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# EXTRACTION OF CADMIUM(II) FROM ACIDIC MEDIUM WITH MACROPOROUS RESIN IMPREGNATED WITH BIS(2-ETHYLHEXYL) AMMONIUM BIS(2-ETHYLHEXYL)DITHIOCARBAMATE

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**ABSTRACT.** Impregnated resin XAD-7 containing a newly synthesized hydrophobic extractant bis(2-ethylhexyl)ammonium bis(2-ethylhexyl)dithiocarbamate (BEABEDC) was prepared using the dry impregnation method and the extraction of cadmium(II) was investigated in different modes. The distribution of cadmium(II) between BEABEDC in heptane or kerosene-10% decanol and aqueous acid solution was examined on liquid-liquid extraction system. Log D values with 0.01 M BEABEDC in kerosene-10% decanol were larger than 3.4 at pH 5-7. The batch wise extraction of cadmium(II) with the impregnated resin was also studied. The distribution ratio with 0.01 M BEABEDC in kerosene was larger $10^{3.2}$ in acidic region and %E more than 95% at ≤ 6 M $H_3PO_4$. The chromatographic extraction of cadmium(II) using a column packed with impregnated resin as a stationary phase was performed. The cadmium(II) retained on the column was quantitatively eluted with 4 M hydrochloric acid.

## INTRODUCTION

Now there is an increasing of environmental legislation limiting the discharge of toxic metals and other wastes. Among these metals, cadmium is a toxic one that often occurs as an impurity in zinc ores and consequently is present in industrial processes for zinc refinement. Cadmium is also present as a contaminant in the wet process acid used for fertilizer manufacture from phosphate. These situations mean that the removal of cadmium in wastes is of capital interest. Solvent extraction [1-3] technologies and ion exchangers having a selective substituents [4,5] have been applied. Macroporous resins impregnated with a selective reagent show similar advantages of liquid-liquid extraction that is specific separation properties [6,7]. The use of hydrophobic extractant to the impregnated resin is promising for designing an efficient separation process. Dithiocarbamates are recognized as good reagents in solvent extraction of cadmium [8,9] owing to their high extractability of this metal. Among the dithiocarbamates, diethyldithiocarbamate (DDTC) have been frequently employed as an extractant of the metal ion, but DDTC is almost insoluble in nonpolar solvent and readily released to an aqueous solution. In this work we synthesized a new hydrophobic extractant bis(2-ethylhexyl)ammonium bis(2-ethylhexyl)dithiocarbamate (BEABEDC), which is insoluble in water and soluble in nonpolar solvents such as heptane and kerosene, in order to examine the extraction behavior of cadmium(II). BEABEDC was impregnated in a macroporous resin XAD-7 and the batchwise extraction of cadmium(II) with the impregnated resin was carried out. The chromatographic separation of cadmium(II) was performed through a column packed with the impregnated resin as a stationary phase.

## EXPERIMENTAL

***Reagents.*** The preparation procedure for dithiocarbamate derivative as described by Linder *et al.* [10] was modified for this work. The following procedure gives a much better yield and a product of greater purity. Bis(2-ethylhexyl)amine (Aldrich) 24.12 g (0.10 mol) was placed in a round bottomed flask with thermometer and carbon disulfide (Aldrich) 3.80 g (0.05 mol) was added dropwise with stirring at room temperature. The temperature was monitored not to exceed 40 $^0$C. The pale yellow mixture was stirred over night and the viscous liquid obtained was analyzed with $^1$H and $^{13}$C NMR spectroscopic methods. The purity was evaluated as >97% by integrating the peaks. Little content of unreacted amine was suggested. The synthesized compound bis(2-ethylhexyl)ammonium bis(2-ethylhexyl)dithiocarbamate (BEABEDC) was used without further purification.

The stability of BEABEDC in kerosene was checked by measuring its UV absorbance at 286 nm. The absorbance decreased to 78% after 28 days. The extractant and its solutions were stored in a refrigerator and used within two weeks after preparation.

