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Purification of Beryllium by Acetylacetone-EDTA Solvent Extraction*

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A solvent extraction process for the purification of beryllium has been described previously in which ethylenediamine tetraacetic acid (EDTA) is used as a masking or sequestering agent to retain metallic impurities in an aqueous phase from which the beryllium is extracted into an organic phase (CCl_4) as a complex with acetylacetone (HX). Subsequent back extraction of the beryllium into nitric acid, followed by the precipitation of beryllium hydroxide, filtering, drying, and calcination to 1000°C, has given BeO products of high purity. Approximately 1300 gm of BeO have been prepared in 23 batches. The average impurity content of these batches (based on BeO) has been very low—less than 10 ppm each of Ca, Al, and Si; less than 5 ppm each of Fe, Mg, and Cu; all other metallic impurities were below the level of detection by the spectrographic method of analysis. The maximum impurity contents for individual metallic species among all these batches were, in ppm BeO, Al-9, Ca-10, Cu-13, Mg-5, Fe-10, Si-11; these are considered to reflect the difficulty of keeping small batches free from contamination by dusty air and should not occur in larger operations.

A quantitative treatment of the extraction equilibria and masking equilibria involved in the process has been undertaken. Spectrophotometric analytic techniques recently applied to the simultaneous determination of acetylacetone and its beryllium complex have greatly facilitated this study; radioactive beryllium-7 has been used as a tracer to make possible the rapid determination of distribution coefficients. The results have generally been as expected; the formation constants for the mono- and di-acetylacetonates of beryllium were calculated (at $I = 0.10$) to be:

$$K_1 = \frac{[BeX^+][H^+]}{[Be^{++}][HX]} = 6.75 \times 10^{-2}$$

$$K_2 = \frac{[BeX_2][H^+]^2}{[Be^{++}][HX]^2} = 4.41 \times 10^{-4}$$

Anomalously high distribution coefficients were noted under conditions associated with the presence of high concentrations of NaCl, and even the disodium salt of EDTA, in the aqueous phase. The significance of the anomalous conditions is discussed in terms of water activity and the degree of hydration of the acetylacetone complex of beryllium.

INTRODUCTION

The purification procedure used in this work was selected and developed on the basis of a literature survey by R. E. Moore (*1*). It was described briefly in the proceedings of the Second Conference on Nuclear Reactor Chemistry (*2*) and in more detail in a recent ORNL report (*3*). Information concerning the properties of pure beryllium oxide is, of course, of interest to many current studies of high-temperature reactors.

PREPARATION OF SMALL QUANTITIES OF BeO

The choice of the acetylacetone-EDTA solvent extraction scheme was based largely on its successful use for the analytical separation of beryllium as described by Adam, Booth, and Strickland in 1952 (*4*), and studied by others since that time (*5*, *6*).

The essential features of the extraction step are the extraction of beryllium into an organic phase as a complex with acetylacetone and the retention

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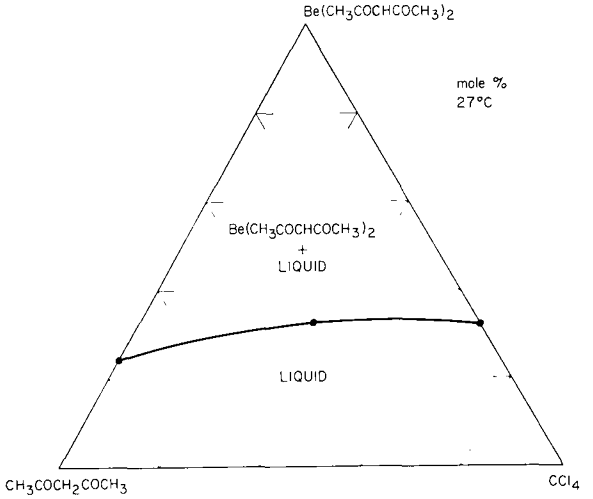

FIG. 1. The system: carbon tetrachloride–acetylacetone–beryllium acetylacetonate.

