Asian Journal of Chemistry Vol. 3, No. 2 (1991), 206–211

SEPARATION OF MACRO AMOUNTS OF METAL PAIRS, II: SEPARATION OF ZINC AND COBALT

A.M. ELKOT
Chemistry Department, Faculty of Science
Zagazig University, Zagazig, Egypt

A systematic study was performed on the separation of zinc and cobalt from various concentrations of cadmium, zinc and cobalt in the original aqueous solutions. Recommended separation can be achieved from macro-concentrations of 0.04M Cd^{2+}, 0.3M Zn^{2+} and 0.4M Co^{2+} by Amberlite LA-2 from 4.5M H_2SO_4 to 0.16M HBr with respect to the three metals.

INTRODUCTION

In a previous paper[1] the extraction and separation of macro amounts of cadmium and cobalt has been reported. In this paper a systematic investigation has been carried out on the extraction and separation of macro-concentration, which is more of practical importance for zinc and cobalt. As solvent Amberlite LA-2 and tri-*n*-butyl phosphate (TBP) have been selected due to their favourable extractive properties and the reversibility of the extraction process so that reextraction from the organic solvent is possible. In addition, equilibrium was found to be attained within short periods of time for the given extraction conditions.

The separation of zinc and cobalt is very important in biological and medical investigations, since they represent the active agents of many pharmaceuticals. On the other hand, the isotopes Zn^{65} and Co^{60} are two of the most important contaminant isotopes, as they have long half-lives and their γ radiations have high energy. The separation of the two isotopes from other elements and isotopes is therefore important in the processing and reprocessing of atomic fuel as well as in the treatment of radioactive wastes.

Best conditions for separation of pairs of elements have been determined.

EXPERIMENTAL

Details of the apparatus, solvents and reagents used have been presented in the previous studies[2].

Radioactive tracers

Radioactive istopes Zn^{65} and Co^{60} with T = 245 d and 5.3 years respectively, were used as tracers of zinc and cobalt and were prepared by dissolution of pile irradiated high purity metals in concentrated hydrochloric or sulphuric acid.

Separation factor ε

The separation factor ε was determined as the ratio of the distribution coefficients *D* of the corresponding elements at the same aqueous and organic phase composition. The value of *D* was determined experimentally[3] by equilibrating a suitably volume (usually 5 ml) of the organic phase with an equal volume of the aqueous phase containing the radioactive tracer through mechanical shaking for 30 min. Preliminary studies showed that this time was sufficient for reaching equilibrium. The two phases were separated by centrifugation and aliquot portions from both phases were taken for radiometric assay. The *D* value was taken as the ratio of activity in the organic and that in the aqueous phase.

RESULTS AND DISCUSSION

Separation of Zinc and Cobalt

The effect of a certain metal ion concentration on the extraction of that metal or another less or more extractable can be best illustrated by the extraction and separation of zinc and cobalt pair by long chain amine (Amberlite LA-2) and organophosphorous solvent (TBP) in the presence of increasing macro amounts of Cd^{2+}, Zn^{2+} and Co^{2+} ions. Cadmium being more extractable and cobalt less than zinc itself. The effect of concentration of $CdSO_4$, $ZnSO_4$ and $CoSO_4$ on the separation of zinc and cobalt by the two solvents is illustrated in Figs. 1, 2 and 3 respectively and are in accordance with expectation. Thus the effect of the three metal sulphate concentrations on Zn extraction increases in the order Co < Zn < Cd. Extraction of Zn is almost unaffected by the presence of macro amounts of cobalt ions. It may be concluded that traces of Zn might be separated quantitatively from a cobalt matrix. The decrease of Zn extraction with the increase of Zn or Cd ion concentration is due to the decrease of the free solvent concentration.

The effect of the concentration of $CoSO_4$, $ZnSO_4$ and $CdSO_4$ on cobalt extraction by the two solvents increases here also in the order Co < Zn < Cd, i.e. in the same order of extractability of the three metals in the given system.

The results of this investigation (Figs. 1–3) indicate that the separation factor ε in all cases increases with increasing concentration of the added metal sulphate, passes through a maximum and then decreases again with further increase of added metal concentration. The maxima represent practical condition for adequate separation and decontamination of the two elements.

In Fig. 1 results are given on the effect of Cd^{2+} ion concentration on separation of zinc and cobalt by the amine and TBP solvents. Excellent separation of metal pairs can thus be achieved from about 0.04 M Cd^{2+} ion concentration by Amberlite LA-2 from 4.5M H_2SO_4 to 0.16M HBr. Note that for $CdSO_4$ the data were given only for a lower concentration range.

The effect of other extractable metal (Zn) halides on separation factor has been investigated for both solvents (Fig.2). The presence of various amounts of Zn^{2+} ion (up to 0.5 M) in the aqueous phase affects the separation in a way dependent on the concentration of Zn^{2+} ion and also on the halogen acid. Better separation is also achieved at 0.3M $ZnSO_4$ by the amine from the bromide solution (0.16M).

