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Solvent Extraction Behavior of Trivalent Metals with Liquid Ion Exchangers

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Abstract

A systematic liquid–liquid extraction behavior of some trivalent metals has been carried out with the high-molecular-weight synthetic carboxylic acid SRS-100 with benzene as diluent. In most cases extraction was quantitative; but in the cases of gallium and antimony the maximum extraction was 97.2 and 65%, respectively. Using pure solvent (without benzene diluent), quantitative extraction (>99%) of gallium was possible with SRS-100 at pH 4.6. Gradual neutralization techniques have been adopted to study the extraction behavior of antimony in the pH range 2.0–6.5. The effect of metal ion concentration, solvent concentration, salting-out agents, diluents, and finally the interferences of associated elements were critically examined. The percentage extraction at various ranges of pH has also been studied. Some important separations have been carried out by exchange reactions. The proposed methods are very simple, rapid, and fairly selective. They can be carried out both at micro and macro levels.

INTRODUCTION

Solutions of SRS-100 in organic solvents act as liquid cation exchangers, the exchange properties of which are similar to those of organic ion exchange resins. These liquid cation exchangers have been used extensively in this laboratory for the extraction of various types of metals (*1–3*). The extraction studies are now extended to trivalent

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metals: gallium(III), indium(III), thallium(III), lanthanum(III), antimony(III) and bismuth(III). In the literature there are reports mainly on the extraction of common metals with naphthenic acids. The liquid cation exchanger SRS-100 (versatic acids) has several advantages over others as it offers fairly rapid extractions. No attempt has yet been made to study the extraction behavior of trivalent metals with versatic acids, particularly with SRS-100. In this paper, systematic studies of trivalent metals with SRS-100 are reported. The optimum conditions for extraction and separation have been carefully selected from a critical study of the various factors involved.

In its simplest form, the over-all process of extraction reaction of trivalent metals with liquid cation exchanger may be expressed as

$$[M^{3+}]_{aq} + [3HR]_{org} \rightleftharpoons [MR_3]_{org} + [3H^+]_{aq}$$

where HR represents the carboxylic acid and the subscripts aq and org refer to the aqueous and organic phases, respectively. The carboxylic acid and the metal chelate formed have very little solubility in the aqueous solutions but are soluble in organic solvents.

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EXPERIMENTAL

Apparatus

The separations were performed in glass separatory funnels (250 ml) by manual shaking. The pH measurements were carried out with an Elico pH meter.

Reagents

SRS-100 (equiv wt 260 to 290), a high-molecular-weight synthetic carboxylic acid (Shell Centre, London), was used as liquid cation-exchanger. All the reagents and chemicals were of analytical grade unless otherwise mentioned.

Gallium chloride solution (5.0 mg/ml). About 2 g of gallium chloride was dissolved in 200 ml of distilled water containing 10 ml of hydrochloric acid. The solution was standardized by the oxine method (*5*).

Indium chloride solution (8.6 mg/ml). About 5 g of $InCl_3 \cdot 4H_2O$ (Fluka) was dissolved in 200 ml of distilled water containing 8.5 ml of concentrated hydrochloric acid. The solution was standardized by the oxine method (*5*).

Thallium(I) nitrate solution (5.3 mg/ml). About 1.8 g of $TlNO_3$ (B.D.H., AR) was dissolved in 250 ml of distilled water containing 2 ml of concentrated nitric acid. The solution was standardized by the chromate method (*6*).

Lanthanum nitrate solution (4.4 mg/ml). About 4 g of $La(NO_3)_4 \cdot 6H_2O$ (B.D.H., AR) was dissolved in 250 ml of distilled water containing 2 ml of concentrated nitric acid. The solution was standardized by complexometric titration with ethylenediaminetetraacetic acid (EDTA) using xylenol orange indicator (*7*).

Bismuth nitrate solution (5.8 mg/ml). About 3 g of $Bi(NO_3)_3 \cdot 5H_2O$ (B.D.H., AR) was dissolved in 250 ml of distilled water containing 10 ml of concentrated nitric acid. The solution was standardized by complexometric titration with EDTA using thiourea indicator (*7*).

