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DETERMINATION OF THE FORMATION QUOTIENTS OF Be-EDTA COMPLEXES BY SOLVENT EXTRACTION

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Abstract—The formation quotient of the Be-EDTA complex, BeY^{2-}, was determined using ligand competition in a solvent extraction system. The distribution quotients of beryllium acetylacetonate were measured by means of γ counting of ^7Be in a system CCl_4–H_2O at a constant ionic strength of 0·1 M $NaNO_3$ at 30°C. The result obtained: $\log\beta_4 = 8{\cdot}68 \pm 0{\cdot}02$ where $\beta_4 = [BeY^{2-}]/[Be^{2+}][Y^{4-}]$, agrees with results listed in the literature.

INTRODUCTION

IN A PREVIOUS paper the formation quotients of several Be-EDTA complexes were measured using a cationic exchange resin[1]. This method presented the possibility that a cationic complex, BeH_3Y^+, could be fixed on the resin, in addition to Be^{2+}. Since the amount of cationic complex on the resin was difficult to determine, the numerical solution was obtained by adding an adjustable parameter to the equations used. In the present work we have tried to confirm the earlier values of the formation quotients. A solvent extraction technique which does not require the use of the above mentioned parameter was employed. The only assumption made is that no mixed anionic complexes were formed in the aqueous phase.

The system consisted on beryllium acetylacetonate-acetylacetone (HX), and ethylenediamine tetraacetic acid (H_4Y) as the competing ligand, distributed between CCl_4 and H_2O. It was known from spectrophotometric measurements that the only beryllium species extracted by the organic phase is the neutral beryllium acetylacetonate[2]. Its distribution quotient Q_{DB}, is related directly to the composition of the organic phase ($[HX]_o + [BeX_2]_o$).

The method consisted in measuring the distribution quotients of beryllium in the presence (Q'_d) and in the absence of EDTA (Q_d) at constant ionic strength of $NaNO_3$ (0·1 M) and at 30°C. The distribution quotients of beryllium in the absence and in the presence of EDTA, being respectively

$$Q_d = \frac{[BeX_2]_o}{[Be^{2+}] + [BeX^+] + [BeX_2]} \qquad (1a)$$

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1. C. E. Bamberger and F. Laguna, *J. inorg. nucl. Chem.* **28**, 1067 (1966).
2. C. E. Bamberger and C. F. Baes, Jr., *Reactor Chemistry Division Ann. Prog. Rep.* ORNL-3262, p. 156 (1962).

and

$$Q'_d = \frac{[BeX_2]'_o}{[Be^{2+}]' + [BeX^+]' + [BeX_2]' + [BeY^{2-}] + [BeHY^-] + [BeH_2Y] + [BeH_3Y^+]} \quad (1b)$$

where the subscript o indicates species in the organic phase, the absence of subscript indicates species in the aqueous phase, and the superscript ' indicates the presence of EDTA in the aqueous phase. Strictly, both denominators of the above equations should include the addition of concentrations of the hydrolytic species, but as will be seen below, the experimental conditions were selected as to make them negligible.

The distribution measurements were performed at constant composition of the organic phase, which from Ref. [3] allows us to state that

$$Q_{DB} = Q'_{DB} = \frac{[BeX_2]_o}{[BeX_2]} = \frac{[BeX_2]'_o}{[BeX_2]'}. \quad (2)$$

Since the neutral species BeX_2 is in equilibrium with Be^{2+} and BeX^+ in the aqueous phase, it can be shown that the beryllium distribution quotients, Q_d

$$Q_d = \frac{[BeX_2]_o}{[Be^{2+}] + [BeX^+] + [BeX_2]} = \frac{[BeX_2]'_o}{[Be^{2+}]' + [BeX^+]' + [BeX_2]'}. \quad (3)$$

