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Liquid-Liquid Extraction of Copper from Ammoniacal Solution with β-Diketones

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NOTE

Liquid–Liquid Extraction of Copper from Ammoniacal Solution with β-Diketones

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Key Words: Liquid–liquid extraction; 1-Phenyl(cyclo)alkane-1,3-diones; LIX 54; Copper extraction; Ammoniacal solution

INTRODUCTION

Some β-diketones such as LIX 51 (Henkel KGaA), Hostarex DK 16 (Hoechst AG), LIX 54 (Henkel KGaA), and MX 80A (Sigma Innovation, Sweden) were developed for technical applications (*1*) but only LIX 54 is commercially available. The use of LIX 54 to separate copper from ammoniacal etch solutions is described by patent applications (*2–4*) and an information paper of Henkel KGaA. The extraction of transition metals with LIX 54 was studied by Ramesh et al. (*5*). LIX 54 in a mixture with neutral donor ligands also proved suitable for the extraction of lanthanide elements (*6*). The active component of LIX 54 and MX 80A was recently identified as a mixture of isomeric 1-phenyl-3-iso-heptyl-1,3-propanediones (*7, 8*). Analogous β-diketones are easily available.

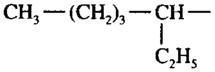
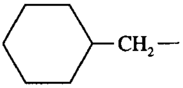
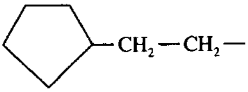
In continuation of previous work (*9*), the extraction behavior of LIX 54 and of some synthesized pure β-diketones of the same type are compared in this paper. The compounds studied are given in Table 1.

EXPERIMENTAL

Extractants

The β-diketones were synthesized by following a literature procedure (*10*) that uses the Claisen condensation of acetophenone with the corre-

TABLE 1
β-Diketones of the Type $C_6H_5—CO—CH_2—CO—R$

No.	R	Symbol	bp (°C)	Analytical data calculated (found) (%)
1	$CH_3—(CH_2)_6—$	■	205–208/10 torr	C 78.01 (78.82) H 9.02 (8.90)
2	 $CH_3—(CH_2)_3—\underset{\underset{C_2H_5}{\vert}}{CH}—$	▲	140–143/10 torr	C 78.01 (78.94) H 9.02 (9.02)
3		⊡	210–230/1 torr	C 78.65 (79.40) H 8.25 (9.08)
4		(◑)	140–145/10 torr	C 78.65 (79.29) H 8.25 (8.96)
5	i-C_7H_{13}- (mixture)	*	190–195/10 torr	LIX 54
6	i-C_7H_{13}- (mixture)	⊙	198–202/10 torr	MX 80 A

sponding phenyl or ethyl esters in the presence of sodium amide. The compounds were purified by vacuum distillation.

Extraction Studies

The conditions for the extraction were: *Concentration:* $c_{Cu^{2+}}$; 10^{-4} M; $c_{\text{extractant}}$; 10^{-2} M; I = 0.1 M KCl or NH_4Cl. *Phase ratio:* $V_{org}:V_{aq}$ = 1:1 (20 mL); temperature, 25°C. *Extraction time:* 10 min (mechanical shaker). *pH adjustment and measurement:* addition of HNO_3 or NaOH, pH meter MV 86 (Präcitronic, Dresden) with glass electrode EGA 50 N (Forschungsinstitut Meinsberg). *Metal determination:* atomic absorption spectrometer AAS-3 (Carl Zeiss, Jena). *Solvent (of the extractant):* kerosene, bp 100–140°C.

All chemicals used were of p.a. quality. A Merck standard solution was used as the stock copper solution.

RESULTS AND DISCUSSION

The reaction of copper with the extractants described here was accomplished within 10 minutes. There is quantitative extraction in the pH 5 to

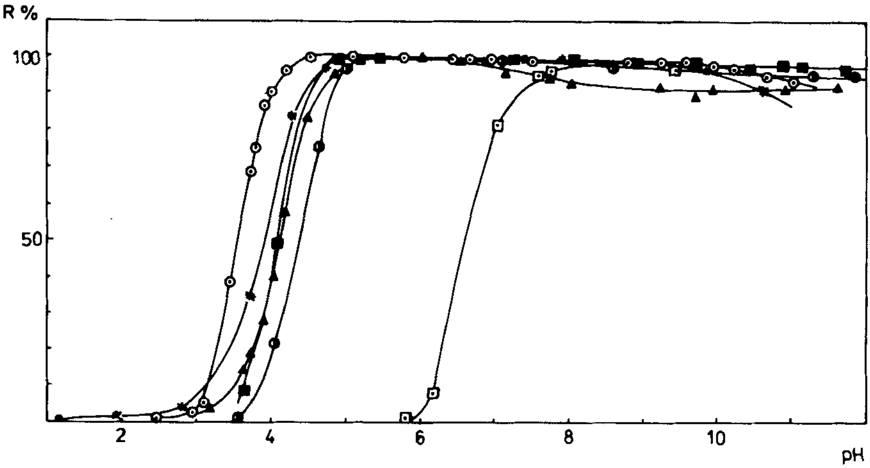


FIG. 1. Extraction of copper with different β-diketones, $R = f$ (pH). $c_{Cu^{2+}}$: 10^{-4} mol/L (I = 0.1 mol/L KNO_3).

