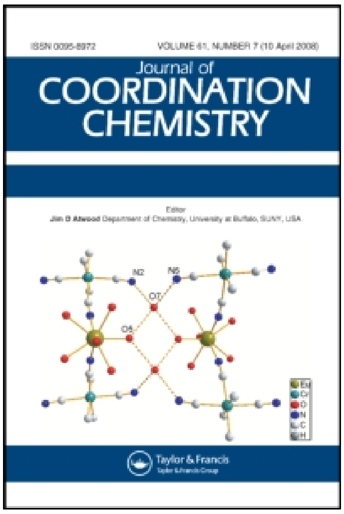

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The effect of diluents on extraction of copper(II) with di(2-ethylhexyl)phosphoric acid

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The effect of diluents on extraction of copper(II) with di(2-ethylhexyl)phosphoric acid

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The liquid–liquid extraction of copper(II) from sulfate medium with di(2-ethylhexyl)phosphoric acid (D2EHPA, HL) at 25°C is studied with the following parameters: pH, concentration of the extractant, and the nature of diluent. The effect of the diluent using polar and nonpolar solvents in the extraction of copper(II) is discussed. The extracted copper(II) species were CuL_2 in 1-octanol and methyl isobutyl ketone and $CuL_2 \cdot 2HL$ in toluene, carbon tetrachloride, and cyclohexane. The extraction constants are evaluated for different diluents.

Keywords: liquid–liquid extraction; copper(II); di(2-ethylhexyl)phosphoric acid; diluent effect

1. Introduction

The recovery of copper(II) from aqueous solutions is very important for environmental protection and the chemical equilibria involved in the extraction processes have been studied [1–8].

Selection of extractants with high efficiency is important; organophosphorus agents have been reported as a good choice with di(2-ethylhexyl)phosphoric acid (D2EHPA) widely used in liquid–liquid extraction for separation and purification of liquid effluents containing various metals [9–13].

The diluent is not only a carrier for the extractant and extracted metal complex, but also a participant in the extraction process. The effect of the diluent is essentially an organic-phase reaction or interaction due to at least one of following two factors [14]: (a) interaction with the extractant molecules, which affects the activity of the extractant and changes the extraction performance of the extractant or (b) interaction with the extracted metal complex, which may change the composition of the complex through coordination and/or substitution of the diluent molecules.

Ritcey and Lucas [15] investigated the effect of the diluent and modifier on extraction performance for several combinations of commercially available extraction systems. They found that an increase in polarity or dielectric constant of the diluent caused a reduction in effectiveness of extraction. A more detailed study of diluent effect was

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carried out by Komasawa [16, 17] who found polar or nonpolar diluents could greatly affect the extraction of metal cations.

The present work describes the results obtained from extraction of copper(II) with D2EHPA in sulfate containing aqueous solutions. The aim of the work is to determine the stoichiometry coefficients of the extracted complexes and their extraction constants and to fully evaluate the nature of the interaction with the diluents for this extraction system. Several polar solvents were employed as diluents in addition to nonpolar solvents.

2. Experimental

2.1. *Reagents and solutions*

D2EHPA (Fluka) of analytical grade was used without further purification. Organic diluents, toluene, carbon tetrachloride, cyclohexane, 1-octanol, and methyl isobutyl ketone (MIBK), were pre-equilibrated with aqueous solutions, which did not contain any metal. The copper sulfate (Merck) and sodium sulfate (Merck) were of analytical reagent grade.

2.2. *Extraction and analytical procedures*

Distribution measurements were performed using a batch technique in thermostatted vessels at 25°C. Equal volumes (25 mL) of both phases were magnetically stirred until equilibrium was reached (max 30 min). The pH was adjusted by 0.1 M NaOH. The initial concentration of copper(II) was 1.57×10^{-3} M and the ionic strength of the aqueous phase was assumed to be unity ($[Na_2SO_4] = 0.33$ M). After the two phases were separated completely, the metal ion concentrations were determined in aqueous phase photometrically at 820 nm using a Philips UV-VIS SP6-36. The metal ion concentrations in the organic phase were calculated from the difference between the metal ion concentrations in the aqueous phase before and after extraction.