By substitution in Equation (1)

$$\frac{1}{Q'_d} - \frac{1}{Q_d} = \frac{[BeY^{2-}] + [BeHY^-] + [BeH_2Y] + [BeH_3Y^+]}{[BeX_2]'_o}$$

$$= \frac{\beta_4[Y^{4-}] + \beta_3[HY^{3-}] + \beta_2[H_2Y^{2-}] + \beta_1[H_3Y^-]}{[BeX_2]'_o/[Be^{2+}]'} \quad (4)$$

where $\beta_1 \ldots . \beta_4$ are the formation quotients of the Be-EDTA complexes. Rearranging (4) we obtain:

$$Z = \left[\frac{1}{Q'_d} - \frac{1}{Q_d}\right] \frac{[BeX_2]'_o}{[Be^{2+}]'} = \beta_4[Y^{4-}] + \beta_3[HY^{3-}] + \beta_2[H_2Y^{2-}] + \beta_1[HY^-]. \quad (5)$$

Thus, measuring the distribution quotients of beryllium in the presence and in the absence of EDTA at various pH values allows to set up systems of equations similar to Equation (5). The quotient $[BeX_2]'_o/[Be^{2+}]'$ in Equation (5) can be calculated using the following relations:

$$\frac{[BeX_2]'_o}{[Be^{2+}]'} = Q_{DB}\ Q_2 \frac{[HX]^2}{[H^+]^2} \quad (6)$$

3. C. E. Bamberger, H. F. McDuffie and C. F. Baes, Jr., *Nucl. Sci. Engng* **22**, 14 (1965).

where

$$Q_2 = \frac{[BeX_2]' [H^+]^2}{[Be^{2+}]' [HX]^2} \tag{6a}$$

and

$$[HX] = \frac{\Sigma HX}{Q_{DX}+1} \tag{6b}$$

in which ΣHX is the total acetylacetone present and Q_{DX} is the distribution quotient of acetylacetone $= [HX]_o/[HX]$.

EXPERIMENTAL

When selecting the experimental conditions, one of the limiting factors was the concentration of H_4Y, which having a low solubility in water[4] provided a small concentration of ligand for competing with the acetylacetonate ion. This led us to test several concentrations of acetylacetone in order to select one which would not yield excessively high distribution quotients. The effect of the concentration of HX in the aqueous phase on the distribution quotient of beryllium was known from previous measurements[3] and this provided the basis for selecting an adequate concentration of HX.

The beryllium (labeled with ^7Be) concentration was small, 10^{-6} M, with respect to the HX concentration in order to keep the organic phase composition constant and also to avoid the formation of beryllium hydrolytic species. The concentration of acetylacetone used was 2×10^{-3} M in CCl_4. The sodium nitrate, the EDTA (ethylenediamine tetraacetic acid), the sodium hydroxide, and the nitric acid were all Reagent grade. When EDTA was present, its concentration was $1{\cdot}3 \times 10^{-3}$ M. The 50 ml aliquots of each phase, organic and aqueous, were shaken in 200 ml glass bottles provided with double stoppers of polyethylene and bakelite. After pH adjustment, the samples were mechanically shaken until the beryllium distribution quotients were reproducible within 5 per cent. The time required was around 200 hr. During this time the pH was adjusted several times when considered necessary. After equilibrium was reached, the γ activity of both phases was measured in a well counter. Distribution quotients were calculated as the ratio of counts/min ml in the organic phase to the counts/min ml in the aqueous phase.

RESULTS AND DISCUSSION

The values of Q_d and Q_d' used were interpolated from the graphically smoothed curves of experimental data (Fig. 1). The values of $[BeX_2]_o'/[Be^{2+}]'$ were calculated using $Q_2 = 4{\cdot}42 \times 10^{-4}$ and $Q_{DX} = 3{\cdot}3$ determined in previous measurements[3]. In the pH range at which the difference between Q_d and Q_d' was significant, Q_{DX} remained constant within 1 per cent. The value of $Q_{DB} = 50$ was estimated from present measurements. The concentration of the anions of EDTA was calculated using the dissociation constants measured by Baetslé and Bengsch [5]. The values of the formation quotients β_n were calculated by least squaring the data shown in Table 1. The results obtained indicated that β_2 and β_1 could not be determined. Since the concentrations of BeH_2Y and BeH_3Y^+ are relatively small at the pH range 5–7, the addition of their concentration by their corresponding formation quotients is a negligible contribution to the value of Z in Equation (5). This is consistent with the shapes of the curves in Fig. 1. It can be seen that at pH values below 5·5 both curves come closer to each other forming a single curve at pH ~ 4·8, which is caused by a significant decrease in the

4. A. J. Barnard, W. C. Broad and H. Flaschka, *Chemist Analyst* **45**, 86 (1956).
5. L. Baetslé and E. Bengsch, *J. Chromatog.* **8**, 265 (1962).

