THE EXTRACTION OF BERYLLIUM AND ALUMINIUM FROM AQUEOUS SULPHATE SOLUTIONS WITH DI-(2-ETHYLHEXYL) PHOSPHORIC ACID*

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The experimental extraction equations are presented for the extraction of beryllium and aluminium from aqueous sulphate solutions with di-(2-ethylhexyl) phosphoric acid solution (EHPA) in kerosene. It is shown that under certain conditions beryllium can be separated from aluminium using this reagent. A structure is suggested for the beryllium complex.

A theory for the extraction of metal ions with weakly acidic chelating agents has been suggested (Morrison and Freiser 1957), and is expressed as the simplified equation (1).

$$D=K^*\left[\frac{[\mathrm{HR}]_o}{[\mathrm{H}^+]}\right]^n, \qquad (1)$$

$$D=\frac{\text{concentration of metal in the organic phase}}{\text{concentration of metal in the aqueous phase}}$$

by taking logarithms

$$\log D=n[\mathrm{pH}+\log [\mathrm{HR}]_o]+\text{constant}. \qquad (2)$$

A similar expression has been derived by Madigan (1959) using corrections for activity coefficients.

$$\log D=n[\mathrm{pH}+\log (c_{\mathrm{HA}})_o\cdot(y^{1/n}_{M^{n+}})_w]+\log K. \qquad (3)$$

This equation has been experimentally verified for the extraction of copper, cobalt, and nickel with EHPA (Madigan 1959).

The experimental work described in the present paper was carried out in an attempt to verify equation (2) for the extraction of beryllium and aluminium from sulphate solutions with EHPA solution in kerosene.

Experimental

Solutions of beryllium sulphate and aluminium sulphate, 0·05M and 0·033M respectively, were prepared by dissolving the hydrated salts in water.

A 0·1M solution of acid form EHPA was prepared by dissolving the reagent in a kerosene fraction distilled at 180–210 °C. Nonanol (4% v/v) was added to the organic solution to prevent any third phase formation. The EHPA was found, by potentiometric titration with ethanolic KOH using an antimony electrode, to be 99·02% di-ester. Various pH values for the aqueous phase at equilibrium were achieved by adding calculated amounts of NaOH or H_2SO_4

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before extraction. Equal volumes of aqueous and organic solutions were mixed thoroughly by rapid stirring at 30 °C for 2 hr to ensure that equilibrium was reached. After separation using ordinary laboratory separatory funnels, the organic phases were analysed for beryllium or aluminium and phosphorus, and the aqueous phases for beryllium or aluminium. The pH of each aqueous phase at equilibrium was measured using a precision pH-meter. It was considered that the amount of sodium extracted in the pH range studied would be negligible.

