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Extraction Equilibria of Copper(II) with D2EHPA in Kerosene from Aqueous Solutions in Acetate Buffer Media

Zhongqi Ren, Weidong Zhang,* Huilin Meng, YiMing Liu, and Yuan Dai

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China

Extraction equilibria of copper(II) from aqueous acetate buffer solutions with di-(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in kerosene and the stripping equilibria were investigated. Results showed that acetate ions can greatly improve the copper(II) extraction efficiency. The distribution coefficients were significantly dependent on the concentration of acetate ions and the pH value in the aqueous phase because of various mechanisms of extraction and complex formation in the organic phase. With the initial pH value of 4.44 and the acetate ion concentration of 0.18 mol·L^{-1}, the maximum distribution coefficient was observed. In addition, mechanisms of copper(II) extraction in acetate buffer media were established. In the stripping process, the ability to back-extract copper(II) from the organic phase is HCl > H_2SO_4 > H_3PO_4.

Introduction

The separation and recovery of copper(II) from aqueous solutions are very important for environment protection and resource re-use in hydrometallurgy, electroplate, and wastewater treatment processes. Solvent extraction, membrane extraction, and liquid membrane techniques are known to be effective methods for this purpose.[1−3]

For the above techniques, the selection of extractants with high efficiency is an important issue. Organophosphorus agents have been reported as a good choice. Among the organophosphorus extractants, di-(2-ethylhexyl)phosphoric acid (D2EHPA) is a commercially used phosphoric acid. It has been widely used in liquid−liquid extraction for the separation and purification of liquid effluents containing various metals.[1−11] Extraction of copper(II) using D2EHPA has been carried out by some researchers.[2,7−10,12] However, the single-stage extraction efficiency of copper(II) from natural aqueous solutions with an equal volume organic phase of D2EHPA in kerosene is 31.6 %, and the distribution coefficient is only 0.44.

Previous studies showed that the addition of certain anionic ligands to the aqueous solution containing metal ions, such as acetate ions, could greatly improve the extraction efficiency.[8,9,13−15] Belkhouche and Didi[8] studied the extraction of copper(II) from aqueous acetate solution with di-(2-ethylhexyl)phosphoric acid dissolved in *n*-heptane. Gu et al.[13] studied the influence of the addition of acetate ions to an aqueous solution containing Co(II) ions, D2EHPA was used as extractant and LOPs (a low odor paraffin solvent) was used as diluent. Simonin et al.[14] studied the effects of sodium acetate on the kinetics of extraction of cobalt(II) and zinc(II) by D2EHPA dissolved in *n*-dodecane. Higher percentage extractions and faster kinetics were observed in the presence of acetate ions.

Van de Voorde et al.[9] studied metals transport using LIX860-I, D2EHPA, Cyanex301 and its mixtures. The influence of the addition of acetate was investigated for copper(II), nickel(II), cobalt(II), and iron(II,III) extraction. Particularly for nickel(II), cobalt(II), and magnesium(II), higher percentage extractions were achieved in the presence of sodium acetate in the aqueous phase. The role of the acetate ions in the formation of the complexes in hexane was examined by registering the infrared and absorption spectra of the metal−organic complexes. The spectra obtained showed that the acetate ions did not participate in the complex formation but acted only as a buffering agent.

Gu et al.[13] suggested that the water molecules in the hexa-aqueous cobalt(II) complex are replaced by the ligand. This ligand−cobalt(II) complex reacts quickly with the extractant and therefore enhances the reaction rate. Sakar and Dhadke[15] studied the extraction of cobalt(II) in the presence of acetate ions, Cyanex reagents were used as extractants diluted in toluene. The plot of log *D* versus log [acetate] showed that acetate ions were present in the organic extract in the ratio 1:2 for Cyanex 272 and 302 while it was 1:1 for Cyanex 301.

However, all these researchers focused on the mechanism and complex formation of the metal−ligand complexes, whereas the influence of the concentration of acetate ions in aqueous solutions on the extraction equilibrium was not taken into account. The experimental data of the distribution coefficient in presence of acetate ions, which plays an important role in many chemical engineering processes and equipment designs especially in solvent extraction, membrane extraction, and liquid membrane processes, are lacking.

Previous studies[8,9,13,15] also showed that the influence of diluents on the extraction process was significant. Satio et al.[16] found that the extraction efficiency may be improved by a discerning choice of pH.

