

Solvent extraction of metals using LIX26 extractant

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Abstract. Solvent extraction of some selected metals from an aqueous buffered solution by LIX26 extractant has been studied. The $pH_{1/2}$ values (at which 50% of metal ion is extracted) for extracting different metals by 1 v/v% LIX26 extractant in methyl isobutyl ketone have been obtained. The order of extraction of metals by LIX26 extractant as a function of $pH_{1/2}$ value is Pd(II) < Cu(II) < Sb(III) < Fe(II) < Co(II) < Zn(II) < Ni(II) < Pb(II) < Mn(II) < Cd(II).

Keywords. LIX26 extractant; $pH_{1/2}$ values; hydrometallurgy.

1. Introduction

The major breakthrough in solvent extraction studies is the development of reagents known as chelating extractants (Ashbrook 1975). Among these extractants, compounds marketed under the trade name "LIX" reagents (Liquid Ion Exchange Reagent) by Henkel Corporation have assumed great importance in the hydrometallurgy of copper (Burkin 1983). These chelating extractants effect efficient and economical separation of copper from virtually all other metals in solution under a wide range of conditions. Very little information is available on the extraction of metals other than copper using LIX extractants. In the present paper, extraction of copper(II), antimony(III), zinc(II), cadmium(II), cobalt(II), nickel(II), manganese(II), palladium(II), lead(II), iron(II), and rhodium(III) with LIX26 extractant has been investigated. Such a study would be helpful in providing basic information required for hydrometallurgical separations and in the development of new analytical methods.

2. Experimental

2.1 Materials

LIX26; HL (containing substituted oxine in kerosene) was kindly supplied by Henkel Corporation, USA. The pH of the aqueous phase was maintained by using mixtures of potassium chloride-hydrochloric acid for pH 1-3, sodium acetate-acetic acid for pH 4-6, ammonium chloride-ammonia for pH 8-10, and ammonium acetate-ammonia for pH 6-8. A constant ionic strength in the aqueous phase was maintained by using potassium nitrate solution. Potassium chloride was used to

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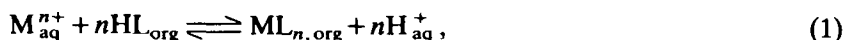
maintain ionic strength where hydrochloric acid was used. Analytical reagent grade methyl isobutyl ketone was used without further purification.

2.2 Extraction procedure

Ten millilitres of an aqueous layer containing an aliquot of metal solution, 5 ml of buffer solution and 1 ml of 1 M potassium nitrate solution was equilibrated with 10 ml of organic layer containing 1 v/v% LIX26 in methyl isobutyl ketone (MIBK). The mixture, in a stoppered bottle, was shaken in a wrist-action mechanical shaker for a period sufficient for the attainment of equilibrium at $35 \pm 1^\circ\text{C}$. After equilibration, pH of the aqueous phase was measured by an expanded scale pH meter (ECIL, India). In the case of extraction from more acidic solutions, hydrochloric acid solution of different molarities was used for attaining the desired concentration of acid in the aqueous phase. The concentration of metal in the aqueous layer was then measured by an SP 191 Pye Unicam Atomic absorption spectrophotometer.

3. Results and discussion

The extraction of a metal ion with a chelating ligand having a replaceable hydrogen ion may be represented by the following equation (Marcus and Kertes 1969).



where HL = LIX26 extractant.

The extraction constant (equilibrium constant) of this reaction is given by

$$K_{\text{ex}} = D[\text{H}^+]_{\text{aq}}^n / [\text{HL}]_{\text{org}}^n, \quad (2)$$

where distribution coefficient D is equal to the ratio $[\text{ML}_n]_{\text{org}} / [\text{M}^{n+}]_{\text{aq}}$. Equation (2) may be rewritten in the logarithmic form

$$\log K_{\text{ex}} = \log D - n\text{pH} - n \log [\text{HL}]_{\text{org}}, \quad (3)$$

Since the LIX26 extractant was supplied to us in a diluted form, the concentration of the extractant was taken on a v/v% basis. At a fixed concentration of the extraction the equilibrium constant (K_{ex}) is proportional to $\text{pH}_{1/2}$ values. The trend in K_{ex} values is known by knowing the trend in $\text{pH}_{1/2}$ values even though the absolute concentration of extractant is not known. LIX reagents used as extractants in commercial solvent extraction operations have, of necessity, to be produced on a large scale and do not have the purity of analytical reagents. It is not advisable (Ashbrook and Ritcey 1984) to do the initial work with refined or purified material in acquiring accurate data and then pilot the process using the commercially available material. In such studies impurities in reagents could render the work useless, since the extraction characteristics could be quite different using a pure material.

The data on the extraction of metals by LIX26 1v/v% in MIBK as a function of $\text{pH}_{1/2}$ values are given in table 1. This agrees partly with the extraction data reported by Sary (1968) for 0.01 M oxine-chloroform solutions as given in table 1. Gentry and Sherrington (1950) also report an order of extraction of metals by oxine

Table 1. Extraction data of some metals using 1 v/v% LIX26 extractant in MIBK.

