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Studies of Solvent Extraction Behavior of Some Divalent Metals with Liquid Ion-Exchanger

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Summary

A systematic study of the comparative extraction behavior of some divalent metals has been carried out with the high molecular weight carboxylic acid, namely SRS-100. Benzene is used as diluent. The study includes the extraction behavior as a function of pH, effect of diluent, metal ion concentration, solvent concentration, and finally interference of the associated elements. In almost all cases nearly quantitative extraction has been achieved. The proposed method is very simple, rapid, and is applicable both at micro and macro levels. The method is applicable to extraction of metal ions in the presence of other commonly interfering ions present at the milligram level.

INTRODUCTION

In a previous communication (*1*) from this laboratory the use of synthetic carboxylic acid, namely SRS-100, for the extraction of transition metals, such as iron(III), cobalt(II), nickel(II), manganese(II), and copper(II), was reported. The studies have now been extended to some divalent metals—iron(II), zinc(II), cadmium(II), mercury(II), lead(II), palladium(II), magnesium(II), calcium(II), strontium(II), and barium(II). All the relevant parameters and factors have been critically studied. The present paper reports on the systematic studies of solvent extraction behavior of these divalent metals and also their separations. Such work has not yet been reported in the literature.

EXPERIMENTAL

Apparatus

Separating funnels (250 ml) were used for extraction. All the pH measurements were carried out with an Elico pH meter.

Reagents

SRS-100 (equiv wt 260–290), a high molecular weight synthetic carboxylic acid (manufactured by Shell Co. Ltd., London). Chemicals and solvents used were all of analytical grade unless otherwise mentioned. Solutions of iron (8.9 mg/ml), zinc (10.5 mg/ml), cadmium (15.8 mg/ml), and magnesium (9.6 mg/ml) were prepared by dissolving a sulfate salt in an appropriate volume of distilled water containing sulfuric acid. Solutions of mercury (7.4 mg/ml), palladium (5.6 mg/ml), and calcium (6.9 mg/ml) were prepared by dissolving the chloride salt in an appropriate volume of distilled water containing hydrochloric acid, and the solutions of lead (10.7 mg/ml), strontium (5.7 mg/ml), and barium (4.7 mg/ml) were prepared by dissolving a nitrate salt in an appropriate volume of distilled water containing nitric acid. The solutions were standardized by conventional methods (*2*, *3*).

Buffer solutions of different pH were prepared by standard procedures: pH 3.3 (acetate–hydrochloric acid) pH 4–6 (acetate–acetic acid) and pH 7.5–10 (ammonia–ammonium chloride) (*3*).

General Procedure

The general procedures for extractions and measurements were the same as described in the previous paper (*1*). The stripping agent in the case of calcium, strontium, barium, and lead was 3 *N* nitric acid. Iron(II), zinc, cadmium, mercury, and magnesium were stripped with 4 *N* sulfuric acid. In the case of palladium, back extraction is not possible, and the amount of metal ion present in the organic phase was calculated by difference. Zinc, cadmium, mercury, lead, palladium, magnesium, calcium, strontium, and barium were estimated by complexometric titration with ethylenediamine tetracetic acid, and iron was estimated volumetrically with potassium dichromate (*2*, *3*).

RESULTS AND DISCUSSIONS

Figures 1 and 2 summarize the comparative studies of extraction behavior of iron(II), zinc(II), cadmium(II), mercury(II), lead(II), palladium(II), magnesium(II), calcium(II), strontium(II), and barium(II), respectively, with SRS-100 over the pH range 3 to 10. From the figures it is evident that the percentage extraction increases with the increase of pH. This is in agreement with the extraction trend expected for a carboxylic acid extractant. The extraction of palladium, lead, zinc, cadmium, and iron starts at comparatively low pH whereas the others, such as magnesium, calcium, strontium, barium, and mercury, start at comparatively higher pH. The recommended optimum conditions of pH as evident from the extraction curves are 5.45 for palladium, 6.9 for lead, 7.1 for zinc, 8.2 for cadmium, 8.75 for barium, 8.8 for calcium and strontium, 9.2 for magnesium, and 9.8 for mercury. In almost all cases quantitative extraction has been achieved, except in the case of iron(II) where the maximum extraction is 90% at pH 6.1. At higher ($pH > 6.1$), iron(II) undergoes hydrolysis, which leads to difficulty in phase separation. Among the divalent metals studied, the nature of extraction for palladium is different. The type of compound formed by palladium with the solvent is so stable that it is very difficult to strip out the metal from the organic phase. The results show that the difference in the extraction behavior of the metals with respect to SRS-100 is very small.

To explore the phenomenon of polymerization in the extraction system, the metal ion concentration was varied from 10 to 50 mg under the specified condition. In this concentration range it was found that the extraction virtually remains unaffected, indicating the absence of polymerization. The addition of ammonium chloride, sodium chloride, and lithium chloride at various concentrations increases the percentage extraction in the case of zinc, cadmium, and mercury, whereas in the case of other metals the percentage extraction decreases. The nature of diluent was varied from benzene to xylene, toluene, diisopropyl ether, butanol, etc. The results are tabulated in Table 1. From the table it is clear that in most cases the diluents having low dielectric constants show extraction similar to benzene, whereas diluents with higher dielectric constants, such as butanol and diisopropyl ether, reduce the extraction somewhat.

