Pak. J. Sci. Ind. Res. 2006 **49**(5) 309-313

Effect of Excess Metal Concentration on the Extraction Potential of Di-(2-Ethylhexyl) Phosphoric Acid

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(received April 19, 2005; revised August 30, 2006; accepted September 2, 2006)

Abstract. The extraction potential of di-(2-ethylhexyl) phosphoric acid (DEHPA) in kerosene increases manyfold on loading calcium into the organic phase before equilibration with aqueous copper feed. The control of pH was unnecessary in the range from pH 5.0 to pH 3.0. It was found that copper can easily replace nickel, sodium and calcium in the organic phase because of the difference in the dissociation constants of copper and other metals studied. The hydrolysis of calcium maintains the pH of the aqueous phase in favour of higher extraction of copper by DEHPA.

Keywords: dissociation constant, di-(2-ethylhexyl) phosphoric acid, copper extraction

Nomenclature

A^- = anions in the aqueous phase
CaR_2 = calcium-DEHPA complex
H^+ = free hydrogen ions
HR = concentration of organic acidic extractant
OH^- = hydroxyl ions
M^{2+}, X^{2+} = free metal ions (M^{2+} refers to free metal ions of low dissociate constants, while X^{2+} refers to free metal ions of high dissociate constants)
MR_2, XR_2 = concentration of metals in the organic phase
R^- = dissociated ions of extractant
XA = concentration of metal salt in the aqueous phase

Introduction

Hydrometallurgical operations using di-(2-ethylhexyl) phosphoric acid (DEHPA) for the extraction of copper have been reported to give lower loadings, as compared with the more expensive second generation extractants (Borowiak-Resterna and Lenarcik, 2004; Cox, 1992; Yoshizuka *et al.*, 1990), such as LIX 864, 865, 984, 622, P5100, 5300, PT5050, SME529, ABF2, and OMG. A number of authors have tried to improve extraction with DEHPA by studying various factors, such as concentration of solvent and solute, effect of pH, influence of sulphate and chloride ions, and the nature of diluents (Cerpa and Alguacil, 2004; Saeed and Jamil, 1998; Ahmed *et al.*, 1994). The principal objective in the application of solvent extraction process is to minimize the control of influencing factors on the separation of competing metals and hence to attain maximum loading of the desired metal in the organic phase.

In order to improve the extraction potential of DEHPA, some researchers (Ajawin *et al.*, 1983; Joe *et al.*, 1966) have used sodium or ammonium salts of DEHPA. The presence of sodium or ammonium ions suppresses the ionization of the metal hydroxide and increases the metal loadings of the organic phase. However, in most cases, a third phase is formed (Ajawin *et al.*, 1983), which reduces the concentration of the metal in the extract phase.

In the present study, a series of experiments were conducted to find out the most suitable metal to form a metal salt of DEHPA that can be employed to achieve maximum extraction. Apropose to this, a number of metal hydroxides, such as sodium hydroxide, calcium hydroxide and nickel sulphate, were initially contacted with DEHPA to make a metal-DEHPA complex before equilibrating it with the aqueous phase. The presence of metal iron in the form of metal-DEHPA complex in the organic phase increased the total metal ions concentration in the equilibrated phases, as compared to the anion concentration in the system. At equilibrium, the exchange of competing metal ions in the aqueous phase was elucidated in the light of much less considered dissociation constants of these metals involved in the process. Other factors, such as concentrations of the solvent and solute and pH of the aqueous phase, were also considered to describe the present process.

Theoretical background. The extraction of metal ions from the aqueous phase by DEHPA in the organic solute has been shown to conform to the following general equation (Ahmed *et al.*, 1994; Rydberg and Serine, 1992):

$$[Cu^{2+}]_a + 2[HR]_o \rightleftharpoons [CuR_2]_o + 2[H^+]_a \qquad (1)$$

This is an ion exchange reaction and the final equilibrium depends on dissociation and distribution constants of the various species in the system. The release of hydrogen ions decreases pH of the aqueous solution causing the formation

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*Author for correspondence; E-mail: drrashid_azri@yahoo.com of non-extractable metal species (Saeed and Jamil, 1998; Yoshizuka *et al.*, 1990), while protonation of the extractant in the aqueous phase results in a very low distribution constant of the metal species (Ahmed *et al.*, 1998; Ritcey and Ashbrook, 1984).