3. Results and discussion

3.1. *General treatment of extraction equilibrium of copper(II) with D2EHPA*

Alkylphosphoric acids exist primarily as the dimer in nonpolar solvents such as alkanes or benzene, and as monomer in polar solvents such as ketones, alcohols, and esters [18]. As the total concentration of copper(II) is at trace levels in this study, it is reasonable to assume that no polynuclear complexes are formed [17, 19]. The extraction of copper(II) from sulfate medium by D2EHPA can be described by the following reaction in nonpolar diluents:

$$M^{2+} + (n+p)/2\overline{(HL)_2} \xrightleftharpoons{K_{ex1}} \overline{(ML_n \cdot p(HL))} + nH^+. \tag{1}$$

The equilibrium constant, K_{ex1}, can be given as a function of molar concentration, provided that the ionic strength of the aqueous solution is kept constant:

$$K_{\mathrm{ex1}} = \frac{\left[\left(\overline{\mathrm{ML}_n \cdot p(\mathrm{HL})}\right)\right]\left[\mathrm{H}^+\right]^n}{\left[\mathrm{M}^{+2}\right]\left[(\overline{\mathrm{HL}})_2\right]^{(n+p)/2}}. \tag{2}$$

In polar diluents one has:

$$\mathrm{M}^{2+} + (n+p)/\overline{(\mathrm{HL})} \xrightleftharpoons{K_{\mathrm{ex2}}} \overline{(\mathrm{ML}_n \cdot p(\mathrm{HL}))} + n\mathrm{H}^+ \tag{3}$$

with

$$K_{\mathrm{ex2}} = \frac{\left[\left(\overline{\mathrm{ML}_n \times p(\mathrm{HL})}\right)\right]\left[\mathrm{H}^+\right]^n}{\left[\mathrm{M}^{+2}\right]\left[(\overline{\mathrm{HL}})\right]^{(n+p)}} \tag{4}$$

where $(\overline{\mathrm{HL}})_2$ and $(\overline{\mathrm{HL}})$ denote dimeric and monomeric extractant in nonpolar and polar diluents; the bar denotes the organic phase species or organic phase concentration, n and p are the stoichiometric coefficients for the ligand and its protonated form.

The distribution coefficient, D, which is defined by the concentration of metal in organic phase divided by that in aqueous phase, for the nonpolar and polar diluents, is expressed by the following equations:

$$\log D = \log K_{\mathrm{ex1}} + (n+p)/2 \log\left[\overline{(\mathrm{HL})_2}\right] + n\mathrm{pH}, \tag{5}$$

$$\log D = \log K_{\mathrm{ex2}} + (n+p)\log\left[\overline{\mathrm{HL}}\right] + n\mathrm{pH} \cdot \tag{6}$$

The extraction equilibrium for each extraction system was analyzed according to the slope analysis method [20] on the basis of some equations derived from equations (5) and (6). If the metal complex is not formed in the aqueous solution and the concentration of the extractant is not changed during the extraction reaction, the slope for the plot of $\log D$ against pH becomes the charge on the aqueous metal ion, n:

$$\left[\frac{\partial \log D}{\partial \mathrm{pH}}\right] = n \quad \text{at constant } [(\overline{\mathrm{HL}})_2] \text{ and } [\overline{\mathrm{HL}}]. \tag{7}$$

In addition, when the equilibrium pH is not changed during the extraction reaction, the plot of $\log D$ against $\log[(\overline{\mathrm{HL}})_2]$ and $\log[\overline{\mathrm{HL}}]$ gives a slope $(n+p)/2$ and $(n+p)$, respectively, from which the value of p can be determined. Therefore, substituting n and p into equations (1) and (3), one can obtain the stoichiometric equations for the extraction reactions and the equilibrium constants can be also determined.

3.2. *Analysis of the extraction equilibrium in nonpolar diluents*

Figure 1 shows the relation between $\log D$ and the equilibrium pH, depending on the concentration of D2EHPA in toluene. Other solvents are in Supplementary Material (online). The linear relation between $\log D$ and pH is described in equation (7) and the value of n calculated from the slope of the straight line is 2 in this system, confirming that the extracted species in organic phase is $\mathrm{CuL}_2 \cdot \mathrm{pHL}$.