The pH values were controlled by partially neutralizing some buffers such as 2-morpholinoethanesulfonic acid (MES, $pK_a$ = 6.15) and 3-morpholinopropanesulfonic acid (MOPS, $pK_a$ = 7.20) with sodium hydroxide. The pH of the solutions was measured by a digital pH meter (TOA AUT-301). The ionic concentration was usually adjusted to 0.1 M with sodium chloride.

Inorganic acids, heptane and kerosene used were of analytical grade.

*Solvent extraction procedure.* 12 mL of an aqueous solution containing 1.10$^{-4}$ M the metal ion adjusted to the desired pH value with a suitable buffer and 3 mL of organic phase containing 1.10$^{-2}$ M or less of BEABEDC were placed in 50 mL stoppered centrifugal glass tube and shaken in a thermostated room 25 $^0$C for 4 h. After centrifuging an aliquot of aqueous phase was taken out. The concentration of the metal ion in aqueous phase was determined with atomic absorption spectrometer (Perkin Elmer 3110). The concentration of metal ion in the organic phase was calculated by mass balance. The results were expressed as the distribution ration D defined as the ratio of the total equilibrium concentration of metal in the organic phase to that in the aqueous phase.

$$D = \frac{[M_o]}{[M_a]} = \frac{V_a}{V_o}\ \frac{[M_i] - [M]}{[M]}$$

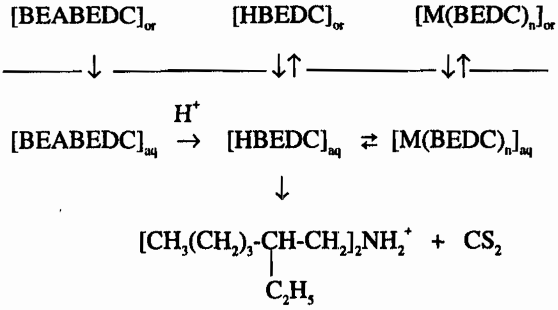
where V signifies the volume of the phases and subscript a and o denote the aqueous phase and organic phase, respectively. Subscript i refers to the initial concentration of metal in the aqueous phase and [M] without script is the equilibrium concentration after extraction.

*Batchwise extraction on impregnated resin.* The extraction of cadmium(II) on resin was examined by placing a resin (0.1 g) impregnated BEABEDC in contact with an aqueous phase (5 mL or 10 mL) containing 2.5.10$^{-4}$ M of cadmium(II) in a thermostated room at 25 $^0$C. After filtration the concentration of the metal ion remaining in the aqueous phase was determined by AAS and the distribution ratio (D) was calculated as the ratio of the content in the resin (mmol/g) and the concentration in aqueous solution [M].

*Column separation.* The impregnated resin was packed into a glass column (1.5 cm internal diameter) and plastic tubes were connected to the inlet and outlet of the column. A sample solution containing cadmium(II) was continuously fed into the column at a flow rate of 24 mL/h using a peristaltic pump. The effluent was collected into portions of 8 mL and the metal concentration in each fraction was determined by AAS.

## RESULTS AND DISCUSSION

The extraction of the metal ion from acidic aqueous solution with BEABEDC is a complex and in general a non-equilibrium process. It may be represented as follows:



$$\begin{array}{ccccc} [BEABEDC]_{or} & & [HBEDC]_{or} & & [M(BEDC)_n]_{or} \\ \downarrow & & \downarrow\uparrow & & \downarrow\uparrow \\ [BEABEDC]_{aq} & \xrightarrow{H^+} & [HBEDC]_{aq} & \rightleftarrows & [M(BEDC)_n]_{aq} \\ & & \downarrow & & \end{array}$$

$$[CH_3(CH_2)_3\text{-}\underset{C_2H_5}{CH}\text{-}CH_2]_2NH_2^+ + CS_2$$

The BEABEDC in solution in kerosene or heptane decomposes rapidly into bis(2-ethylhexyl) dithiocarbamic acid HBEDC and bis(2-ethlhexyl)amine when the two phases are shaken together. Thus HBEDC is the chelating agent under these conditions and over 99% of HBEDC should be in the organic phase. As BEABEDC is very hydrophobic the aqueous concentration of the complex is negligible. In acidic aqueous solution HBEDC may decompose into carbon disulfide and protonated bis(2-ethylhexyl)amine [8].