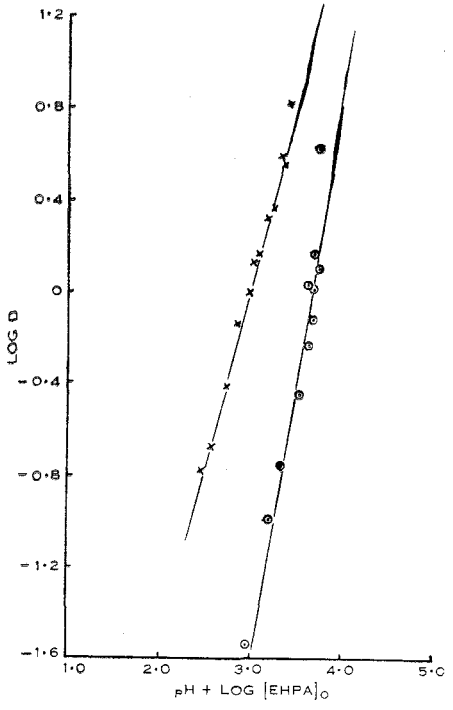


Fig. 1

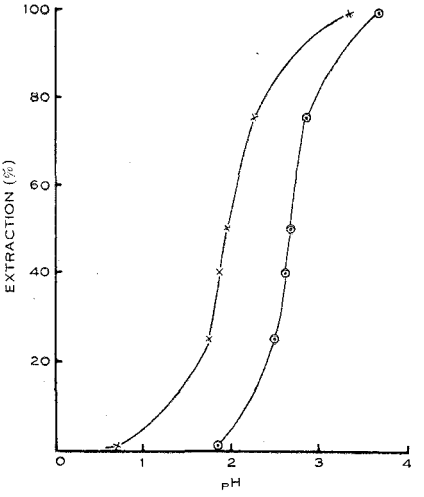


Fig. 2

Fig. 1.—Extraction of beryllium and aluminium by EHPA.
×—× Beryllium-slope 1·55; ⊙—⊙ aluminium-slope 2·38.

Fig. 2.—Extraction of beryllium and aluminium. Log $[EHPA]_o = 1$.
×—× Beryllium; ⊙—⊙ aluminium.

Discussion

(*a*) *The Extraction Equations.*—The results are graphically represented in Figure 1 by plotting log D against $[pH + \log[EHPA]_o]$. A straight-line relationship is obtained for both beryllium and aluminium. From Figure 1 the experimental extraction equations for beryllium and aluminium are obtained, and are shown below in equations (4) and (5).

Extraction equation for beryllium

$$\log D = 1 \cdot 55[pH + \log[EHPA]_o] - 4 \cdot 63. \quad (4)$$

Extraction equation for aluminium

$$\log D = 2 \cdot 38[pH + \log[EHPA]_o] - 8 \cdot 77. \quad (5)$$

The values for n obtained from Figure 1 are lower than the theoretical values of 2·0 and 3·0 for beryllium and aluminium respectively. This is to be expected because of the assumptions made in the derivation of the theoretical extraction equation (2).

The possibility of separating beryllium and aluminium by a solvent extraction process using EHPA may be evaluated as shown below. If the concentration of EHPA in the organic phase is kept constant at 10 mM/l, this value being chosen for convenience, then equations (4) and (5) may be written as

$$\log D = 1 \cdot 55[\mathrm{pH} + 1] - 4 \cdot 63, \tag{6}$$

$$\log D = 2 \cdot 38[\mathrm{pH} + 1] - 8 \cdot 77. \tag{7}$$

The extraction percentage E is related to D, the distribution ratio, as follows :

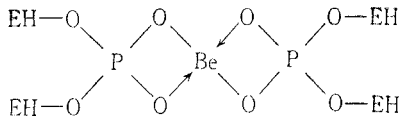
$$D = E/(100 - E). \tag{8}$$

Thus from equations (6), (7), and (8) the values of the pH for various values of extraction percentage can be calculated.

Figure 2 shows the extraction percentage of beryllium and aluminium for various calculated values of pH. It can be seen that by choosing the correct pH conditions it should be possible to separate beryllium and aluminium using a suitable number of extraction stages. At pH 2·2 the amounts of beryllium and aluminium extracted are 70 and 12% respectively, giving a separation factor which is defined as

$$D_{\mathrm{Be}}/D_{\mathrm{Al}} \quad \text{of 17.}$$

(*b*) *The Beryllium Complex.*—The beryllium complex was prepared by dissolving the stoichiometric weights of beryllium sulphate and EHPA in ethanol and boiling under reflux for several hours. The ethanol was then evaporated and the residue was boiled with water to remove any water-soluble impurities. The soap-like mass obtained was dissolved in benzene and poured into a water–acetone mixture. This procedure was repeated, yielding a soap-like compound which was shown by analysis to contain two EHPA molecules for each beryllium ion. The complex is probably a tetrahedral one formed by sp^3 hybridization of the beryllium ion.



EH = ethylhexyl

The compound as depicted above has two coordinate bonds from two oxygen atoms to the beryllium ion and two valence satisfying covalent bonds from the other two oxygen atoms. The suggested complex is neutral, with the EHPA groups placed tetrahedrally about the central beryllium ion.

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References

MADIGAN, D. C. (1959).—*Aust. J. Chem.* **13**: 58–66.

MORRISON, G. H., and FREISER, H. (1957).—"Solvent extraction in Analytical Chemistry." pp. 50–7. (John Wiley & Sons Inc.: New York.)