Antimony(III) solution (5.7 mg/ml). About 3.4 g of Sb_2O_3 (B.D.H.) was dissolved in 0.1 *M* hydrochloric acid and diluted to 500 ml with 0.1 *M* hydrochloric acid. The solution was standardized by the iodimetric method, using starch indicator (*6*).

Buffer solutions of different pH were prepared by different procedures (*6*); pH 1.5 to 2.5 (chloroacetate), pH 3.3 (acetate–hydrochloric acid), pH 4 to 6.5 (acetate–acetic acid), pH 7.5 to 9.5 (ammonia–ammonium chloride).

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General Procedure

The general procedure for extraction and measurement was the same as discussed in the previous papers (*1–3*). In case of thallium, thallous(I) was oxidized to thallic(III) with bromine water, and the excess bromine was removed by warming the solution before mixing with the buffer solutions. Antimony, bismuth, and lanthanum tend to hydrolyze at higher pH. In the cases of bismuth and lanthanum this was avoided by carrying out extraction in the presence of citrate as masking agent. The appropriate quantities of masking agents were introduced to the experimental solution before mixing with the buffer solution. Extraction studies of antimony have been carried out by the gradual neutralization technique (*4*). In all cases the volume of the aqueous phase was kept to 15 ml and that of the organic phase was 10 ml. The aqueous feed solution at the desired pH was equilibrated with the organic solvent (SRS-100:benzene = 1:2) for 5 min. The solutions were then allowed to settle for 10 min before the phases were separated. To remove the traces of organic solvent extrained in the separated aqueous phase, the latter

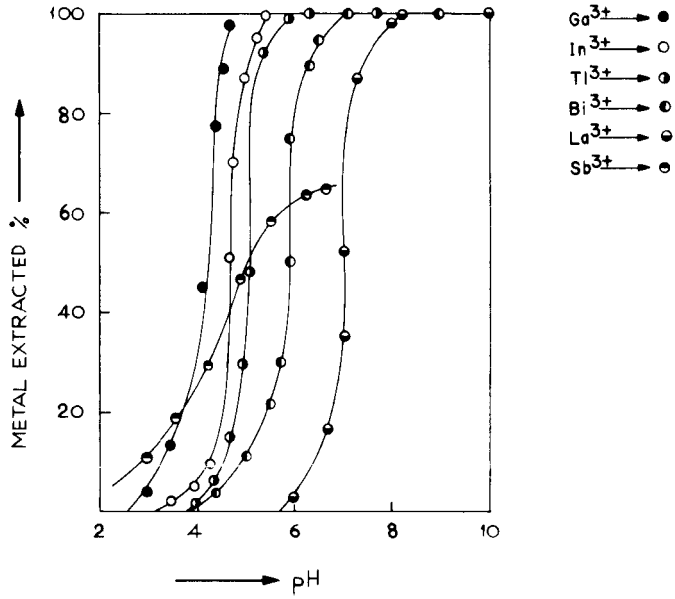

FIG. 1. Extraction with SRS-100 as a function of pH (SRS-100:benzene = 1:2).

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was washed with 5 ml of benzene. The resulting benzene extract was added to the separated organic phase. The metal ion present in the organic phase was stripped twice with 10 ml of (2–4 *N*) sulfuric acid. The metal ions in both phases were determined by the standard methods. Gallium was estimated complexometrically with EDTA using pyrocatechol violet indicator, indium and thalium(III) with Eriochrome black T indicator, and lanthanum and bismuth with xylenol orange indicator (*6*). Antimony(III) was estimated iodimetrically (*5*). In the case of thallium, the solution was oxidized with bromine water before estimation, and the excess bromine was removed by warming the solution.