The main objective of this paper was to study the extraction equilibrium of copper(II) in aqueous acetic acid−acetate buffer solutions using D2EHPA in kerosene. The influences of temperature, initial Cu^{2+} concentration, acetate ion concentration, pH, and D2EHPA concentration on the extraction equilibrium were investigated. Using HCl, H_2SO_4, and H_3PO_4 as stripping reagents, the stripping processes were also studied. Equilibrium data were presented, and the mechanism of extraction was also probed simply.

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* Corresponding author. E-mail: zhangwd@mail.buct.edu.cn.

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Experimental Section

Reagents. Di-(2-ethylhexyl)phosphoric acid (D2EHPA), from the Tianjin Guangfu Chemical Co. Ltd., was of chemical reagent quality with a purity > 95.0 %. Commercial aviation kerosene, from the Tianjin Damao Chemical Reagent Plant, was washed twice with 20 % (vol) H_2SO_4 to remove aromatics and then with deionized water three times. Anhydrous copper sulfate, from the Shanghai Tingxin Chemical Reagent Plant, was an analytical grade reagent with a purity > 99.0 %. Acetic acid glacial and anhydrous sodium acetate, from the Tianjin Fuxing Chemical Reagent Plant, were analytical grade reagents with purity > 99.0 %. All chemical reagents were used without further purification except the commercial aviation kerosene.

Extraction Experiments. The aqueous phase was prepared by dissolving a weighed amount of $CuSO_4$ in acetate buffer media, in which the pH was adjusted. All the extraction experiments were conducted with 150 mL stoppered flasks at (20 ± 0.1) °C (except for determining the effect of temperature) in a thermostated bath shaker. Solvent (50 mL) and 50 mL of the aqueous solution were added to each flask. The flask containing the mixture was shaken for about 30 min, and then the mixture was left to equilibrate for (1 to 2) h. It was observed that this time was sufficient to establish the equilibrium between the two phases. It was noted that, after extraction, no significant volume change was observed. The mixture was then transferred to a separating funnel and allowed to settle for at least 30 min, which was shown in previous experiments to be sufficient for a complete phase separation. After separation of the phases, the aqueous phase sample was taken for pH and solute concentration analysis. All extraction experiments were carried out three or five times, and the reproducibility was found to be ± 5 %.

Stripping Experiments. The organic phase was obtained from the extraction experiments. All the stripping experiments were conducted using the same procedures and conditions described for extraction experiments.

Sample Analysis. A digital precision ionometer model PXS-450 (Shanghai Dapu Co. Ltd.) with a combined glass electrode was used for pH measurements (± 0.01 pH). The meter was standardized against 4.01, 6.85, and 9.14 standard buffer solutions. The copper(II) concentration in the aqueous phase was analyzed with the sodium diethyldithiocabamate spectrophotometric method (GB7474-87, P.R. China), and the copper(II) concentration in the organic phase was calculated from mass balance.

Results and Discussion

Extraction Process. All the extraction equilibrium data are given in Tables 1 to 5. The extraction distribution coefficient D_E of copper(II) is defined as follows:

$$D_E = \frac{\overline{[Cu^{2+}]}}{[Cu_{aq}^{2+}]} \tag{1}$$

where the bar indicates the species in the organic phase, aq represents the aqueous phase, and E represents the extraction process. The distribution coefficients increase with increasing temperature as shown in Table 1 and decrease with increasing initial concentration of copper(II) in the aqueous phase as shown in Table 2.

Table 1. Effect of Temperature on Extraction of Copper(II) at $[AC^-] = 0.24\ mol\cdot L^{-1}$, [D2EHPA] = 10 % (vol)

T	initial/equilibrium	equilibrium $[Cu^{2+}]$ concentration/$mg\cdot L^{-1}$		
K	pH	organic phase	aqueous phase	D_E
273.2	3.53/3.45	806.7	55.9	14.43
283.2	3.53/3.45	810.6	52.2	15.54
293.2	3.53/3.45	812.4	50.4	16.11
303.2	3.53/3.44	815.6	47.2	17.28
313.2	3.53/3.44	816.3	46.5	17.55