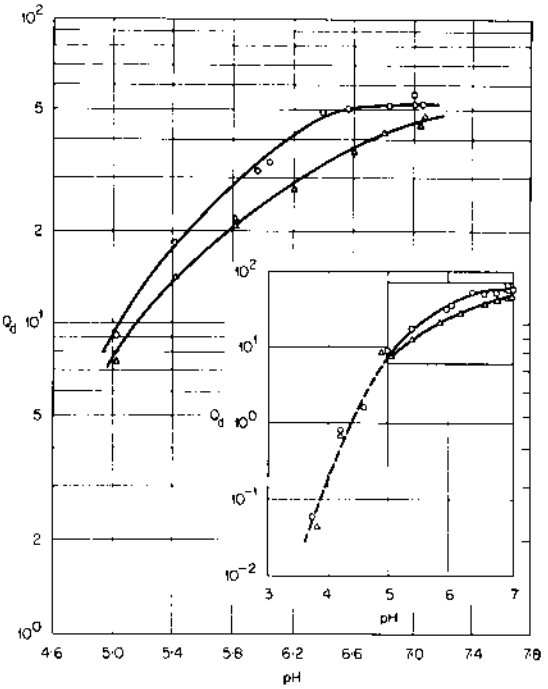

Fig. 1. Distribution quotients of beryllium, in the presence of $1{\cdot}3 \times 10^{-3}$ M EDTA (Δ) and in the absence of EDTA (o) as a function of pH.

Table 1. Data from distribution measurements of beryllium in the acetylacetone CCl_4–H_2O system at 30°C

$$\left(Z = \left[\frac{1}{Q'_d} - \frac{1}{Q_d}\right] \frac{[BeX_2]'_o}{[Be^{2+}]'}\right)$$

pH	Z	$[Y^{4-}] \times 10^8$	$[HY^{3-}] \times 10^4$
5·5	5·7765	1·654	2·077
5·6	9·6541	2·515	2·515
5·7	21·6657	3·790	2·995
5·8	22·6052	5·680	3·581
5·9	37·5949	8·387	4·207
6·0	55·5705	12·28	4·887
6·1	83·1600	17·74	5·603
6·2	128·0790	25·29	6·341

concentration of Y^{4-} and HY^{3-} while the concentration H_2Y^{2-} and H_3Y^- (ions of relatively much lower complexing ability) increases. In the pH range of 5·5 to 6·5 the difference between Q_d and Q'_d is maximum, making this pH range the most suitable for calculating β_4 and β_3. Increasing the pH above 6·5 causes both curves to come together because although the concentration of the ions Y^{4-} and HY^{3-} increases with pH the dissociation of HX also increases with pH causing

an increase in the BeX_2 concentration which is a more stable complex than the competing Be-EDTA complexes.

The above mentioned considerations limited the application of this solvent extraction system to the determination of only two formation quotients, β_4 and β_3, in a narrow range of pH.

Least squares analysis of the data with unit weights indicated that even the contribution of the species $BeHY^-$ was negligible in the solvent extraction system used. The result obtained for β_4 was $8{\cdot}68 \pm 0{\cdot}02$ (one standard deviation) which alone accounts for the data within the estimated experimental error. However, the data are also consistent with values for β_4 of 8·6 and β_3 of 4·0 which agree with those previously determined by ion exchange, respectively 8·4 and 3·7 [1].

The complex BeY^{2-} is the least stable of the EDTA complexes with any divalent or polyvalent cation, except for Ba^{2+} [6]. This accounts for the successful use of EDTA in most separation schemes of beryllium from other ions in analytical chemistry.

6. L. G. Sillén and A. E. Martell, *Stability Constants of Metal-Ion Complexes*. The Chemical Soc., London (1964).