RESULTS AND DISCUSSION

The extraction behavior of gallium(III), indium(III), thallium(III), lanthanum(III), antimony(III), and bismuth(III) has been investigated as a function of pH. Figure 1 shows the extraction of these metals

as a function of pH. At pH 4.7, 97.2% extraction of gallium has been achieved. At higher pH gallium(III) hydrolyses. Quantitative extraction of gallium requires two consecutive equilibrations at pH 4.5. The extractions were carried out in the presence of tartaric acid which, however, inhibits the extraction. Indium is extracted quantitatively at pH 5.4. Without benzene diluent SRS-100 extracts indium quantitatively at pH 5.2. The respective optimum conditions for quantitative extractions are indium at pH 5.4, thallium at pH 6.2, lanthanum at pH 8.2, and bismuth at pH 7.0. Antimony is extracted to the extent of 65% at pH 6.5. With further increases of pH the extraction remains constant. Extraction studies have been carried out for lanthanum and bismuth using citrate as the masking agent. Citrate, tartrate, and oxalate interfere in the extraction of antimony, and so the extraction of antimony has been carried out by using the gradual neutralization technique (4) to avoid precipitation of metal hydroxide, i.e., the pH of the solution was gradually raised by the slow addition of a neutralizing agent (ammonia) during the extraction period. The optimum pH ranges for quantitative extraction are: thallium 6.2–7.5, lanthanum 8.3–10.0, and bismuth 7.0–9.0.

In order to study the effect of metal ion concentration on extraction, the amount of metal ions was varied from 5 to 25 mg under the optimum conditions, and it was found that the recommended procedure held good. Only gallium undergoes hydrolysis at higher concentrations. These results indicate the absence of polymerization in the organic phase. The shaking period was varied from 2 to 15 min. It was found that in most cases complete extraction requires 4 min. In each case the optimum shaking period was 5 min. Ammonium chloride, magnesium chloride, and sodium chloride in the aqueous phase exert a salting-out effect. This

TABLE 1

Percentage Extraction of Metals as a Function of Solvent Concentration

Solvent (SRS-100): benzene ratio	Gallium (III) (%)	Indium (III) (%)	Thallium (III) (%)	Lanthanum (III) (%)	Bismuth (III) (%)
1:2	97.2	99.5	100.0	100.0	100.0
1:4	94.6	98.6	99.3	99.5	99.0
1:9	84.8	91.6	88.4	87.6	89.6

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TABLE 2

Effect of Diluent on Percentage Extraction of Metals

Diluent	Dielectric constant	Ratio, solvent: diluent	Gallium (III) (%)	Indium (III) (%)	Thallium (III) (%)	Lanthanum (III) (%)	Bismuth (III) (%)
Benzene	2.3	1:2	97.2	99.5	100.0	100.0	100.0
Xylene	2.4	1:2	95.8	99.2	99.4	98.9	99.6
Toluene	2.4	1:2	96.4	97.9	99.4	98.1	99.6
Diisopropyl-ether	3.9	1:2	92.5	98.6	99.4	96.1	99.6
Butanol	16.1	1:2	93.4	94.6	98.7	89.8	98.7

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leads to enhanced extraction in the cases of gallium, indium, and thallium, whereas in the cases of bismuth and lanthanum extraction decreases. The effect of reagent concentration on extraction was investigated by varying the solvent (SRS-100) concentration from 1:2 to 1:9, using benzene as diluent. The results are tabulated in Table 1. From Table 1 it is clear that dilution of SRS-100 lowers the extraction to an appreciable extent. In the case of pure solvent (without benzene diluent), the emulsion-forming tendency is increased. In order to avoid emulsion formation and to achieve quantitative extraction, most of the extraction has been carried out using solvent:diluent in a 1:2 ratio. Benzene has been used as diluent.

The role of diluent in extraction has been studied by varying the nature of diluent from benzene to xylene, toluene, diisopropyl ether, butanol, etc. The results are given in Table 2. The results show that the nature of diluent has very little effect on extraction. Xylene and toluene show extraction almost similar to benzene, whereas butanol and diisopropyl ether reduce the extraction a small extent.

A qualitative selectivity scale of extraction has been drawn up from the optimum conditions obtained with SRS-100, the order being $Ga^{3+} > In^{3+} > Tl^{3+} > Bi^{3+} > La^{3+} > Sb^{3+}$.