Table 2. Effect of Initial Aqueous Concentration of Copper(II) on Extraction Equilibrium at Initial pH = 3.59, $[AC^-] = 0.23\ mol\cdot L^{-1}$, [D2EHPA] = 10 % (vol), *T* = 293.2 K

initial aqueous concentration of $[Cu^{2+}]$	equilibrium $[Cu^{2+}]$ concentration/$mg\cdot L^{-1}$		
$mg\cdot L^{-1}$	organic phase	aqueous phase	D_E
784.3	748.7	35.6	21.06
695.5	665.9	29.5	22.55
586.0	562.2	23.8	23.67
484.9	465.8	19.1	24.40
413.0	398.7	14.3	27.85
334.2	323.1	11.2	28.95

Table 3. Effect of Concentration of Acetate Ions on Extraction of Copper(II) at [D2EHPA] = 10 % (vol), *T* = 293.2 K

$[AC^-]$	initial/equilibrium	equilibrium $[Cu^{2+}]$ concentration/$mg\cdot L^{-1}$		
$mol\cdot L^{-1}$	pH	organic phase	aqueous phase	D_E
0.00	4.09/2.10	274.6	621.5	0.44
0.09	4.44/4.11	858.7	12.0	71.50
0.17	4.44/4.17	841.5	4.6	181.17
0.25	4.44/4.25	831.5	8.8	94.09
0.31	4.44/4.28	800.4	10.3	77.63
0.44	4.44/4.29	810.1	11.9	68.32
0.53	4.44/4.30	824.1	12.7	65.14
0.12	4.02/3.31	838.7	29.2	28.73
0.17	4.02/3.67	865.6	8.0	108.89
0.28	4.02/3.81	826.8	10.3	80.19
0.50	4.02/3.91	788.3	13.1	60.24
0.69	4.02/3.93	805.0	17.0	47.48
0.88	4.02/3.93	777.3	22.6	34.45

Table 4. Effect of pH on Extraction of Cu(II) at [D2EHPA] = 10 % (vol), *T* = 293.2 K

initial/equilibrium	$[AC^-]$	equilibrium $[Cu^{2+}]$ concentration/$mg\cdot L^{-1}$		
pH	$mol\cdot L^{-1}$	organic phase	aqueous phase	D_E
5.00/4.77	0.19	876.4	24.6	35.57
4.70/4.44	0.18	890.8	10.3	86.76
4.44/4.10	0.18	896.2	4.8	186.78
4.22/3.96	0.19	907.8	9.5	96.07
3.70/3.49	0.19	867.6	38.6	22.48
3.25/3.10	0.18	770.1	50.3	15.31
7.04 /5.18	0.97	814.2	51.2	15.89
5.34/4.95	0.97	869.2	39.7	21.89
4.97/4.74	0.97	856.7	31.4	27.28
4.65 /4.45	0.97	849.3	25.6	33.24
4.44/4.27	0.97	874.3	23.2	37.71
3.88/3.71	0.98	869.2	39.7	21.89
3.44 /3.31	0.97	900.7	49.7	18.12
2.24 /2.03	0.97	238.9	636.0	0.38

As indicated in Table 3, the distribution coefficient of Cu(II) between D2EHPA in kerosene and pure water (no acetate) is small, 0.44. Because D2EHPA is a Lewis acidic complexing agent, the acidic organophosphorus extractants extract most Lewis base functional groups by forming a complex with neutral molecules or by ion exchange. However, copper(II) is a common Lewis acidic group. The reaction mechanism can be described

Table 5. Effect of the Concentration of D2EHPA in Kerosene on Extraction Equilibrium at [AC$^-$] = 0.18 mol·L^{-1}, T = 293.2 K

organic concentration of [D2EHPA]	initial/equilibrium	equilibrium [Cu^{2+}] concentration/mg·L^{-1}		
v/v	pH	organic phase	aqueous phase	D_E
0.03	4.44/4.22	866.9	34.2	25.36
0.05	4.44/4.20	885.8	15.3	57.98
0.08	4.44/4.15	892.4	8.6	103.40
0.10	4.44/4.10	896.2	4.8	186.78
0.12	4.44/4.06	897.3	3.8	238.92
0.13	4.44/4.03	897.8	3.2	280.87
0.14	4.44/4.01	898.2	2.9	312.15

as follows:[8−11]

$$\mathrm{Cu_{aq}}^{2+} + \overline{(\mathrm{H_2R_2})} \rightleftharpoons \overline{\mathrm{CuR_2}} + 2\mathrm{H_{aq}}^{+} \tag{2}$$

where H_2R_2 represents the dimeric form of D2EHPA in kerosene, and the bar indicates the species in the organic phase.