Now, consider a metal M^{2+} forming a metal-DEHPA complex (MR_2) in the organic phase, which is equilibrated with an acidic aqueous solution containing a divalent metal X^{2+} and anions A^{2-}. The reaction mechanism in the aqueous phase may be described by the following equations:

$$[MR_2] \rightleftharpoons [M^{2+} + 2R^-] \tag{2}$$

$$[XA] \rightleftharpoons [X^{2+} + A^{2-}] \tag{3}$$

$$[HR] \rightleftharpoons [H^+ + R^-] \tag{4}$$

$$[X^{2+} + 2\,R^-] \rightleftharpoons [XR_2] \tag{5}$$

The amount of metal ions (X + M) in the system exceeds the stoichiometric proportion of anions A^{2-}. The condition of electrical neutrality in the aqueous phase at pH 4.29 requires that the metal ions can only be equal to the anions in the aqueous phase. Therefore, the excess metal (X or M) transfers into the organic phase and remains there in undissociated form. The condition of electrical neutrality in the aqueous phase requires that:

$$2[X^{2+}] + 2[M^{2+}] + [H^+] = 2[A^{2-}] + [OH^-] \tag{6}$$

The pH of the aqueous phase is 4.29, thus the total concentration of hydrogen and hydroxyl ions can be neglected as compared to total cations and anions. Therefore, equation (6) may be simplified as:

$$2[X^{2+}] + 2\,[M^{2+}] = [A^{2-}] \tag{7}$$

The amount of metal, in excess, is equal to the total metal in the system minus anions. Therefore, this excess metal will remain in undissociated form in the organic phase so as to maintain electrical neutrality in the aqueous phase. The distribution constant of the undissociated complex has been reported to be very high (Marcus and Kertes, 1969). In the present study, the M^{2+} ions (calcium, sodium, or nickel) chosen had a higher dissociation constant than that of X^{2+} ions (copper). Therefore, M^{2+} ions will be more in the dissociated form and remain in the aqueous phase allowing X^{2+} ions to be extracted into the organic phase.

It is clear from these facts that the exchange of two metals between the organic and aqueous phases depends on their dissociation and distribution constants of their undissociated species formed with DEHPA. Moreover, this process enhances the extraction potential of DEHPA manyfolds because of the presence of a large amount of metal species as compared to anions in the system.

Materials and Methods

To determine the extractability of DEHPA, a series of tests were carried out which can be divided into two groups. The first set of experiments was conducted with DEHPA diluted in kerosene as a solute. In each case, 50 ml of the organic phase was equilibrated with 50 ml of aqueous copper solution of varying pH in 200 ml bottles. The bottles were shaken continually for 30 min at room temperature to ensure complete equilibrium. Equilibrated phases were allowed to be disengaged and the aqueous phase was withdrawn for analysis. The concentration of metal ions was analysed using Spectronic-20 spectrophotometer. The pH of the aqueous phase was measured with Toptronic pH meter. The concentration of metal ions in the organic phase was obtained by difference. To ensure the accuracy of the analysis, the organic phase was stripped with 1 N sulphuric acid and analysed for copper concentration.

The second set of experiments was performed with nickel-DEHPA, sodium-DEHPA and calcium-DEHPA complexes. The experimental procedures were the same as adopted in the first set of experiments. The analysis technique used for copper, nickel, calcium and sodium was described earlier (Ahmed *et al.*, 1989). The concentration of metals in the aquous phase was analyzed spectophotometrically.

All the chemicals used in the present investigation were of reagent grade (E. Merck), except kerosene. Commercial kerosene was washed with distilled water to remove colour or any other impurities and centrifuged prior to its use.