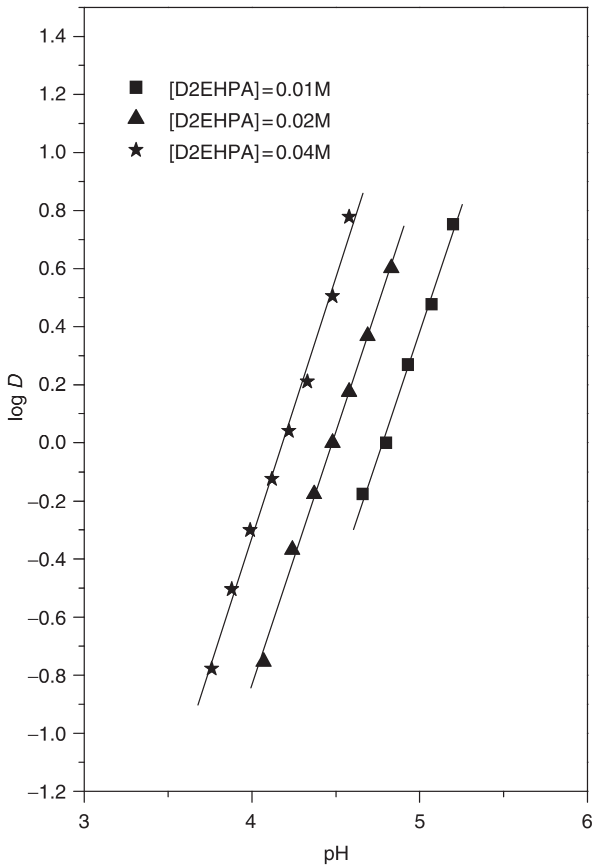

Figure 1. Effect of pH on the extraction of copper(II) with D2EHPA in toluene.

To determine the amount of free D2EHPA involved in the extracted species, the extraction of metal at various concentration of D2EHPA in toluene, carbon tetrachloride and cyclohexane solvents was carried out at constant pH; the number of di(2-ethylhexyl)phosphoric acid molecules involved in the monomeric species can be determined from the slope of the plots of log D against log $[\overline{(\mathrm{HL})_2}]$, as shown in figure 2. The values of $[\overline{(\mathrm{HL})_2}]$ were calculated by assuming: $[\overline{(\mathrm{HL})_2}] \approx 0.5\,\mathrm{C_{HL}}$, with $\mathrm{C_{HL}}$ the total acid concentration, $(n+p)/2$ is determined to be 2 and the value of p thus becomes 2, and the composition of the extracted species is $\overline{\mathrm{CuL_2 \cdot 2HL}}$. This agrees with the published results for the extraction of copper(II) with D2EHPA into toluene from perchlorate medium [19].

The extraction equilibrium constants were determined to be $\log K_{\mathrm{ex1}} = -4.95 \pm 0.01$ for toluene, $\log K_{\mathrm{ex1}} = -4.60 \pm 0.02$ for carbon tetrachloride, and $\log K_{\mathrm{ex1}} = -4.21 \pm 0.01$ for cyclohexane.

3.3. *Analysis of the extraction equilibrium in polar diluents*

Depending on the concentration of D2EHPA in 1-octanol and MIBK, a linear relation between log D and pH is found as described in equation (7), with the value of n

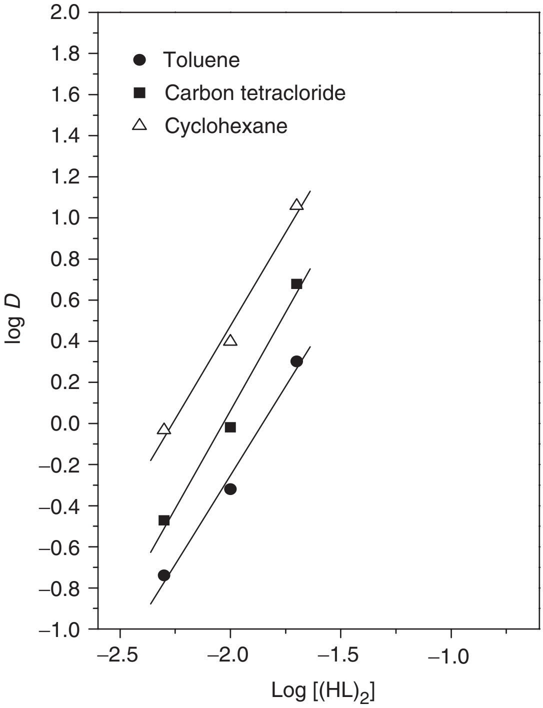

Figure 2. Effect of the extractant concentration on the extraction of copper(II) at pH = 4.4.