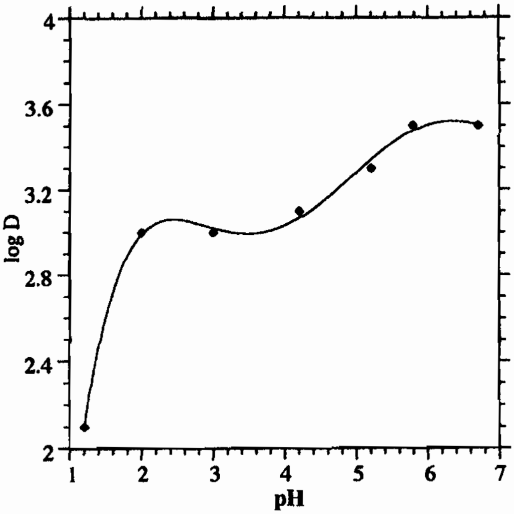


Figure 1. Distribution ratio of cadmium(II) between aqueous phase and heptane containing 0.01 M of BEABEDC as a function of pH: [Cd] = $10^{-4}$ M, $V_a$ = 12 mL, $V_o$ = 3 mL, shaking time = 4 h.

*Solvent extraction.* In preliminary experiments, the extraction of Cd(II) with $10^{-2}$ M BEABEDC solution in heptane or kerosene were investigated as a function of shaking time. These results show that the equilibrium was reached within 3 h. Hence we fixed the shaking time of the solvent extraction process to 4 h.

The relationship between log D and pH is shown in Figure 1. Cadmium(II) was quantitatively extracted from acidic aqueous phase to the organic phase yielding values of around 3.5 in pH region of 5-7.

Plots of log D against log BEABEDC in heptane or kerosene for the extraction of cadmium(II) gave straight line with slop 1.90 (Figure 2). This observation can be interpreted by a mechanism in which two molecules of BEABEDC are involved in the extracted species. This observation is in agreement with those reported for this type of metal ion and other dithiocarbamate extractant [11,12].

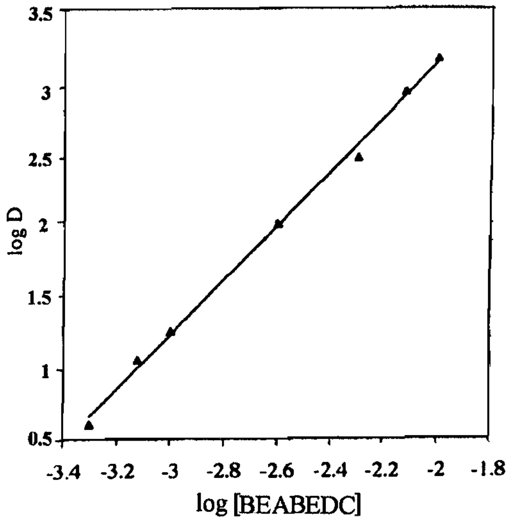


Figure 2. Distribution ratio of cadmium(II) between kerosene and aqueous phase as a function of BEABEDC concentration, [Cd(II)] = $10^{-4}$ M, $V_a$ = 12 mL, $V_o$ = 3 mL, pH = 5.2.