Extractive Separation

Figure 1 shows the typical extraction behavior of gallium(III), indium(III), thallium(III), lanthanum(III), antimony(III), and bismuth(III) in various ranges of pH. The metal ion pairs which are

separable can be found from the figure. The separation procedures are very simple and rapid, requiring only an adjustment of pH values of the solutions from which the metals are to be extracted. In some cases the interfering ions are eliminated either by using a masking agent or by preliminary extraction of the interfering ions under different conditions. Quantitative separations have been achieved in most cases.

The following extractive separations have been carried out:

Gallium(III) from thallium(I), iron(III), aluminum, lanthanum, lead, palladium, zirconium, platinum, molybdenum, tungsten, zinc, cadmium, mercury, copper, manganese, cobalt, nickel, calcium, magnesium, barium, and strontium.

Indium from thallium(I), aluminum, iron(III), lanthanum, lead, palladium, platinum, molybdenum, tungsten, cobalt, nickel, copper, manganese, zinc, cadmium, mercury, calcium, magnesium, strontium, and barium.

Thallium(III) from lanthanum, iron(III), cobalt, nickel, copper, palladium, platinum, molybdenum, tungsten, calcium, magnesium, strontium, and barium.

Bismuth from aluminum, gallium, indium, thallium(III), iron(III), cerium(IV), zirconium, thorium, molybdenum, tungsten, palladium, platinum, calcium, magnesium, strontium, and barium.

Lanthanum from cerium(IV), zirconium, thorium, iron(III), gallium, indium, thallium(III), palladium, platinum, molybdenum, tungsten, and mercury.

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Exchange Reaction

The order of extraction of a metal ion with carboxylic acids is the order of relative stabilities of the metal carboxylates. Thus an exchange reaction is possible between a metal carboxylate in the organic phase and a more acidic metal in the aqueous phase. The reaction for trivalent metal ions may be expressed as

$$[M_1R_3]_{org} + [M_2^{3+}] \rightleftharpoons [M_2R_3]_{org} + [M_1^{3+}]_{aq}$$

where the metal M_2 is more acidic than the metal M_1. This exchange extraction procedure has been employed especially in those systems where the coextraction of the interfering metal ions are appreciable. The results of the exchange extraction studies are shown in the Table 3.

The procedure of the exchange reaction is very simple. The test

TABLE 3

Exchange Reactions and Separations

Initial organic phase, metal ion M_1 (mg)	Aqueous raffinate, metal ion M_2 (mg)	Organic extract	
		Back washed M_1 (%)	Extracted M_2 (%)
Tl, 10.6	Ga, 10.0	Tl, 99.2	Ga, 96.4
La, 8.8	Ga, 10.0	La, 99.6	Ga, 98.0
Bi, 11.6	Ga, 10.0	Bi, 98.5	Ga, 96.8
In, 12.9	Fe, 12.9	In, 98.6	Fe, 98.9
La, 8.8	In, 12.9	La, 99.4	In, 98.4
In, 12.9	Zr, 10.0	In, 98.4	Zr, 97.8
Co, 9.4	In, 12.9	Co, 98.9	In, 98.4
Tl, 10.6	Fe, 12.9	Tl, 99.2	Fe, 99.6
La, 8.8	Cu, 8.4	La, 99.4	Cu, 99.8
La, 8.8	Bi, 11.6	La, 99.4	Bi, 98.6

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solution containing the metal M_1 was extracted by 10 ml of solvent with benzene diluent under optimum pH condition of M_1. After equilibration the aqueous phase was separated and the metal M_1–loaded organic phase M_1R_3 was again equilibrated for 10–15 min with 15 ml of buffer solution containing the metal M_2 to be exchanged, the pH of the latter being adjusted to the optimum value of extraction of the latter (M_2). The two phases were allowed to settle and then separated. The metal M_1 present in the aqueous phase was estimated. The metal M_2 present in the organic phase M_2R_3 was back-extracted with (2–4 *N*) sulfuric acid and estimated.

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