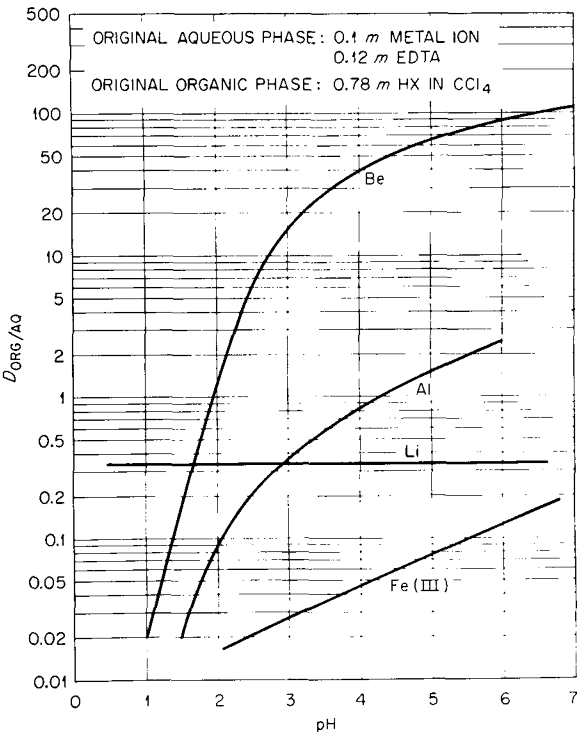

FIG. 2. Distribution coefficients versus pH

of many metallic impurities in the aqueous phase as complexes with EDTA. The steps, in the process which was used for the first phase of the program, are:

1. $Be(OH)_2$ is dissolved in a solution of acetylacetone and carbon tetrachloride.

2. The organic solution is washed with deionized water.

3. The organic solution is extracted several times with an aqueous phase saturated with ethylenediamine-tetraacetic acid (EDTA) which retains metallic impurities as EDTA complexes.

4. The purified organic solution is back-extracted with nitric acid.

5. $Be(OH)_2$ is precipitated by addition of pure aqueous NH_4OH.

6. Pure BeO is obtained by calcining the pure $Be(OH)_2$. (Polyethylene equipment used to avoid contamination from glassware).

Figure 1 shows the miscibility of acetylacetone with carbon tetrachloride and the high solubility of the beryllium complex in the organic phase. This, of course, would permit a large scale process to operate with reasonably small volumes of the organic phase. Figure 2 shows distribution coefficients versus pH for beryllium and several typical impurities under particular concentration conditions. A corresponding figure in ref. *3* also presented values for the distribution of magnesium. Other references do not show the extraction of magnesium, and the earlier results have not been confirmed by later tests; it is not now believed that magnesium is extracted under our conditions. Table I shows the results of spectrographic analyses of 23 batches of purified material and illustrates the agreement between the results from two different spectrographic laboratories. The total amount of BeO included in these batches was approximately 1300 gm. The recoveries in each batch were quite low. Because of incomplete separation of acetylacetone in the back-extraction step, the precipitated $Be(OH)_2$ in early experiments was found to contain large amounts of organic beryllium acetylacetonate—material which interfered with the calcination. A partial neutralization to pH 2.8–3.0 and re-extraction with carbon tetrachloride, following the back-extraction step, removed all the acetylacetone from the aqueous phase, allowing a pure final product to be obtained. But this treatment also re-extracted substantial amounts of beryllium into the organic wash. To achieve higher yields, the acetylacetone could be removed from the aqueous back extract by multiple washings with an organic stripping agent.