The influence of iron(III) and copper(II) on the extraction of cadmium(II) was examined. The extraction results of synthetic mixture of Cd(II), Cu(II) and Fe(III) by BEABEDC in kerosene-10% decanol from phosphoric acid medium are represented in Figure 3 in which the percentage of extraction (%E) of Cd(II), Cu(II) and Fe(III) are represented as a function of $H_3PO_4$ concentration. Figure 3 shows that %E of metal ions decreases with increasing $H_3PO_4$ concentration. The %E extracted were 10.5%, 75.2%, 95% for Fe(III), Cd(II), and Cu(II), respectively, at 3 M $H_3PO_4$. The separation of Fe(III) from Cd(II) and Cu(II) can be expressed using the separation factor $S_{cd(II)/Fe(III)}$ and $S_{cu(II)/Fe(III)}$ which is the parameter of the efficiency of the separation system for the couple of metal ions. It is defined by the ratio of the distribution coefficients of the metal ions:

$$S_{Cd(II)/Fe(III)} = \frac{D_{Cd(II)}}{D_{Fe(III)}}$$

The maximum separation factor obtained is 80.5 (Table 1), when the $H_3PO_4$ concentration was 3 M.

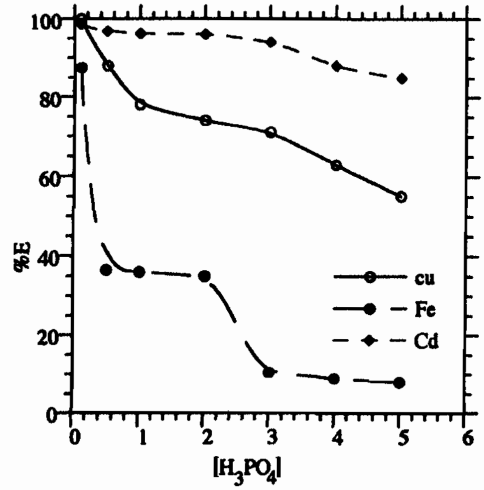


Figure 3. Effect of phosphoric acid concentration on extraction of a mixture of cadmium(II), copper(II) and iron(III): [Cd(II)] = 1.8 x $10^{-4}$ M, [Cu(II)] = 3.15 x $10^{-4}$ M, [Fe(III)] = 3.6 x $10^{-4}$ M in aqueous phase. BEABEDC = 0.04 M in kerosene.

Table 1. Distribution ratio and separation factor of metal ions at different concentration of $H_3PO_4$.

| $[H_3PO_4]$ | $D_{Cu}$ | $D_{Cd}$ | $D_{Fe}$ | $S_{Cu/Fe}$ | $S_{Cd/Fe}$ |
|---|---|---|---|---|---|
| 0.1 | 9.08 | 2.52 | 0.39 | 25.13 | 6.46 |
| 0.5 | 4.97 | 3.25 | 0.39 | 12.74 | 8.33 |
| 1 | 3.39 | 3.00 | 0.23 | 14.74 | 13.00 |
| 2 | 3.30 | 3.00 | 0.099 | 33.33 | 30.30 |
| 3 | 2.79 | 2.90 | 0.036 | 77.55 | 80.50 |
| 4 | 2.55 | 2.72 | 0.036 | 70.83 | 78.33 |
| 5 | 1.93 | 2.72 | 0.036 | 48.05 | 75.55 |

The effect of BEABEDC concentration on extraction of Cd(II), Cu(II) and Fe (III) from a synthetic mixture of these three metal ions was examined when phosphoric acid concentration was 0.1 M. Figure 4 shows that at 0.04 M concentration of BEABEDC, the three metal ions are extracted all together with a good percentage of extraction. The %E were 86.78, 97.71 and 99.69%, respectively, for Fe(III), Cd(II), and Cu(II). But at low concentration of BEABEDC (0.01M), Fe(III) can be separated from Cu(II) or Cd(II) with separation factor of 80.5.

