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Separation Science and Technology

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article De, Anil K. and Roy, Uday Sankar(1971) 'Solvent Extraction Behavior of Transitional Metals with Liquid Ion-Exchangers', Separation Science and Technology, 6: 1, 25 — 33
To link to this Article: DOI: 10.1080/00372367108055548
URL: http://dx.doi.org/10.1080/00372367108055548

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SEPARATION SCIENCE, 6(1), pp. 25–33, February, 1971

Solvent Extraction Behavior of Transitional Metals with Liquid Ion-Exchangers

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Summary

A systematic study of the comparative extraction behavior of some transitional metals has been performed with the high molecular weight carboxylic acids, SRS-100 and Versatic-9, using benzene as diluent. The study includes the extraction behavior as a function of pH, effect of diluent, metal ion concentration, solvent concentration, salting-out agent, and finally interference of the associated elements. Exchange reaction for several systems are reported. In almost all cases nearly quantitative extraction has been achieved. It has been found that the extraction is rapid and complete within 3–4 min but the optimum period of extraction is kept at 5 min. In some cases quantitative separations have also been carried out.

INTRODUCTION

There are several reports in the literature on the extraction of metal ions with the aid of carboxylic acids. Gindin et al. (*1, 2*) investigated with C_7–C_9 acids while Fletcher et al. (*3–6*) worked with commercially available naphthenic acids and with Versatic acids. Spitzer et al. (*7*) showed that Versatic acid could be selectively used as extractants to separate iron(III) from copper(II) and copper(II) from cobalt(II) and nickel by liquid–liquid extraction, but they used the technique of gradual neutralization to avoid precipitation of metal hydroxide, i.e., the pH of the solution was gradually changed by slow addition of a neutralizing agent during the extraction period. A mechanical stirrer was used at the rate of 2000 rpm. This procedure has been much simplified in our preposed method which employs simple manual batch extraction at controlled pH.

In this communication systematic studies are reported on the use of liquid cation exchanger, Versatic-9 and SRS-100, synthetic carboxylic acids manufactured by Shell from C_9- and C_{15}-olefins. Such systematic studies have not been reported so far. Versatic-9 is a mixture of highly branched saturated aliphatic acids containing nine carbon atoms (C_9) while SRS-100 consists of approximately 50% highly branched predominantly tertiary, high molecular weight Versatic acids (C_{15}) and approximately 50% neutral oil. Both cation exchangers are suitably soluble in organic solvents. These liquid ion-exchangers have been used for the extraction of some transitional metals, iron(III), cobalt(II), nickel, manganese (II), and copper(II), and their separations. All the relevant parameters have been critically studied. The extraction of a metal ion with a high molecular weight carboxylic acid may be considered to proceed in a manner analogous to the reaction of a metal ion with a cation exchange resin. In its simplest form, the extraction equilibrium expression may be written:

$$[M^{n+}]_{aq} + n[HR]_{org} \rightleftharpoons [MR_n]_{org} + n[H^+]_{aq}$$

where M is an n-valent cation, RH represents carboxylic acids, and the subscripts aq and org refer to the aqueous and organic phases, respectively. The extraction is thus dependent on the pH of the aqueous phase.

EXPERIMENTAL

Apparatus

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

Reagents

SRS-100, a high molecular weight synthetic carboxylic acid (equiv wt 260 to 290), and Versatic-9 (both manufactured by Shell Co. Ltd., London) were used as liquid ion-exchangers. The chemicals and solvents used were all of analytical grade unless otherwise mentioned.

Solutions of Fe (6.4 mg/ml), Co (5.5 mg/ml), Ni (5.6 mg/ml), Mn (5.6 mg/ml), Cu (4.2 mg/ml), Zn (10.5 mg/ml), and Cd (15.8 mg/ml) were prepared by dissolving a sulfate salt in an appropriate volume of distilled water containing sulfuric acid. Solution of Hg (7.4 mg/ml) was prepared by dissolving mercuric chloride in an appropriate volume of distilled water containing hydrochloric acid. Standardization was effected by accepted analytical methods (*8*, *9*).

Buffer solutions of different pH were prepared by standard procedures: pH 1.5 to 2.5 (chloroacetate); pH 3.3 (acetate–hydrochloric acid); pH 4 to 6 (acetate–acetic acid), and pH 7.5 to 10 (ammonia–ammonium chloride) (*9*).