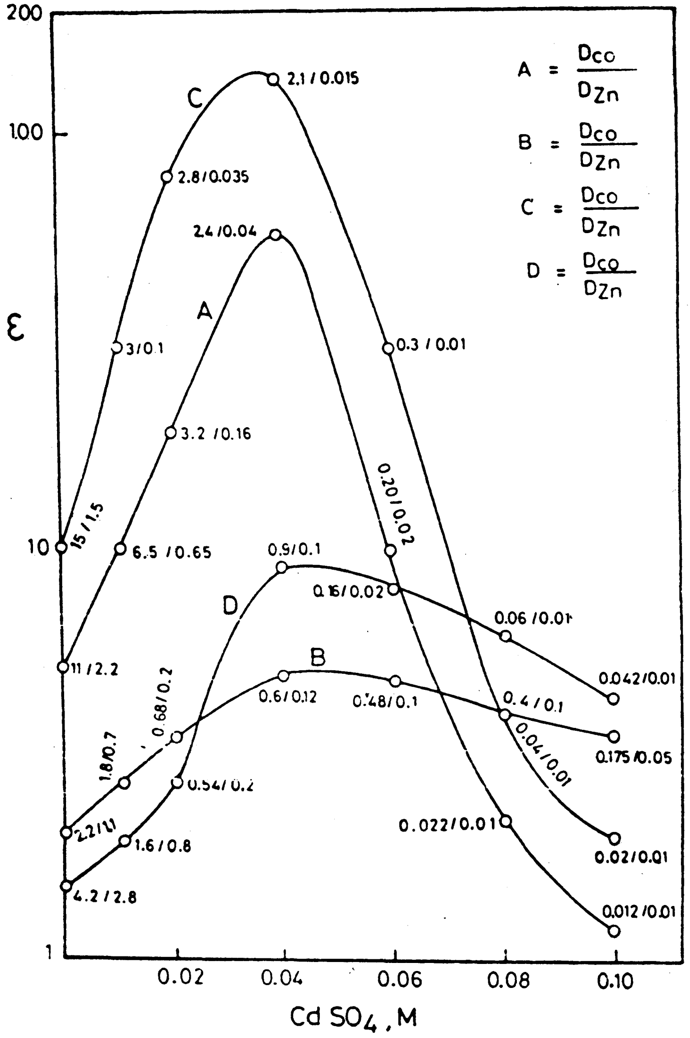

Fig. 1 Effect of $CdSO_4$ concentration on separation factor of Zn and Co from 4.5M H_2SO_4 in the presence of:
A—0.12M HCl, 5% Amberlite LA-2;
B—0.12M HCl, 50% TBP,
C—0.16M HBr, 5% Amberlite LA-2;
D—0.16M HBr, 50% TBP.

In Fig. 3 the variation of the separation is shown as a function of the original $CoSO_4$ molarity in the aqueous phase with Amberlite LA-2 and TBP from 4.5M

H_2SO_4 in the two acids HCl and HBr. The better separation appeared at 0.4M $CoSO_4$ from 0.16M bromide solution by LA-2.

It is obvious that 5% LA-2 should be considered the best choice among the two solvents studied not only because of the higher separation factors determined,