Metal	pH _{1/2} (50% extraction)	pH for complete extraction	Shaking (min)	pH _{1/2} 0.01 M oxine in CHCl ₃ [†]
Mn(II)	6.75	≥ 7.9	30	6.66
Co(II)	5.00	6.7	30	5.08
Ni(II)	6.15	≥ 7.8	30	3.16
Cd(II)	6.95	≥ 8.6	60	6.65
Zn(II)	5.40	≥ 6.7	30	5.20
Cu(II)	Complete extraction in the pH range 1.5–9		5	1.77
Pb(II)	6.40	≥ 8.5	30	6.04
Sb(III)	< 1.5	1.5	30	—
Rh(III)	only 25% extraction		120	—
Fe(II)*	3.8	≥ 5.0	60	—
Pd(II)	< 1	—	30	< 0

* Chloroform as solvent; † Stary (1968)

as a function of pH_{1/2} values. It seems most likely that the extraction of metals by LIX26 extractant will generally follow that for metal oxinates. Since LIX26 resembles oxine in its extractive properties towards metals, it seems reasonable to suppose that similarities exist in their properties. There is also good agreement between extraction studies with LIX26 and Kelex 100 extractants. LIX26 possesses a K_{DR} of 3 orders of magnitude larger and a rather small K_a value than does oxine (Bag and Freiser 1982). Hence LIX26 offers an opportunity to study the mechanisms of metal extraction in acidic system not possible with oxine because of its low hydrophobicity as compared to LIX26 extractant.

The pH isotherms of LIX26 extractant with these selected metals are shown in figure 1. The order of extraction of metals by LIX26 extractant as a function of pH_{1/2} values is as follows:

Pd(II) < Cu(II) < Sb(III) < Fe(II) < Co(II) < Zn(II) < Ni(II) < Pb(II) < Mn(II) < Cd(II).

Except for Ni(II) and Cd(II) all the extraction data for LIX26 systems agree well with oxine systems (Stary 1968). Cadmium(II) forms hydrated complexes with oxine (CdL₂2HL) and with Kelex 100 forms complexes of the type CdL₂ (Lakshmanan *et al* 1974). Since hydrated complexes are better extracted into oxygenated solvents, cadmium extraction with LIX26 is effected at higher pH values as compared to oxine.

The order of extraction of metals by Kelex 100 as a function of pH_{1/2} value has been given as (Ma and Freiser 1984; Zhu and Freiser 1983):

Pd(II) < Cu(II) < Ni(II).

The extraction behaviour of these selected metals by LIX26 extractant can be briefly summarised as follows:

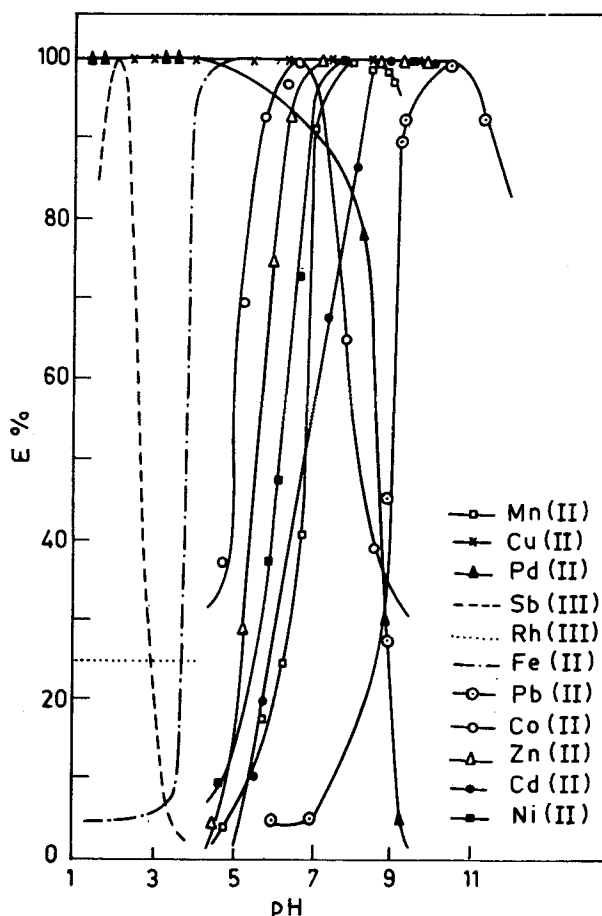


Figure 1. The pH isotherms of some selected metals using 1% v/v LIX26 extractant in MIBK. In case of Pb(II) the X-axis has been shifted by 2.0 pH units towards the +ve direction.

(i) Copper(II), antimony(III) and palladium(II) are extracted from acidic solutions. Antimony(III) gets extracted around pH 9 (Sandell 1959) with oxine, whereas with LIX26 an effective complete extraction is possible around pH 1.5. Palladium is extracted from highly acidic solutions thereby providing high selectivity in the recovery and purification of palladium. Effective separation of palladium is also achieved from nickel using this extractant.

(ii) Maximum extraction shown by rhodium(III) was only 25% above which no extraction was possible. At higher pH values extraction of cobalt(II) falls rapidly.

(iii) Complete extraction of copper(II), manganese(II), nickel(II), zinc(II), lead(II), cadmium(II) and iron(II) by using LIX26 extractant is around pH 8.6, though copper(II) is also extractable from acidic solutions.

Thus a single extraction at pH 8.6 from a dilute solution of metals into a smaller volume of the organic solvent will be a rapid and effective method of preconcentration of metals before atomic absorption spectrophotometric deter-

mination (Cresser 1978). Since LIX26 is soluble to a good extent in many organic solvents, both microscale as well as macroscale operations are possible.

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