General Procedure

An aliquot (1.5–2.0 ml) of the test solution containing 8–12.75 mg of the metal ion under investigation was mixed in a 250-ml separatory funnel with 10 ml of the appropriate buffer solutions. In experiments involving diverse ions, the foreign ions were added before the buffer solutions were introduced. The pH of the solution was adjusted as desired and extraction was accomplished with 10 ml solvent by shaking for 5 min, using benzene as diluent (solvent:diluent = 1:2). Only in the case of iron was 10 ml of pure solvent used without diluent because the addition of diluent would have necessitated extraction at a higher pH where iron(III) precipitates as hydroxide. In each case the volume of the aqueous phase was made 15 ml and that of the organic phase 10 ml. The shaking period was varied from 2–15 min in each case and it was found that the optimum shaking period is 5 min. The two phases were allowed to settle after equilibrium. The aqueous phase was then separated and the equilibrium pH was measured. To remove any traces of organic solvent entrained in the separated aqueous phase, the latter was washed with 5 ml benzene in a separately funnel. The resulting benzene extract was added to the separated organic phase. The amount of metal ion present in the aqueous phase was estimated by conventional methods. The metal ion in the organic phase was stripped with (2–4 N) sulfuric acid and estimated by conventional methods. Cobalt, nickel, manganese, zinc, cadmium, and mercury were estimated by complexometric titration with ethylenediamine tetracetatic acid. Copper was estimated iodometrically and iron volumetrically with potassium dichromate (*8*, *9*).

RESULTS AND DISCUSSION

Figures 1 and 2 summarize the comparative studies of the extraction behavior of iron(III), cobalt(II), nickel, manganese(II), and

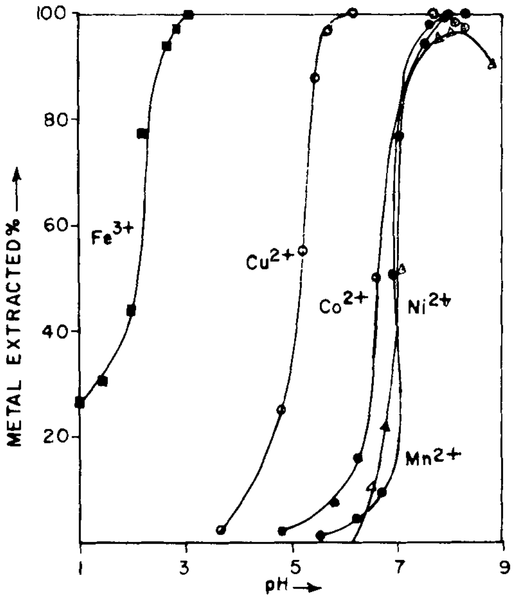

FIG. 1. Extraction with SRS-100 as a function of pH. Solvent:diluent = 1:2. C_6H_6 as diluent. ■, Fe(III); ○, Cu(II); ⊗, Co(II); △, Ni(II); ●, Mn(II).

copper (II) with SRS-100 and Versatic-9 over the pH range 1 to 9. From these it is evident that the percentage extraction increases with the increase of pH and becomes quantitative at the optimum pH. This is in good agreement with the conclusion drawn from the extraction equilibrium studies. The extraction of iron(III) starts at a lower pH (<1) and becomes quantitative at pH 3.15 with SRS-100 whereas in the case of Versatic-9 the extraction of iron(III) under the above condition is 95%. However, under the optimum condition (at pH $>$ 3.10) a slight turbidity appeared, leading to difficulty in phase separation. This could be avoided by carrying out neutralization and extraction simultaneously. Metals such as cobalt, nickel, manganese, copper, zinc, cadmium, and mercury start to extract at higher pH (>3.15). Thus, under this same condition iron can be extracted selectively in a single extraction in the presence of these elements.

The recommended optimum conditions of pH for the quantitative extractions are cobalt pH 8.2, nickel pH 8.3, manganese pH 7.95, and copper pH 6.15 with SRS-100, whereas with Versatic-9 the respective conditions are cobalt, pH 8.1, nickel, pH 7.5, manganese pH 7.05, and copper pH 6.2.