calculated from the slope of 2 in this system. This result confirms that the extracted species in the organic phase should be $CuL_2 \cdot pHL$.

The extraction of metal at various concentration of D2EHPA in 1-octanol and MIBK solvents was carried out at constant pH and the number of di(2-ethylhexyl) phosphoric acid molecules involved in the monomeric species can be determined from the slope of plots of $\log D$ against $\log[\mathrm{HL}]$, as shown in figure 3. The values of $[\overline{\mathrm{HL}}]$ were calculated by assuming: $[\overline{\mathrm{HL}}] \approx C_{\mathrm{HL}}$, the straight lines with a slope of $(n+p)$ are 2 and the value of p thus becomes 0 and the composition of the extracted species is $\overline{\mathrm{CuL}_2}$. This agrees with the published results for the extraction of copper(II) with D2EHPA from perchlorate medium into 1-octanol [19].

The extraction equilibrium constants were determined to be $\log K_{\mathrm{ex2}} = -3.69 \pm 0.02$ for 1-octanol and $\log K_{\mathrm{ex2}} = -4.57 \pm 0.01$ for MIBK.

3.4. *Analysis of the extraction equilibrium in nonpolar and polar diluents*

Extraction of copper(II) with D2EHPA is achieved with toluene, carbon tetrachloride, cyclohexane, 1-octanol, and MIBK as shown in figure 4.

The stoichiometries of the extracted copper(II) species with D2EHPA in different solvents and their extraction constants, summarized in table 1, decreased in the order 1-octanol > cyclohexane > MIBK > carbon tetrachloride ≥ toluene. The extraction constant in MIBK is very close to that in carbon tetrachloride.

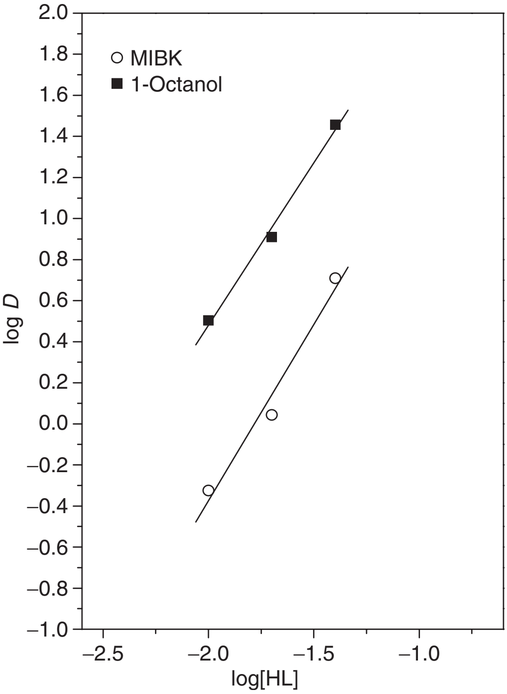

Figure 3. Effect of the extractant concentration on the extraction of copper(II) at pH = 4.4.