QUANTITATIVE TREATMENT OF THE EXTRACTION SCHEME

The objectives of this phase of the program were: (1) to formulate expressions for the equilibrium constants for the complexing of beryllium by acetylacetone (in the absence of EDTA) and to relate these to experimentally determined parameters in an all-aqueous system, (2) to convert these rela-

TABLE I

Comparative Spectrographic Analyses of 23 Batches of Purified Material

Prep. No.	Analysis I[a] Impurities reported (ppm)	Analysis II[b] Impurities reported (ppm)
A1	None	None
A2	Na <10 t; Mg <5 t	None
A3	Si <25 ft; Mg 6; Fe 10	—
A4	Na <10 t; Mg <5 ft	—
A5	Al, Mg, Fe 5; Si, Ca 10; Na <10 t	—
A6	Ca 5; B <1 t; Na <10 t; Al <5 t	None
JA1	Li 30; Cu 2	Cu 7; Al, Fe, Si 4
JA2	Cu 2	Cu, Si 5
JA3	Cu 2	Cu 7; Al, Si 5, Mg 4
JA4	Si 20; Mg, Cu 5	Cu, Si 4
JA5	Al 7, Si 10; Mg 8, Cu <5 t	Fe, Si 4
JA6	Al, Mg 5; Si 20; Cu 18	Cu 9; Si 5; Mg 4
JA7	Al, Mg, Cu 5; Si 10; Ca <10 t	Cu, Si 5
JA8	Al, Mg, Cu 5; Si 10	Cu 5; Fe, Si 4
JA9	Si 15, Mg 5; Ca <10 t; Pt − ft	Mg, Si 4
JA10	Al, Si 10; Mg <5 t; Pt − t	Al, Si 5
JA11	Mg <5 t; Si 10; Pt − t	Si, 11; Al 9; Mg 5; Fe 4
JA12	Si <10 t; Mg 5; Pt − ft	Al, Cu, Si 4
JA13	Al 10; Si <10 t; Mg <5 t; Pt − t	Si 11; Al 7; Fe 4
PA2		Al 5; Cu 14; Si 11
PA3		Al, Cu, Si 5; Mg 4
PA4		Al 4; Si 7
PA5		Al, Fe 5; Si 9

[a] J. A. Norris, Z. Combs, and co-workers, ORNL Analytical Chemistry Division. Except those reported, other impurities were not detected or, if present, were below the quantitatively detectable levels which generally were as follows: Al, Ba, Cr, K, Ni, Rb, Si, Fe, Ca <10; Co, Mn, Mo, Pb, Mg, Cu <5; B <1; Ti <20; Zn <25; Li, Na, Sn <5–10; V <5–20; Sr <10–20 ppm. The symbols t and ft refer to trace and faint trace.

[b] W. D. Harman *et al.*, Y-12 Plant Spectrographic Laboratory. The quantitatively detectable levels for elements in Analysis II are as follows: Ag, Cr, Ni, Sn, Ga, Mo, Al, Cu, Mg, Ti, Au, Ge, B, Fe, Mn, Pb, Hf, Ba, Co, Si <4; W, Nb, Sr, Zr, Tl, Ta <11; Cd <36. The values were reported originally in terms of ppm in beryllium metal and were rounded off to the nearest ppm after conversion to ppm in BeO. The alkali metals and calcium were not reported in Analysis II.

tionships to an expression from which the equilibrium constants could be determined, and to see how these constants were affected by various parameters, (3) to use these constants, plus other experimentally determined relationships involving the *organic* phase to calculate distribution ratios for beryllium in organic-aqueous systems, and (4) to test the calculated constants against experimentally measured values of the distribution ratio.

Equations (1) and (2) show the formation of the mono- and diacetylacetonates of beryllium. For convenience acetylacetone is shown as HX.

$$Be^{++} + HX = BeX^{+} + H^{+} \qquad (1)$$

$$Be^{++} + 2HX = BeX_2 + 2H^{+} \qquad (2)$$

Equations (3) and (4) define the formation quotients of BeX^+ and BeX_2.

$$K_1 \equiv \frac{[BeX^+]_{aq}[H^+]_{aq}}{[Be^{++}]_{aq}[HX]_{aq}} \qquad (3)$$

$$K_2 \equiv \frac{[BeX_2]_{aq}[H^+]^2_{aq}}{[Be^{++}]_{aq}[HX]^2_{aq}} \qquad (4)$$