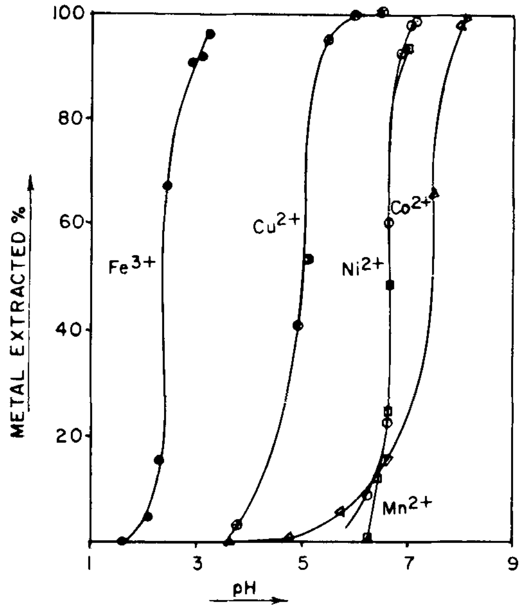

FIG. 2. Extraction with Versatic-9 as a function of pH. Solvent:diluent = 1:2. C_6H_6 as diluent. ●, Fe(III); ⊗, Cu(II); △, Co(II); ⊙, Ni(II); ⊡, Mn(II).

The results show that the difference in extraction of the metals with SRS-100 and Versatic-9 are very small, except that the tendency for emulsion formation at higher pH is greater in the case of SRS-100. The optimum shaking period of extraction for Versatic-9 is 3 min, which shows that the rate of extraction is more rapid with Versatic-9 than with SRS-100.

In order to explore the polymerization phenomenon in the extraction system the metal ion concentration was varied from 20–50 mg under the optimum conditions. In this concentration range it was found that the extraction remains virtually unaffected, indicating the absence of polymerization. The addition of ammonium chloride, sodium chloride, and aluminium chloride at various concentrations reduces the extraction, probably because of masking action.

The nature of diluent was varied from benzene to toluene, xylene, diisopropyl ether, butanol, etc. The results are tabulated in Table 1. From Table 1 it is evident that in most cases xylene and toluene showed a similar type of extraction, but with butanol and diisopropyl ether the extraction decreases.

TABLE 1

Effect of Diluent on Percentage Extraction of Metals

Diluent	Dielectric constant	Ratio solvent: diluent	Iron (III)	Cobalt (II)	Nickel	Manganese (II)	Copper (II)
Benzene	2.3	1:2	97.90	99.47	96.96	99.82	99.9
Xylene	2.4	1:2	97.60	96.98	96.45	98.58	99.7
Toluene	2.4	1:2	96.93	94.80	95.43	97.86	99.2
Diisopropyl ether	3.9	1:2	95.90	84.56	87.08	95.64	99.6
Butanol	16.1	1:2	96.10	76.28	91.62	97.11	98.8

The concentration of the solvent (SRS-100) was varied from 1:2 to 1:9 with benzene as diluent. The effect on extraction was noted at different solvent concentrations and is tabulated in Table 2. From Table 2 it is clear that dilution of solvent lowers the extraction.

A qualitative selective scale of extraction can be drawn up from the optimum extraction condition, which gives the following order of extraction with SRS-100 and Versatic-9: $Fe^{3+} > Cu^{2+} > Mn^{2+} > Co^{2+} > Ni^{2+}$. This selective scale is in agreement with that of Shikheeva (*6*) drawn up for naphthenic acid.

Extractive Separations

Figures 1 and 2 show typical extraction behavior of iron(III), cobalt(II), nickel(II), manganese(II), and copper(II) at different pH values. The degree of separation of metal ion pairs may be evaluated by comparing data on the extraction of metals over a range of pH values. The separation procedure is very simple, requiring only pH

TABLE 2

Percentage Extraction of Metals as a Function of Solvent Concentration

Solvent (SRS-100): benzene ratio	Iron (III)	Cobalt (II)	Nickel	Manganese (II)	Copper (II)
1:2	97.34	99.61	96.96	99.82	99.87
1:4	95.3	93.56	84.9	96.62	95.49
1:9	90.05	90.52	66.8	93.32	91.11

control. Iron (12.75 mg) can be separated from cobalt, nickel, manganese, copper, zinc, cadmium, mercury, palladium, calcium, and magnesium when they are present at the 100-mg level. The interfering anions are phosphate, tartrate, citrate, oxalate, fluoride, and EDTA. Cobalt, manganese, and mercury do not interfere in the extraction of copper. The noninterfering anions are phosphate, fluoride, and tartrate. The interference of vanadium during extraction can be eliminated by using tartaric acid as a masking agent. Chromium interferes seriously with both iron and copper. The interference of nickel during the extraction of copper can be eliminated by using dilute solvent (SRS-100:benzene = 1:10). In this procedure about 92.5% of the copper can be separated from a mixture of copper and nickel.