*Batchwise extraction in impregnated resin.* Solvent impregnated resin containing BEABEDC were prepared by direct adsorption of the extractant on to amberlite XAD-7 using the dry impregnation method [13,14]. The kinetic of extraction of cadmium(II) with BEABEDC impregnated resin was investigated. The BEABEDC impregnated resin (0.1g) was shaken with aqueous phase (5 mL) containing 2.5.$10^{-4}$ M of cadmium(II) and 0.1 M phosphoric acid. The log D value increased with shaking time: 2.2 at 15 min, 3.4 at 30 min and 3.5 at 1 h and after that remained constant for 10 h. Hence we fixed the shaking time to 3 h in subsequent experiments.

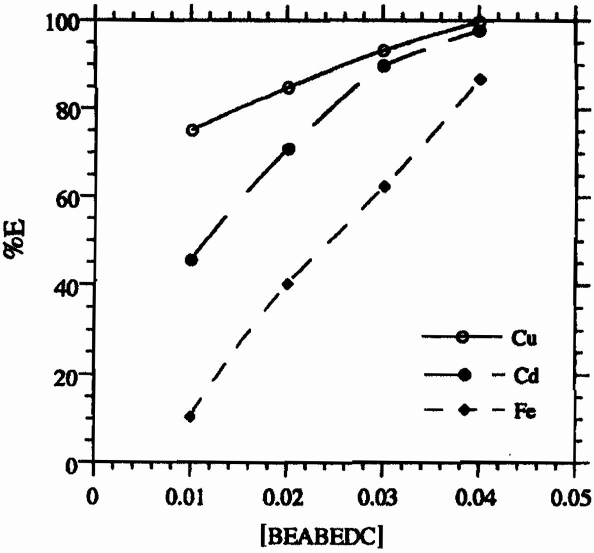


Figure 4. Effect of BEABEDC concentration in kerosene on extraction of mixture of cadmium(II), copper(II) and iron(III): [Cd(II)] = 1.8 x $10^{-4}$ M, [Cu(II)] = 3.15 x $10^{-4}$ M, [Fe(III)] = 3.6 x $10^{-4}$ M in aqueous phase, [$H_3PO_4$] = 0.1 M.

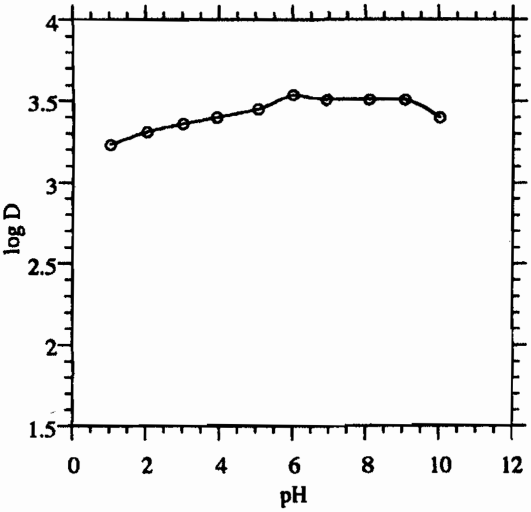


Figure 5. Distribution ratio of cadmium(II) between BEABEDC impregnated resin and aqueous phase as a function of pH. $V_a$ = 5 mL, $W_r$ = 0.01g.

The effect of pH on the distribution ratio of cadmium(II) was examined in the impregnated resin system. Figure 5 shows that cadmium(II) was quantitatively extracted at pH 1-10, with a maximum log D value of 3.5 at pH 6-9. The extraction of Cd(II) into impregnated resin with BEABEDC would effectively accomplished in the acidic region.

We studied the extraction of mixture of cadmium(II) and copper(II) containing about $1.8.10^{-4}$ M of cadmium(II) and $3.6.10^{-4}$ M of copper(II) with BEABEDC impregnated resin as a function of phosphoric acid concentration. Table 2 shows that Cd(II) and Cu(II) are quantitatively extracted when concentration of $H_3PO_4$ are $\leq 3$ M. The percentage of extraction in Table 2 shows that Cd(II) and Cu(II) can be extracted from phosphoric acid medium up to 12 M.