The experimental technique used in the determination of K_1 and K_2 involved a potentiometric titration with a glass electrode. A solution of controlled ionic strength containing, initially, known amounts of BeX_2 and HX was placed in a stirred vessel at 25°C. Nitric acid was then added stepwise in known amounts; following each addition the pH of the resulting solution was measured. As seen from Eqs. (1) and (2), any hydrolysis of BeX_2 would be accompanied by the consumption of hydrogen ions. The difference between the measured hydrogen ion concentration and that which would have been obtained in the absence of hydrolysis, $[H^+]_f$, provided a measure of the extent of the hydrolysis resulting from each incremental addition of nitric acid. Equation (5) defines ΔH^+ as this difference and indicates its relationship to changes in HX concentrations and to changes in the concentrations of aqueous beryllium species.

$$\begin{aligned}\Delta H^+ &\equiv [H^+]_f - [H^+]_{aq} \\ &= \Delta[HX]_{aq} = [HX]_{aq} - [HX]_i \\ &= 2[Be^{++}]_{aq} + [BeX^+]_{aq} \qquad (5)\end{aligned}$$

Two new quantities, Y and $\bar{n}$, are defined in Eqs. (6) and (7) in terms of parameters that can be measured experimentally.

$$Y \equiv \frac{[HX]_{aq}}{[H^+]_{aq}} = \frac{[HX]_i + \Delta H^+}{[H^+]_{aq}} \qquad (6)$$

$$\bar{n} \equiv \frac{\Delta H^+}{\sum Be_{aq}} = \frac{2[Be^{++}]_{aq} + [BeX^+]_{aq}}{\sum Be_{aq}} \qquad (7)$$

Then, in Eq. (8), the total beryllium in the solution is indicated as consisting of three species that can be evaluated using K_1, K_2, Y, and Be^{++}_{aq}.

$$\begin{aligned}\sum Be_{aq} &= [Be^{++}]_{aq} + [BeX^+]_{aq} + [BeX_2]_{aq} \\ &= [Be^{++}](1 + K_1Y + K_2Y^2)\end{aligned} \qquad (8)$$

TABLE II[a]