Exchange Reactions

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 hydrocarbon solutions and a more acidic metal in the aqueous phase. The reaction for divalent ions may be represented by:

$$[BR_2]_{org} + [A^{2+}]_{aq} \rightleftharpoons [AR_2]_{org} + [B^{2+}]_{aq}$$

where the metal A is more acidic than the metal B. Thus a solution of copper carboxylate (copper extracted in the organic phase) exchanges with iron quantitatively in one stage from aqueous solutions, since the difference in the optimum pH conditions for iron and copper is quite appreciable. Further, the exchange reaction procedure is applied to such metal ion pairs as Fe^{3+}/Cu^{2+}; Fe^{3+}/Co^{2+}, Fe^{3+}/Ni^{2+}, Fe^{3+}/Mn^{2+}, Fe^{3+}/Zn^{2+}, Fe^{3+}/Cd^{2+}, Cu^{2+}/Zn^{2+}, Cu^{2+}/Cd^{2+}, Cu^{2+}/Co^{2+}, and Cu^{2+}/Ni^{2+}. In most of these cases the optimum pH conditions are well separated. Exchange reactions are particularly useful in cases such as Cu/Zn, Cu/Cd, and Cu/Ni where coextraction of the second metal seriously limits extractive separations.

Table 3 shows the exchange reaction scheme in detail. The procedure of the exchange reaction is very simple. An aliquot (1.5–2.0 ml) of the test solution containing (8–12.75 mg) of metal iron (M_1) was taken and extracted with 10 ml solvent (SRS-100) under the optimum pH condition using benzene as the diluent in a 1:2 solvent:diluent ratio. The aqueous phase was separated and the metal (M_1)-loaded

TABLE 3

Exchange Reactions and Separations

Initial organic phase	Aqueous raffinate	Organic extract	
Metal ion (M_1), (mg)	Metal ion (M_2), (mg)	Back washed % (M_1)	Extracted % (M_2)
Cu, 8.44	Fe, 12.75	Cu, 99.31	Fe, 98.57
Zn, 15.77	Fe, 12.75	Zn, 99.63	Fe, 99.59
Co, 9.38	Fe, 12.75	Co, 99.17	Fe, 99.08
Ni, 11.58	Fe, 12.75	Ni, 98.13	Fe, 99.08
Mn, 11.28	Fe, 12.75	Mn, 98.54	Fe, 99.34
Zn, 15.77	Cu, 8.44	Zn, 99.63	Cu, 99.54
Co, 9.38	Cu, 8.44	Co, 98.77	Cu, 99.31
Cd, 20.54	Cu, 8.44	Cd, 99.01	Cu, 99.54
Ni, 11.58	Cu, 8.44	Ni, 95.01	Cu, 99.31
Mn, 11.28	Cu, 8.44	Mn, 98.04	Cu, 99.54
Hg, 18.42	Co, 9.38	Hg, 97.67	Co, 98.14

organic phase was equilibrated with 15 ml buffer solution containing the metal (M_2) to be exchanged, the pH of the latter being the optimum value of extraction of the latter metal (M_2). After equilibrium, the two phases were allowed to settle. The aqueous phase was then separated and the amount of metal (M_1) present in the aqueous phase was estimated by conventional methods. The metal ion (M_2) in the organic phase was stripped with (2–4 *N*) sulfuric acid and estimated by conventional methods. From Table 3 it is clear that in almost all the cases nearly quantitative exchange has been achieved.

Acknowledgments

The authors are thankful to the Council of Scientific and Industrial Research, New Delhi, for the award of a fellowship to U.S.R. They are indebted to Shell Centre, London, for the gift samples of SRS-100 and Versatic-9.

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Received by editor March 7, 1970