As indicated by eq 2, in the extraction process, H^+ exchanges with Cu^{2+} and enters the aqueous phase. As such, the equilibrium pH of the aqueous solution was always lower than the initial pH. Since the concentration of H^+ in the aqueous solution increases with decreasing pH, this does not benefit the reaction represented by eq 2. For copper(II) extraction from pure water, the increase in the concentration of H^+ is large, which restrains the extent to which eq 2 can proceed.

As indicated in Table 3, the distribution coefficients can be greatly improved in the presence of acetate ions. Because CH_3COO^- is a Lewis base group, copper(II) was extracted from aqueous acetate buffer solutions as $CuCH_3COO\cdot(HR_2)$ where the anion of acetate participates in the formation of the metal complex as shown in Figure 1.[8,17] The reaction mechanism can be given as follows:[8,17]

$$\mathrm{Cu_{aq}}^{2+} + \mathrm{CH_3COO_{aq}}^{-} + \overline{(\mathrm{H_2R_2})} \rightleftharpoons \overline{\mathrm{CuCH_3COO\cdot(HR_2)}} + \mathrm{H_{aq}}^{+} \tag{3}$$

The distribution coefficients increase with increasing acetate concentration and then decrease. There is a maximum distribution coefficient at an acetate concentration of around 0.17 mol·L^{-1}, as shown in Figure 2 and Table 3. At low acetate concentration, variations of pH and concentration of H^+ decrease with increasing acetate ions concentration, which is of benefit to eq 3. At high concentrations of acetate in the aqueous phase, the increasing concentration of acetate opposes the diffusion of copper to the organic phase. Copper(II) will more strongly react with acetate to form an aqueous complex $Cu(CH_3COO)^+$ and Na^+ will compete with Cu^{2+}. As the Na^+ concentration increases, Na^+ is extracted instead of Cu^{2+}. The metal complex formed in the organic phase is NaR·HR, and the reaction mechanism may be given by the following equation:[18]

$$\mathrm{Na_{aq}}^{+} + \overline{(\mathrm{H_2R_2})} \rightleftharpoons \overline{\mathrm{NaR\cdot HR}} + \mathrm{H_{aq}}^{+} \tag{4}$$

The influence of pH in the aqueous solution on copper(II) extraction is shown in Table 4 and Figure 3. The distribution coefficients increase with increasing pH and then decrease. When the initial pH of the aqueous phase equals 4.44, a maximum distribution coefficient occurred. The pH of the aqueous solution depends on the ratio of acetate acid and sodium acetate in the buffer solution. At lower pH, the media becomes more acidic, the formation of CH_3COOH would be favored, and the cation $(CuCH_3COO)_{aq}^+$ dissociates to the Cu^{2+} form where the metal complex formed is CuR_2, metal is released from the organic phase to the aqueous phase. The reaction mechanism of extraction of copper in strongly acidic media can be given as in eq 2. At higher pH, the H^+ concentration is lower, which does not benefit the reaction represented by eq 3 because a certain quality of protons are required to drive the complex reaction. The distribution coefficients increase with increasing D2EHPA concentration in kerosene as shown in Table 5 because of the increase of the complex ligands.

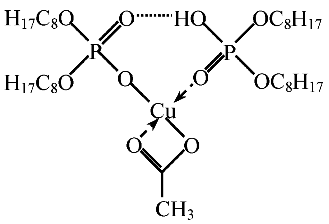

Figure 1. Copper(II) complex structure.

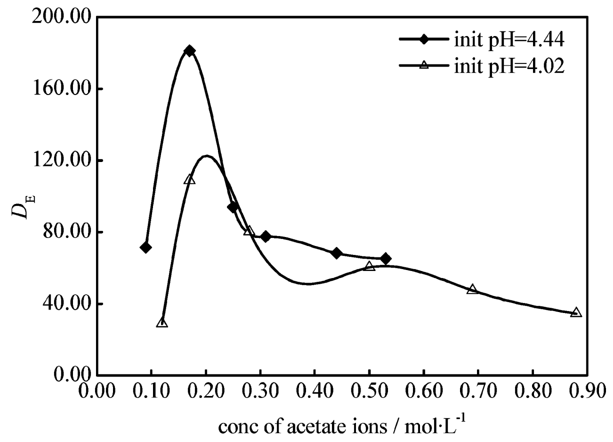

Figure 2. Influence of acetate ions concentration in aqueous phase on extraction of copper(II) at [D2EHPA] = 10 % (vol), T = 293.2 K.