EFFECT OF IONIC STRENGTH ON K_1 AND K_2

pH	ΔH^+	$\bar{n}$	Y
$I = 0.1$ (KNO$_3$)			
5.11	9.348×10^{-4}	9.772×10^{-2}	$1.434 \times 10^{+3}$
4.91	1.395×10^{-3}	1.465×10^{-1}	9.390×10^{2}
4.75	1.849×10^{-3}	1.952×10^{-1}	6.713×10^{2}
4.62	2.298×10^{-3}	2.438×10^{-1}	5.146×10^{2}
4.40	3.179×10^{-3}	3.406×10^{-1}	3.299×10^{2}
4.31	3.613×10^{-3}	3.889×10^{-1}	2.759×10^{2}
4.23	4.041×10^{-3}	4.370×10^{-1}	2.364×10^{2}
4.15	4.462×10^{-3}	4.849×10^{-1}	2.016×10^{2}
4.00	5.289×10^{-3}	5.803×10^{-1}	1.500×10^{2}
3.85	6.087×10^{-3}	6.741×10^{-1}	1.114×10^{2}
3.72	6.861×10^{-3}	7.669×10^{-1}	8.586×10^{1}
3.60	7.620×10^{-3}	8.585×10^{-1}	6.797×10^{1}
3.49	8.332×10^{-3}	9.485×10^{-1}	5.477×10^{1}
3.28	9.680×10^{-3}	1.122	3.610×10^{1}
3.07	1.084×10^{-2}	1.279	2.338×10^{1}
2.78	1.217×10^{-2}	1.474	1.263×10^{1}
2.54	1.299×10^{-2}	1.613	7.490×10^{1}
2.36	1.344×10^{-2}	1.711	5.002×10^{1}
$I = 0.6$ (KNO$_3$)			
4.51	3.657×10^{-3}	0.368	$4.31 \times 10^{+2}$
4.18	5.450×10^{-3}	0.550	$2.28 \times 10^{+2}$
3.75	8.360×10^{-3}	0.850	$1.01 \times 10^{+2}$
3.57	9.770×10^{-3}	0.990	7.18×10^{1}
3.38	1.111×10^{-2}	1.13	4.95×10^{1}
3.02	1.353×10^{-2}	1.38	2.41×10^{1}
2.76	1.510×10^{-2}	1.55	1.41×10^{1}
2.53	1.622×10^{-2}	1.67	8.69
2.35	1.702×10^{-2}	1.76	5.90
2.20	1.747×10^{-2}	1.82	4.25
2.07	1.755×10^{-2}	1.83	3.16
$I = 2.0$(KNO$_3$)			
5.05	1.063×10^{-3}	2.247×10^{-1}	$1.285 \times 10^{+3}$
4.60	2.113×10^{-3}	4.477×10^{-1}	4.972×10^{2}
3.98	4.150×10^{-3}	8.850×10^{-1}	1.378×10^{2}
3.69	5.102×10^{-3}	1.090	7.544×10^{1}
3.45	5.997×10^{-3}	1.284	4.580×10^{1}
3.22	6.791×10^{-3}	1.457	2.829×10^{1}
2.99	7.408×10^{-3}	1.593	1.728×10^{1}
2.80	7.868×10^{-3}	1.696	1.136×10^{1}
2.64	8.190×10^{-3}	1.773	8.017
2.51	8.410×10^{-3}	1.824	6.003
2.41	8.630×10^{-3}	1.876	4.821
2.32	8.750×10^{-3}	1.906	3.941
2.24	8.770×10^{-3}	1.915	3.271
2.18	8.930×10^{-3}	1.954	2.870
2.11	8.770×10^{-3}	1.923	2.421
2.01	8.740×10^{-3}	1.925	1.915
1.93	8.670×10^{-3}	1.922	1.575

[a] The numbers in the table have a significance which is established by the accuracy and precision associated with the pH readings. Readings are estimated to the nearest hundredth of a pH unit and the precision is considered to be ±0.01 unit.

(Terms involving hydrolyzed beryllium species were considered, but their effect was insignificant in our experiments because of the high ratio of HX to uncomplexed beryllium above pH 3.) An analogous treatment of the numerator of Eq. (7) and substitution of Eq. (8) for the term in the denominator permits $\bar{n}$ to be related to K_1, K_2, and Y as shown in Eq. (9).

$$\bar{n} = \frac{[\mathrm{Be}^{++}](2 + K_1 Y)}{[\mathrm{Be}^{++}](1 + K_1 Y + K_2 Y^2)} = \frac{2 + K_1 Y}{1 + K_1 Y + K_2 Y^2} \tag{9}$$

As is common with schemes involving only mononuclear products, the aqueous beryllium ion concentration cancels from this last expression. Equation (9) may be rearranged into Eq. (10) in which K_1 and K_2 appear as the slope and intercept of a linear relationship.

$$\frac{2 - \bar{n}}{\bar{n} Y^2} = K_1 \frac{(\bar{n} - 1)}{\bar{n} Y} + K_2 \tag{10}$$

Table II presents the results of experiments at three different ionic strengths. Figure 3 displays these results according to Eq. (10) and shows the values of K_1 and K_2 which were obtained.

Since an important objective of the work was to develop a quantitative treatment of the entire