Results and Discussion

The influence of pH on the extraction of copper ions solely with DEHPA and with various metal complexes of DEHPA in the organic diluent kerosene are shown in Fig. 1 and Fig. 2. The **curve-1** (Fig. 1) depicts that copper and sulphate ions are in stoichiometric proportion, giving a very low distribution constant of copper for the system. It is evident from equation (1) that for every mole of copper extracted into the organic phase, 2 moles of H^+ ions are released into the aqueous phase to maintain electrical potential of the system. So, in this system, one of the parameters that controlled the reaction was the acid contents (H^+ ions) of the aqueous phase. At pH 4.29 of the aqueous solution, copper extracted was 0.165 g/l from the total feed concentration of 3.0 g/l copper with 0.1 M DEHPA. The **curve-2** shows an improvement in the extraction of copper from 3.0 g/l copper solution of pH 4.29 with 0.1 M nickel-DEHPA complex. The total metal ions present in the system were in excess of the stoichiometric amount of sulphate ions. The dissociation constant of the nickel-complex is higher than the copper complex, therefore, some of the nickel-DEHPA complex dissociates in the aqueous phase and nickel is replaced by copper to form copper-DEHPA complex in the aqueous phase. The copper-DEHPA complex was extracted into the organic phase because of the low dissociation constant of copper. The release of H^+ ions in this system was much less than that of the results given in **curve-1** (Fig. 1), hence, resulting in a favourable pH of the aqueous phase to give higher extraction of copper as illustrated in **curve-2** (Fig. 1). The loading of copper in the organic phase was 0.182 g/l for this system, which was better than the results illustrated in **curve-1** (Fig. 1).

These results confirm the presented theory that as the amount of excess metal in the system increased, the amount of copper extracted in the organic phase also increased. This exchange of two metals between the organic and aqueous phases is the result of dissociation constants and distribution constants of their undissociated species formed with DEHPA.

Considering the above findings, metal hydroxides of calcium and sodium were chosen because they have much higher dissociation constants as compared to copper. The extraction of copper from the aqueous phase with calcium or sodium complexes of DEHPA is illustrated in Fig. 2. The curves in Fig. 2 illustrate significantly higher extraction potential of DEHPA as compared to the results presented in Fig. 1.

It was found that sodium concentrations in 0.1 M DEHPA can be increased upto 20 g/l. However, theoretically, 0.1 M DEHPA can only load metal ions equivalent to its molar concentrations, whereas sodium ions present in the organic phase were almost nine times higher. The higher concentration is attributed to the ability of kerosene to dissolve sodium hydroxide solution, as such, which consequently results in an increase in the volume of the organic phase. Moreover, the sodium-DEHPA complex formed, presumably had very low concentration. The higher concentrations of excess metal in the system improved the extraction of copper as compared to the results given in **curve-1** and **curve-2** (Fig. 1). Copper extracted was 1.080 g/l from the total metal concentration of 23 g/l (3 g/l copper + 20 g/l sodium) in the system with the DEHPA concentration of 0.1 M. Moreover, the third phase was not observed under the present conditions of the system.

The influence of calcium ions, as an excess metal in the system, is also shown in Fig. 2. The results indicate that calcium had a greater effect on the extraction of copper than any other metal studied. Copper extracted was 2.12 g/l from the total metal concentration of 4.64 g/l (3.0 g/l copper + 1.64 g/l calcium) with the DEHPA concentration of 0.1 M. This is an increase of 1.955 g/l, 1.938 g/l and 1.04 g/l over the results reported in **curve-1** and **curve-2** (Fig. 1) for solely DEHPA and nickel-DEHPA complex and the sodium-DEHPA curve in Fig. 2, respectively, under similar conditions.

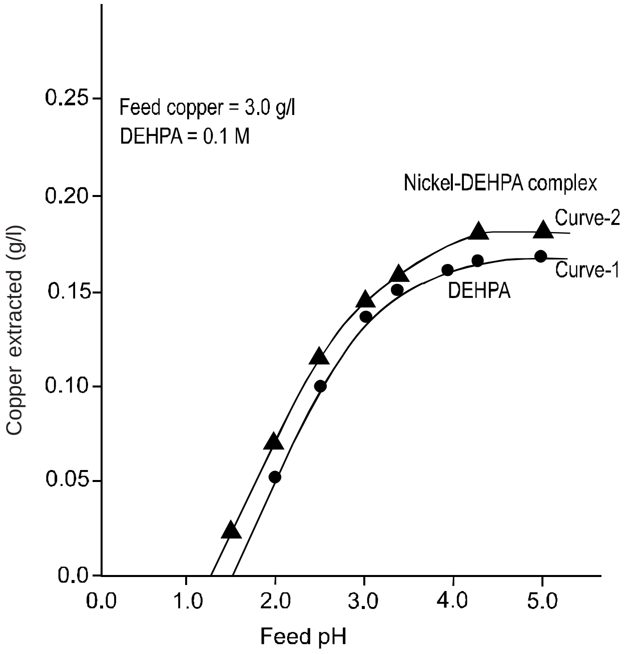

Fig. 1. Extraction of copper with di-(2-ethylhexyl) phosphoric acid (DEHPA) and nickel-DEHPA complex.

