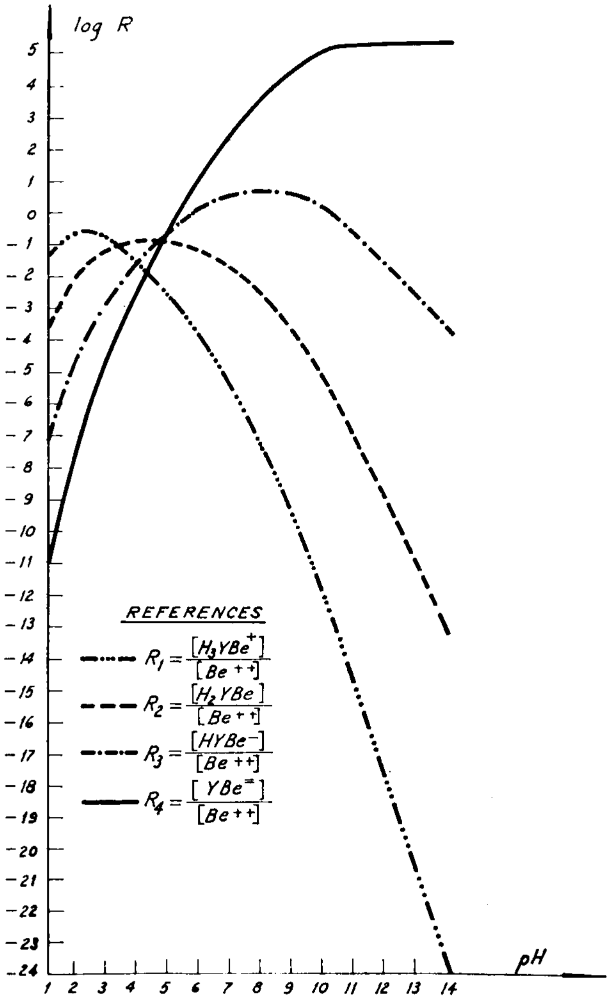

FIG. 2.—Ratio of complexed beryllium to uncomplexed beryllium (EDTA solution: 10^{-3} M).

which may be established by calculating α_4 and α_3 and further confirmed with the results shown on Fig. 2.

STAROSTIN and co-workers(4) obtained the values $\log \beta_4 = 10{\cdot}8$ and $\log \beta_5{}^* = 5{\cdot}4$. Obviously, the limitation involved is the use of the solubility product data for beryllium hydroxide. This was taken as $7{\cdot}3 \times 10^{-22}$ but the literature lists some other values which differ by up to five orders of magnitude(10) and which might cause $\log \beta_4$ to vary between 5·8 and 10·8.

Finally, RINGBOM(11) lists $\log \beta_4 = 9{\cdot}3$ at 0·1 ionic strength giving no further details.

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* $$\beta_5 = \frac{(BeOHY^{3-})}{(BeY^{2-})(OH^-)}$$

(10) J. BJERRUM, G. SCHWARZENBACH and L. G. SILLÉN, *Stability Constants of Metal Ion Complexes.* Pt. II. The Chem. Soc. London (1958).

The values of the formation quotients thus obtained show that the BeY^{2-} complex is roughly 10,000 times more stable than $BeHY^-$ and even more stable than BeH_2Y and BeH_3Y^+, although the actual concentration of each complex in solution is a function of pH only (see Fig. 2).

From this review it may also be seen that our values of the formation quotients are somewhat lower than those obtained by other authors. This is consistent with the fact that the ratios $K_d{}^\circ/K_d{}'$ have been fractionated among four species instead of two.

Because of this, the simultaneous determination of the four formation quotients giving two new values (β_1 and β_2), contributes to the accuracy of the two quotients previously determined.

The values obtained of $k(H_3Y^-) = 0{\cdot}07$–$0{\cdot}01$, corresponding to the ratio of complexed to free beryllium in the resin, are consistent with an estimated higher ionic potential for the uncomplexed beryllium ion.⁽¹²⁾

Acknowledgement—The authors like to express their gratitude to Dr. A. SUÑER for many helpful discussions regarding this work.

(11) A. RINGBOM, *Complexation in Analytical Chemistry* (1st Ed.) p. 332. Interscience, New York (1963).

(12) R. KUNIN, *Ion Exchange Resins* (2nd. Ed.), p. 27, J. Wiley, New York (1958).