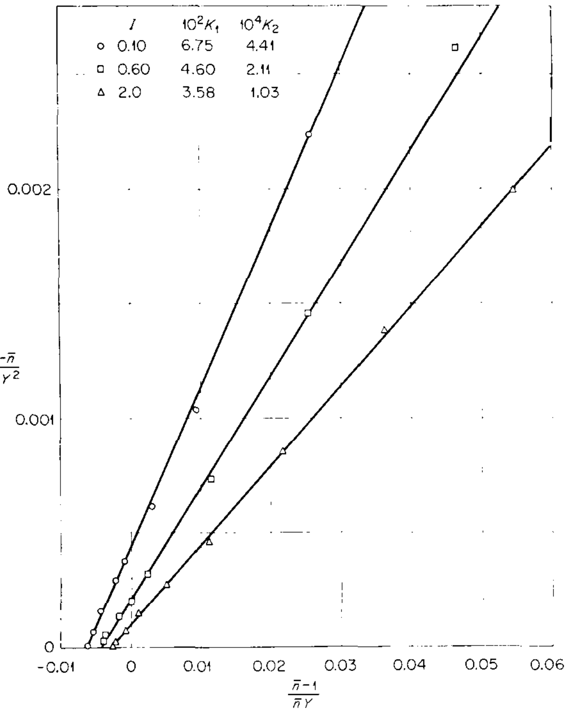

FIG. 3. Determination of K_1 and K_2

extraction scheme, it was next necessary to introduce the distribution of the BeX_2 complex between the aqueous and organic phases for a two-phase system. Equation (11) defines this distribution.

$$K_{DB} \equiv \frac{[BeX_2]_o}{[BeX_2]_{aq}} \tag{11}$$

In this work it has been assumed that BeX_2 is the only beryllium-containing species in the organic phase. Solubility measurements for BeX_2 in pure water and in carbon tetrachloride show that the ratio of concentrations in saturated solutions corresponds to a K_{DB} of about 110, but this may not be appropriate for dilute solutions where activity coefficients are closer to unity. Equation 12 defines D as the total beryllium in the organic phase divided by the total in the aqueous phase.

$$\begin{aligned} D &\equiv \frac{\sum Be_o}{\sum Be_{aq}} \\ &= \frac{[BeX_2]_o}{[Be^{++}]_{aq} + [BeX^+]_{aq} + [BeX]_{aq}} \end{aligned} \tag{12}$$

Introducing K_1, K_2, Y, and K_{DB} into Eq. (12) we obtain Eq. (13).

$$D = \frac{K_{DB}}{(1/K_2 Y^2) + (K_1/K_2 Y) + 1} \tag{13}$$

Examination of this relationship shows that the terms in the denominator involving K_1, K_2, and Y become insignificantly small as the pH of the system is increased (since Y becomes large). Consequently, values of K_{DB} for a particular ionic strength can be obtained from measurements of D at high pH.

A series of extraction measurements in the absence of EDTA in which D was determined as a function of pH using beryllium-7 and in which the distribution of HX between the aqueous and the carbon tetrachloride phases was determined spectrophotometrically are presented in Table III. Figure 4 shows a comparison of the observed D values from these measurements with calculated D values from Eq. (13). The K_{DB}, K_1, and K_2 values used here were corrected for the expected effect of the change in ionic strength involved in the measurements (K_{DB} varied from 76.8 to 82.0, K_1 varied from 0.068 to 0.061, K_2 varied from 0.00044 to 0.00036). The very small, but systematic discrepancy at lower values for D may be related to the difficulty of

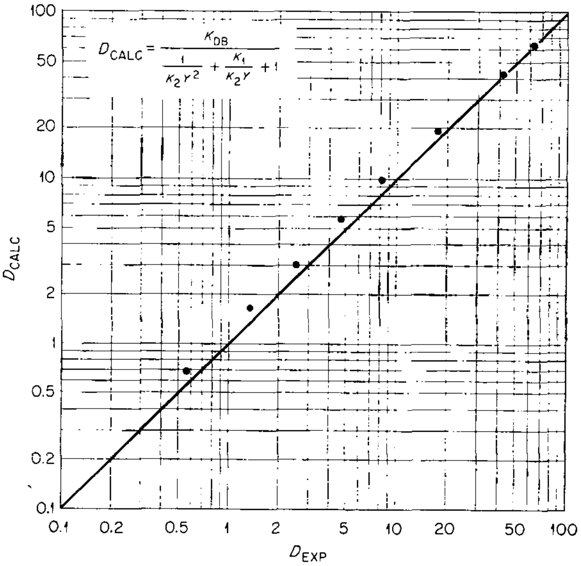

FIG. 4. Agreement between calculated and experimental values of D.