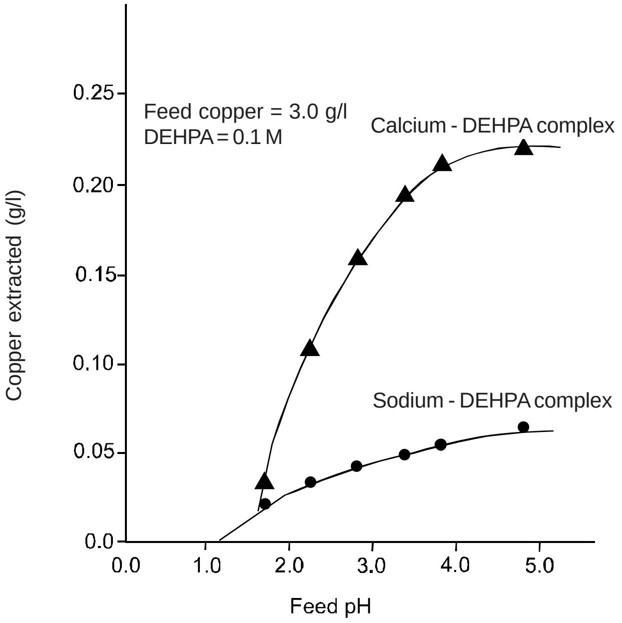

Fig. 2. The effect of excess metal on the equilibrium distribution of copper, using calcium and sodium-di-(2-ethylhexyl) phosphoric acid (DEHPA) complexes.

These results prove that the introduction of calcium ions as an excess metal in the organic phase improves the extraction potential of DEHPA as compared to the other metals examined. Therefore, a series of distribution data was obtained to investigate the influence of other salient parameters on the extractability of DEHPA. These salient parameters were pH, concentrations of DEHPA and copper, solvent losses, and solubility of DEHPA in the aqueous phase.

The extraction of copper from 1 g/l to 5 g/l copper in the aqueous feed solution at pH 4.29, with calcium-DEHPA complex, is shown in Table 1. The results show that the extraction of copper did not increase proportional to its increase in concentration in the aqueous feed solution. It is attributed to the release of large sulphate ions into the aqueous phase which are associated with copper salt, since 1 g of copper is associated with 1.511 g of sulphate ions as given in Table 1. In 1 g/l copper in the aqueous feed solution having total metal ions concentration of 3.36 g/l (2.36 g/l calcium), the concentration of sulphate ions was less than half, i.e., 1.511 g/l. It resulted in giving a distribution coefficient of 1.179. As the concentration of aqueous copper feed solution increased to 5 g/l, the concentration of associated sulphate ions also increased to 7.554 g/l in the system. The sulphate ions were thus more than the total concentration of metal ions (5 g/l copper + 2.36 g/l calcium) resulting in a very low distribution coefficient of 0.414. This trend is evident from Table 1 for the other concentrations of copper, i.e., 2 g/l, 3 g/l and 4 g/l.

Moreover, the results given in Table 1 show that 0.5 M DEHPA carries only 1.818 g/l to 2.155 g/l total metal (0.053 M copper + 0.037 M calcium). If the extracted complex is represented by XR_2, according to equation (1), then it would appear that only a small proportion of DEHPA molecules is directly involved in the formation of metal complex. This shows that the process demanded further contacts of the loaded extract phase with fresh copper feed to involve all molecules of DEHPA for maximum extraction of metal ions from the aqueous feed.

The results given in Table 2 give feed pH, equilibrium pH, sulphate ions added, and distribution of copper and calcium in the conjugate phases at equilibrium. The influence of sulphate ions becomes more evident on the extraction capacity of DEHPA as shown in Table 2. The concentration of sulphate ions was increased by the addition of sulphuric acid, whereas concentration of total metal (copper + calcium) ions was kept constant. The distribution of both metals decreased as the concentration of sulphate ions increased. It is due to excess sulphate ions in the aqueous phase. These excess sulphate ions function as coordinating ligands (Marcus and Kertes, 1969; Joe *et al.*, 1966) and compete with DEHPA for the metal ions resulting in reduced extraction of metal by DEHPA.