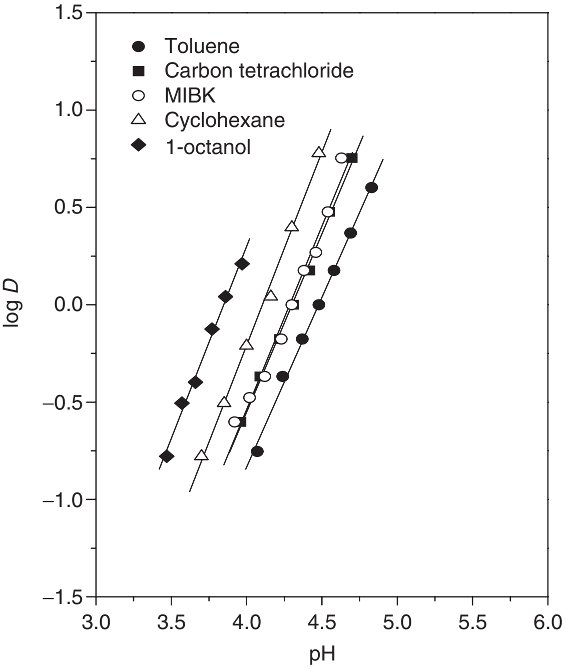

Figure 4. Effect of pH on the extraction of copper(II) into different diluents. $C_{D2EHPA} = 0.02$ M; $C_{Cu} = 1.57 \times 10^{-3}$ M.

Table 1. Stoichiometries and extraction constants of D2EHPA in different diluents.

Diluents	Extraction equilibrium	Log K_{ex}
Toluene	$Cu^{2+} + 2\overline{(HL)_2} \xrightleftharpoons{K_{ex1}} \overline{CuL_2 \cdot 2HL} + 2H^+$	-4.95 ± 0.01
Carbon tetrachloride		-4.60 ± 0.02
Cyclohexane		-4.21 ± 0.01
1-octanol	$Cu^{2+} + 2\overline{HL} \xrightleftharpoons{K_{ex2}} \overline{CuL_2} + 2H^+$	-3.69 ± 0.02
MIBK		-4.57 ± 0.01

The effect of diluent on the self-association of D2EHPA may be explained in the same way as the partition of D2EHPA. Cyclohexane, carbon tetrachloride, and toluene are inert diluents in which the interaction with D2EHPA is not of primary importance. In MIBK and 1-octanol the interactions between diluent molecules and D2EHPA species play an important role [21].

$$\overline{HL} + \bar{S} \xrightleftharpoons{K_S} \overline{(HL)S} \tag{8}$$

where S is the molecule of diluent.

The thermodynamic activity of D2EHPA is lowered by chemical interaction with diluent molecules according to equation (8), influencing the free ligand concentration, $[L^-]$ [22].

In 1-octanol, the extraction efficiency is high in spite of chemical interaction between extractant and diluent molecules (formation of hydrogen bonds), due to the low degree of dimerization of HL so that the free ligand concentration in the aqueous phase is rather high, with copper(II) extracted in the organic phase as $\overline{CuL_2}$.

Comparing with other nonpolar diluents, the extraction of copper(II) in cyclohexane was clearly improved to the presence only of the dimeric form of the molecules of extractant in the organic phase extracting copper(II) as $\overline{CuL_2 \cdot 2HL}$ and the total absence of interactions between D2EHPA and the solvent. Cyclohexane is a good solvent for the extraction of copper(II) with D2EHPA [6].

For carbon tetrachloride, the extraction of copper(II) is weaker than in cyclohexane from the interactions between extractant and the diluent in the organic phase.

The extraction of copper(II) in toluene is weakest due to stronger interactions between D2EHPA and the diluent than that in carbon tetrachloride, decreasing the activity of D2EHPA.

In the case of the MIBK, which is a more polar solvent, the extraction of copper(II) is not improved as in 1-octanol, probably due to the solubility of the MIBK in the aqueous phase, forming a complex $CuSO_4(MIBK)_4$ in addition to $\overline{CuL_2}$ in the organic phase. Barkat *et al.* [23] reported formation of $ZnSO_4(MIBK)_4$ during extraction with acidic chelating extractants.

4. Conclusion

The solvent effect in the extraction of copper(II) with D2EHPA was studied, employing nonpolar and polar solvents showing: (1) The extraction increased with the concentration of D2EHPA. (2) By using the method of slope analysis, the extracted copper(II) species with D2EHPA were CuL_2 in 1-octanol and MIBK and $CuL_2 \cdot 2HL$ in toluene, carbon tetrachloride, and cyclohexane. (3) The extraction is better according to the following order: 1-octanol > cyclohexane > MIBK > carbon tetrachloride $\geq$ toluene.

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