Table 2. %E of cadmium(II) and copper(II) with BEABEDC impregnated resin. ($W_r = 0.1$g; $V_a = 5$ mL; Cd(II) = Cu(II) = $2.5 .10^{-4}$ M).

| $[H_3PO_4]$ | %E of Cd(II) | %E of Cu(II) |
|---|---|---|
| 0.1 | 100 | 100 |
| 0.5 | 100 | 100 |
| 1 | 100 | 100 |
| 2 | 99.5 | 100 |
| 3 | 98.7 | 100 |
| 4 | 97.2 | 99.3 |
| 5 | 96.8 | 97.8 |
| 6 | 95.1 | 96.9 |
| 8 | 92.9 | 95.7 |
| 10 | 91.7 | 95.3 |
| 12 | 90.3 | 94.9 |

*Chromatography procedure.* The chromatographic removal of cadmium(II) was attempted by using a column packed with BEABEDC impregnated resin (5 g, 1.4 x 15 cm). A solution containing $10^{-4}$ M of cadmium(II) was continuously passed through the column and the concentration of cadmium(II) in the effluent was determined. Figure 6 shows the breakthrough curve of cadmium(II). For almost 50-fold volume of the column, the cadmium(II) concentration was kept under $2.10^{-7}$ M.

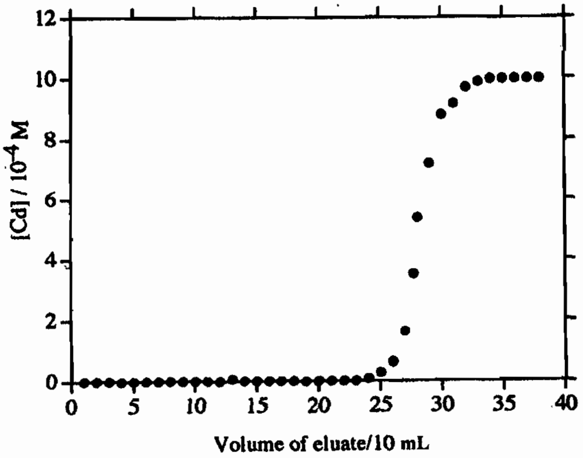


Figure 6. Breakthrough curve of cadmium(II) through the column packed with BEABEDC impregnated resin. Column: 1.5 cm (i.d) x 15 cm, Cd(II) = $10^{-3}$ M.

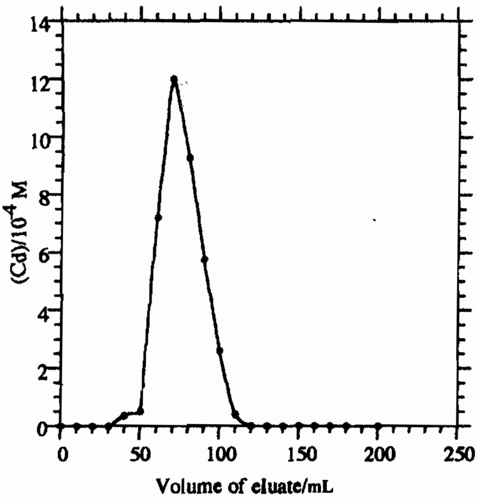


Figure 7. Elution curve of cadmium(II) retained on the BEABEDC impregnated resin column. Column: 1.5 cm (i.d.) x 15 cm. Flow rate = 24 mL/h.

The elution of cadmium(II) was performed with 4 M hydrochloric acid after the retention of a known amount of cadmium(II) in the column. Figure 7 shows that cadmium(II) retained was readily eluted out of the column yielding the quantitative recovery of 99.87%. The BEABEDC impregnated resin was proved to have some potentials for retention of cadmium(II) in industrial phosphoric or for preconcentration of cadmium(II) from diluted solutions.

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