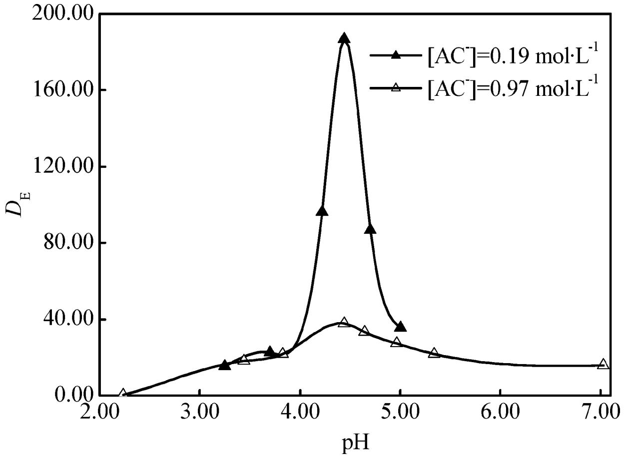

Figure 3. Influence of aqueous pH on extraction of copper(II) at [D2EHPA] = 10 % (vol), T = 293.2 K.

Table 6. Stripping Equilibrium Data of Copper(II) between Water and HCl, H_2SO_4, H_3PO_4 + D2EHPA in Kerosene at 293.2 K

initial concentration of [Cu^{2+}] in organic phase	initial concentration in aqueous phase/mol·L^{-1}				
mg·L^{-1}	[H$^+$]	[Cl$^-$]	[SO$_4^{2-}$]	[PO$_4^{3-}$]	D_S
886.0	2.01	2.01			2.97
886.0	4.02	4.02			3.19
886.0	6.01	6.01			8.68
886.0	8.03	8.03			0.71
886.0	6.03		3.02		2.33
886.0	6.02			2.01	1.89

Table 7. Effect of the Temperature on Stripping Equilibria at [HCl] = 6.00 mol·L^{-1}, T = 293.2 K

T	total equilibrium concentration of [Cu^{2+}]/mg·L^{-1}		
K	aqueous phase	organic phase	D_S
293.2	751.8	55.1	13.64
303.2	762.9	47.7	15.99
313.2	770. 5	41.9	18.39
323.2	777.2	38.3	20.28
333.2	780.6	35.6	21.91
343.2	789.9	31.5	25.06

Stripping Process. The stripping equilibrium data are given in Tables 6 and 7. The stripping distribution coefficient D_S of copper(II) is defined as

$$D_S = \frac{[\mathrm{Cu_{st}}^{2+}]}{[\overline{\mathrm{Cu}^{2+}}]} \qquad (5)$$

where st represents the strip phase, the bar indicates the species in the organic phase, and S represents the stripping process.

As indicated in Table 6, when HCl was used as a stripping agent, Cl^- greatly affects the back-extraction. There is a maximum distribution coefficient when the concentration of [HCl] is around 6.00 mol·L^{-1}. At the same concentration of [H^+], the ability to back-extract copper(II) from the organic phase is HCl > H_2SO_4 > H_3PO_4. The stripping distribution coefficients also increase with increasing temperature as shown in Table 7.

Conclusions

In this work, the extraction equilibria of copper(II) from aqueous acetate buffer solutions with di-(2-ethylhexyl)phosphoric acid (D2EHPA) dissolved in kerosene and the stripping equilibria were studied. Extraction and stripping equilibrium data were presented. Results showed that acetate ions can greatly improve the extraction efficiency. The distribution coefficients increase with increasing acetate concentration and pH and then decrease due to the various mechanisms of extraction and complex formation. The distribution coefficients increase with increasing temperature and the D2EHPA concentration in kerosene and decrease with increasing initial concentration of copper(II) in the aqueous phase. There is a maximum distribution coefficient when the initial pH value is 4.44 and the acetate ion concentration is 0.18 mol·L^{-1}, the single stage extraction efficiency is > 99.5 %. In stripping processes, the ability to back-extract copper(II) from the organic phase is HCl > H_2SO_4 > H_3PO_4.