The concentration of the solvent was varied from 1:2 to 1:9 with

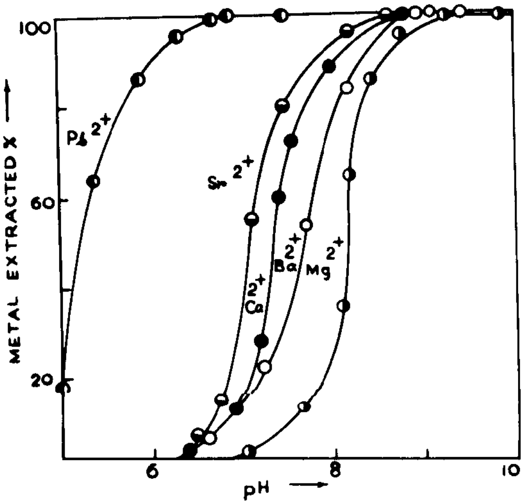

FIG. 1. Extraction with SRS-100 as a function of pH (SRS-100:benzene = 1:2).

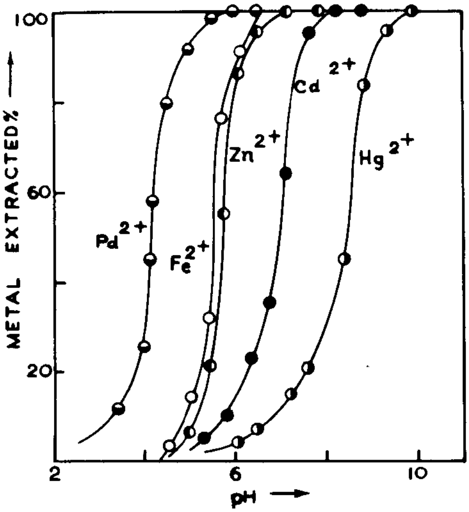

FIG. 2. Extraction with SRS-100 as a function of pH (SRS-100:benzene = 1:2).

TABLE 1

Effect of Diluent on Percentage Extraction of Metals

Diluent with ratio 1:2	Di-electric const.	Iron(II)	Zinc(II)	Cadmium(II)	Mercury(II)	Lead(II)	Palladium(II)	Magnesium(II)	Calcium(II)	Strontium(II)	Barium(II)
Benzene	2.3	91.0	99.6	99.4	99.4	99.5	100	98.9	99.6	99.8	99.8
Xylene	2.4	90.5	98.8	98.7	98.9	99.5	97.9	98.9	99.6	99.8	99.8
Toluene	2.4	91.7	99.2	99.4	99.4	99.5	98.2	98.7	99.6	99.5	99.2
Diisopropyl ether	3.9	89.3	99.6	99.4	99.4	98.2	100	98.9	98.2	98.6	97.9
Butanol	16.1	86.7	98.2	98.7	97.9	96.9	100	97.9	98.2	96.4	96.7

TABLE 2

Percentage Extraction of Metals as a Function of Solvent Concentration

Solvent (SRS-*100*): benzene ratio	Iron(II)	Zinc(II)	Cadmium(II)	Mercury(II)	Lead(II)	Palladium(II)	Magnesium(II)	Calcium(II)	Strontium(II)	Barium(II)
1:2	91.0	99.6	99.4	99.4	99.5	100	98.9	99.6	99.8	99.8
1:4	86.3	93.6	92.8	91.6	92.3	95.6	83.5	88.7	91.4	90.3
1:9	78.4	90.4	87.9	77.3	85.6	90.3	73.5	78.3	81.6	76.5

benzene as diluent. The effect on extraction was noted at different solvent concentrations and tabulated in Table 2. From the table it follows that dilution of solvent lowers the extraction. A qualitative scale of selectivity can be drawn up from the optimum extraction conditions and gives the order as follows:

$$Pd^{2+} > Fe^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Ba^{2+}, Ca^{2+}, Sr^{2+} > Mg^{2+} > Hg^{2+}$$

Extractive Separations

Figures 1 and 2 show typical extraction behavior of iron(II), zinc(II), cadmium(II), mercury(II), lead(II), palladium(II), magnesium(II), calcium(II), strontium(II), and barium(II) at various ranges of pH. The degree of separation between the metal ion pairs may be found by comparing the data on the extraction of metals over a range of pH values. The separation procedure is very simple and requires only the control of pH.

(a) Palladium has been separated from iron, cobalt, nickel, zinc, copper, manganese, lead, cerium, zirconium, thorium, gallium, indium, and thallium. These metals are separated from palladium using (3–4 *N*) sulfuric or nitric acid as stripping agent. (b) The separation of iron(III) from iron(II) is effected by preliminary extraction of iron(III) at pH 3.10 with SRS-100. Calcium, magnesium, mercury, and palladium do not interfere in the extraction of iron(II). (c) Lead is separated from palladium, calcium, magnesium, mercury, cerium, and zirconium by pH adjustment. (d) Zinc is separated from mercury, palladium, calcium, magnesium, and barium.

The mutual separation of magnesium, calcium, strontium, and barium in the presence of one another is not possible by a simple extraction procedure. Separation of cadmium from zinc is also not possible whereas cadmium can be separated from mercury and magnesium.

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