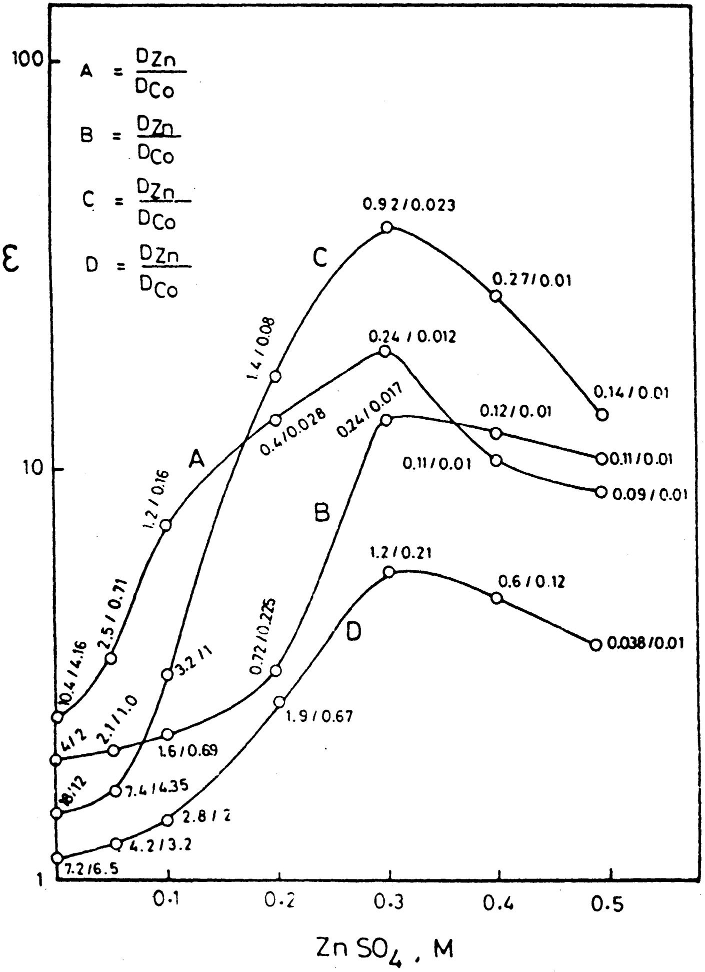

Fig. 2 Effect of $ZnSO_4$ concentration on separation factor of Zn and Co from 4.5M H_2SO_4 in the presence of:
A—0.12M HCl, 5% Amberlite LA-2;
B—0.12M HCl, 50% TBP,
C—0.16M HBr, 5% Amberlite LA-2;
D—0.16M HBr, 50% TBP.

but also because of the better properties as an extractant, viz., lower density than the 50% TBP solvent, affecting quicker disengagement of the aqueous and organic phases in addition to the establishment of equilibrium within shorter periods of time.

In the light of the above results one may suggest that the halides of zinc and cobalt form extractable complexes with TBP and Amberlite LA-2 and that these complexes are extracted from sulphuric acid solutions, possibly according to the following mechanism:

$$MX_2 + n\mathrm{TBP} \rightleftharpoons MX_2 . n\mathrm{TBP} \qquad (1)$$

$$MX_2 + nR_3NHX \rightleftharpoons MX_{2+n}^{n-} . nR_3NH^+ \qquad (2)$$

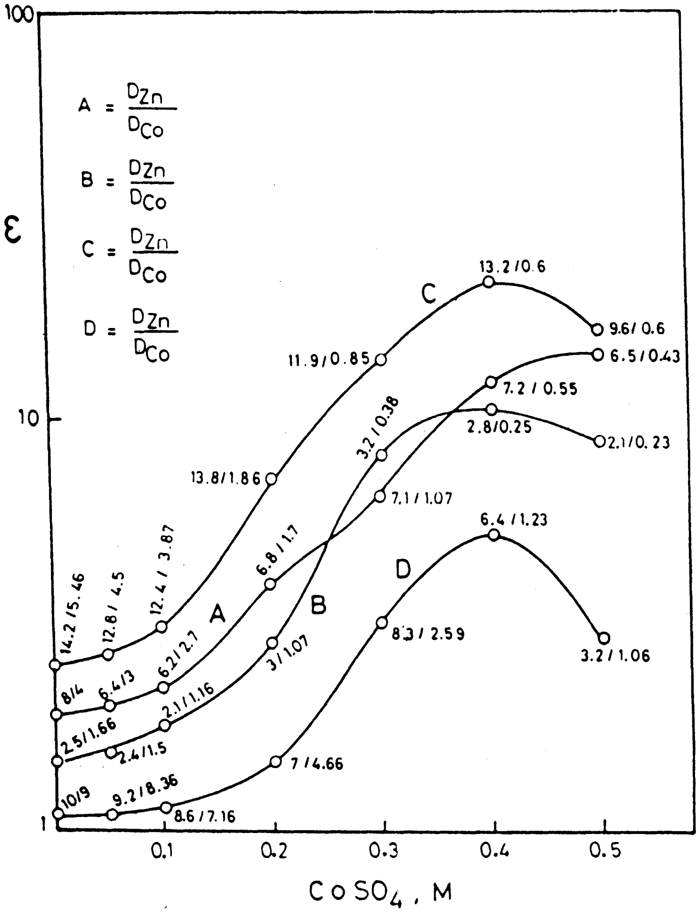

Fig. 3 Effect of $CoSO_4$ concentration on separation factor of Zn and Co from 4.5M H_2SO_4 in the presence of:
A—0.12M HCl, 5% Amberlite LA-2;
B—0.12M HCl, 50% TBP,
C—0.16M HBr, 5% Amberlite LA-2;
D—0.16M HBr, 50% TBP.

In the presence of high sulphuric acid concentrations, it is expected that amines form salts with hydrochloric or hydrobromic acids even if one of the latter two acids is present in a much lower concentration[4]. It has been postulated that in the presence of excess hydrochloric or hydrobromic acids zinc and cobalt halides exist as complex ions:

$$MX_2 + nHX = nH^+ + MX_{2+n}^{n-} \tag{3}$$

If one of the two acids is partially replaced by sulphuric acid the latter will help in removing water needed for proton solvation and this causes reaction (3) to be shifted to the left and hence a higher extraction is obtained.

REFERENCES

1. A.M. El-Kot, Isotopenpraxis (1989) (in press).
2. A. Alian, A.M. El-Kot and S. Abdelhalem, *J. Radioanal. Chem.,* **57**, 373 (1980).
3. A. Alian, A.M. El-Kot, A. Badran, M.S. El-Bassiouny, *J. Radioanal. Chem.*, **27**, 383 (1975).
4. C.F .Colemann, *Atomic Energy Reviews*, **2**, 3, (1964).

[Received: 1 November 1989 ; Accepted: 8 May 1990] AJC–171