Literature Cited

(1) Wang J. D.; Chen J. Y. *Handbook of Solvent Extraction*; Chemical Engineering Press: Beijing, 2001.
(2) Szymanowski J. *Hydroxyoximes and Copper Hydrometallurgy*; CRC Press: Boca Raton, FL, 1993.
(3) Chmielewski, A. G.; Urbanski, T. S.; Migdal, W. Separation technologies for metals recovery from industrial wastes. *Hydrometallury* **1997**, *45*, 333−344.
(4) Elyahyaoui, A.; Bouhlassa, S. Extraction of cadmium and iodocadmat species by di-(2-ethylhexyl)phosphoric acid from perchloric and phosphoric media. *Appl. Radiat. Isot.* **2001**, *54*, 921−926.
(5) Lee, M. S.; Ahn, J. G.; Lee, E. C. Solvent extraction separation of indium and gallium from sulphate solutions using D2EHPA. *Hydrometallurgy* **2002**, *63* (3), 269−276.
(6) Kongolo, K.; Mwema, M. D.; Banza, A. N.; Gock, E. Cobalt and zinc recovery from copper sulphate solution by solvent extraction. *Miner. Eng.* **2003**, *16* (12), 1371−1374.
(7) Chakravorty, J.; Bhattacharya, C.; Datta, S. Extraction of copper(II) and nickel(II) from wastewater by emulsion liquid membrane. *J. Inst. Eng. (India): Chem. Eng. Div.* **2004**, *85*, 1−4.
(8) Belkhouche, N. E.; Didi, M. A. Separation of nickel and copper by solvent extraction using di-(2-ethylhexyl)phosphoric acid-based synergistic mixture. *Solvent Extr. Ion Exch.* **2005**, *23*, 677−693.
(9) Van de Voorde, I.; Pinoy, L.; Courtijn, E.; Verpoort, F. Influence of acetate ions and the role of the diluents on the extraction of copper(II), nickel(II), cobalt(II), magnesium(II) an iron(II, III) with different types of extractants. *Hydrometallurgy* **2005**, *78*, 92−106.
(10) Ihm, S. K.; Lee, H. Y.; Huilee, D. Kinetic study of the extraction of copper(II) with di-2-ethyhexyl phosphoric acid in a Lewis-type cell. *J. Membr. Sci.* **1988**, *37*, 181−191.
(11) Huang, T. C.; Tsai, T. H. Separation of cobalt and nickel ions in sulfate solutions by liquid-liquid extraction and supported liquid membrane with di(2-ethylhexyl)phosphoric acid dissolved in kerosene. *J. Chem. Eng. Jpn.* **1991**, *24*, 125−132.
(12) Juang, R. S.; Huang, H. L. Mechanistic analysis of solvent extraction of heavy metals in membrane contactors. *J. Membr. Sci.* **2003**, *213*, 125−135.
(13) Gu, Z. M.; Wasan, D. T.; Li, N. N. Ligand-accelerated liquid membrane extraction of metal ions. *J. Membr. Sci.* **1986**, *26*, 129−142.
(14) Simonin, J. P.; Hendrawan, H.; Dardoize, F.; Clodic, G. Study of salt effects on the kinetics of extraction of cobalt(II) and zinc(II) at trace level by D2EHPA in *n*-dodecane. *Hydrometallurgy* **2003**, *69*, 23−38.
(15) Sarkar, S. G.; Dhadke, P. M. Extractive spectrophotometric determination of cobalt(II) using cyanex reagents. *Can. J. Anal. Sci. Spectrosc.* **1999**, *44* (3), 75−79.
(16) Satio, K.; Murakami, S.; Muromatsu, A.; Sekido, E. Liquid−liquid extraction of copper(II) with cyclic tetrathioethers. *Anal. Chim. Acta* **1994**, *294*, 329−335.
(17) Sella, C.; Bauer, D. Diphasic acido-basic properties of organophosphorus acids. *Solvent Extr. Ion Exch.* **1988**, *6*, 819−833.
(18) Sato, T.; Nakamura, T. The complexes formed in the divalent transition metalsuphuric acid−di-(2-ethylhexyl) phosphoric acid extraction systems−cobalt(II), nikel(II) and copper(II) complexes. *J. Inorg. Nucl. Chem.* **1972**, *34*, 3721−3730.

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