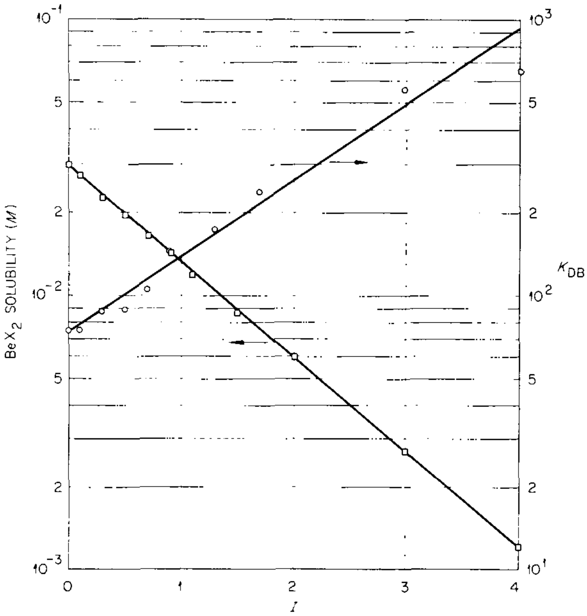

FIG. 5. Effect of ionic strength on BeX_2 solubility and on K_{DB}.

TABLE III[a]

VARIATION OF D WITH pH AND $[HX]_{aq}$

pH	D	$[HX]_{aq}$	Y	I
7.35	76.8	0.0297	5.3×10^5	0.100
4.43	63.5	0.0297	8.0×10^2	0.100
3.85	41.3	0.0297	2.1×10^2	0.100
3.32	17.3	0.0300	64.1	0.103
3.01	8.2	0.0330	33.8	0.110
2.78	4.7	0.0355	21.4	0.119
2.53	2.5	0.0404	13.7	0.137
2.31	1.35	0.0463	9.5	0.157
2.01	0.57	0.0550	5.6	0.186

[a] Initial $[BeX_2]_o \sim 0.1\ M$. Phase ratio ~1.

establishing a sufficiently precise material balance for H^+ at low pH's where the accuracy of the glass electrode is taxed.

ENHANCEMENT OF *D*

The effect of the EDTA was expected to be straightforward, and it mostly was. Information in the literature suggested that it should form strong complexes with many metallic impurities (*7*) and a relatively weak complex with beryllium (*8*). When the EDTA concentration in the aqueous phase was varied, it was somewhat surprising to find that the values for D appeared to increase with increasing concentrations of EDTA. But then it was found that dissolved NaCl could cause even more remarkable elevation in the D value; this elevation is believed due to the classical "salting-out" effect in which a neutral species, BeX_2, is forced out of aqueous solution by the lowering of water activity upon increasing the ionic strength. Figure 5 shows how great were the changes in both the BeX_2 solubility and K_{DB} upon raising the ionic strength. Both series of measurements were made in the presence of excess HX at pH 5–7 so that dissociation of BeX_2 in solution can be neglected. Hence the measurements of solubility and of D ($\sim K_{DB}$) may be related more or less directly to the aqueous activity of BeX_2. If it is *assumed* that the effect is due entirely to hydration and related to the change in the water activity, then *calculations* from these data indicate that approximately 18 water molecules are associated with each molecule of BeX_2 in the aqueous phase. It is believed that, whatever the cause of the effect, it is probably the same as that which is responsible for the relatively greater sensitivity of K_2 than K_1 to changes in ionic strength.

CONCLUSION

Studies of the extraction process are being extended to include tests of possible synergistic combinations of extractants, and examination of kinetic factors in the process, particularly those relating to the formation of the BeX_2 complex. New facilities have just been completed at our laboratory in which larger quantities of pure BeO are to be prepared using the precipitation technique recently described by Bamberger (*9*), in order to have material for spectrographic standards, for irradiation and other testing, and for studies of the effects of controlled amounts of additives on the sintering properties of BeO.

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