The results in Table 2 show that change in the feed pH from 4.29 to 3.40 gives almost the same distribution of copper for 5 g/l copper feed solution extracted with 0.5 M Ca-DEHPA complex. Similarly, an increase in pH to 5.0 by the addition of sodium hydroxide gives the same distribution of copper. The pH of the aqueous feed solution reduces the extraction of copper as shown in Fig. 1, Fig. 2 and Table 2. The extraction of copper at pH 4.29 was 0.995 g/l, and at pH 1.50 it reduced to only 0.165 g/l. This shows that the effect of pH on the extractability of DEHPA was more profound at the pH values lower than 2.0.

Another interesting fact emerging from Table 2 is that the pH of the aqueous phase, after achieving equilibrium, was higher than that of the aqueous feed pH. This increase of pH of the equilibrated aqueous phase may be explained by considering the following reactions occurring in the aqueous phase:

Table 1. Distribution of copper and calcium in the equilibrated phases*

Total copper (g/l)	Associated SO_4^{2-} ions (g/l)	Organic phase copper (g/l)	Organic phase calcium (g/l)	Aqueous phase copper (g/l)	Aqueous phase calcium (g/l)	Distribution coefficient
1	1.511	0.338	1.480	0.662	0.88	1.179
2	3.022	0.500	1.385	1.500	0.975	0.762
3	4.533	0.650	1.325	2.350	1.035	0.583
4	6.043	0.800	1.263	3.200	1.097	0.480
5	7.554	0.995	1.160	4.005	1.200	0.414

* = calcium = 2.36 g/l; di-(2-ethylhexyl) phosphoric acid (DEHPA) = 0.5 M; feed pH = 4.29

Table 2. Effect of sulphate ions on the extraction of copper*

Feed pH	Equilibrium pH	Added SO_4^{2-} ions (g/l)	Organic phase copper (g/l)	Organic phase calcium (g/l)	Aqueous phase copper (g/l)	Aqueous phase calcium (g/l)
4.29	4.16	-	0.995	1.160	4.005	1.200
3.40	4.10	0.017	0.960	1.092	4.040	1.268
2.50	3.79	0.149	0.750	1.088	4.250	1.272
2.00	3.50	0.478	0.472	1.015	4.528	1.345
1.50	2.89	0.518	0.165	0.900	4.835	1.460
5.00	4.15	-	0.995	1.150	4.005	1.210

* = di-(2-ethylhexyl) phosphoric acid (DEHPA) = 0.5 M; feed copper = 5 g/l; calcium = 2.36 g/l

$$[CaR_2]_o + [Cu^{2+}]_a \rightleftharpoons [CuR_2]_o + [Ca^{2+}]_a \quad (8)$$

$$[CaR_2]_o + 2\,[H^+]_a \rightleftharpoons 2\,[HR]_o + [Ca^{2+}]_a \quad (9)$$

These equations show that a large number of calcium ions are transferred to the aqueous phase as is also evident from Table 1. These calcium ions hydrolyse and consequently increase or maintain pH of the aqueous phase (Sato *et al.*, 1977). It is also apparent from these equations that calcium ions have higher dissociation constant and are suitable to replace copper by an ion exchange mechanism.

It has been reported (Cox, 1992; Yoshizuka *et al.*, 1990; Korodosky *et al.*, 1987) that Salicylaldoxime (strong copper extractant) as in higher series, and Ketoxime (moderate copper extractant) LIX65N, SME 529, OMG and ABF 2 are widely used extractants for extraction purposes. Ketoxime can load upto 5.0 g/l copper at about 20% concentration in kerosene, however, this resulted in viscous, hard to handle, organic phase. The salicylaldoxime shows very high distribution constant but is sparingly soluble in the aqueous phase showing excessive losses. However, the results presented for the extraction of copper with DEHPA show high extraction without becoming viscous, and the losses by evaporation or absorption in the aqueous phase are minimal which agree with earlier findings (Cox, 1992; Joe *et al.* 1966).

It is evident from the results given in Tables 1 and 2 that the extraction potential of DEHPA was greatly influenced by the presence of excess metal. The added metal ions remained in the organic phase and can be replaced by repeated contact of the organic phase with fresh feed. It will obviously give higher loadings of only copper ions in the extract phase. In other words, the real benefit of the cheap DEHPA may be achieved by the addition of excess metal in the system and by using multistage extraction process.

Conclusion

The overall distribution of metal ions depends on the amount of total metal concentration and total anions present in the system. The pH of the aqueous phase may be unnecessary to control when using this process. The number of extraction stages in a mixer-settler would be reduced due to quick exchange of metal ions by this process.

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