10 region (Fig. 1), whereas 1-phenyl-3-cyclohexylmethyl-propane-1,3-dione gives satisfactory results only above pH 6. Copper forms the expected 1:2 complex compound with the extractant, as can be seen from the slope of the log D/pH plot in Fig. 2. A comparison of the different extractants is given by Table 2. According to the values of K_{ex} and pH 0.5, the order of extractability as dependent on the alkyl substituent is cyclohexylmethyl < cyclopentylethyl < n-heptyl < 2-ethylpentyl < LIX 54 < MX 80 A. However, there are only small differences between these extractants because of the similarities in acidity, complex stability, and the solubilities of the extractant and its metal complex in the organic solvent. The best results were obtained by using highly branched 1-phenyl-3-alkyl-propane-1,3-diones which are the active components of LIX 54. For the mean efficiency of 1-phenyl-3-cyclohexylmethyl-propane-1,3-dione, no simple explanation except a possible steric hindrance was found.

Figures 3 and 4 show the extraction of copper from ammoniacal solution. With an ionic strength (I) of 0.1 M (NH_4Cl), no difficulties occurred up to pH 10, but then the copper extraction is significantly hindered due to the large increase in ammonia concentration in the aqueous phase (Fig. 4). The reason for this is the competitive reaction leading to the copper ammine complex.

Generally, highly branched extractants of the LIX 54 type are preferred as reagents. The excellent solubility of the copper complex in special hydrocarbon solvents is a good basis for hydrometallurgical applications.

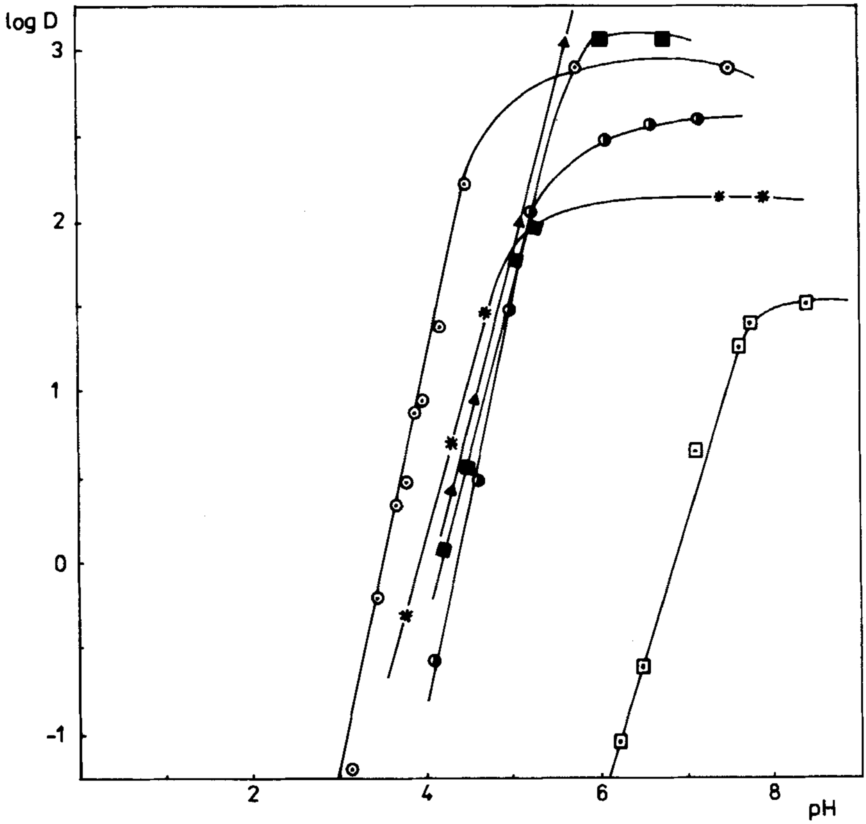


FIG. 2. Extraction of copper with different β-diketones, lg $D = f\,(\mathrm{pH})$. $c_{\mathrm{Cu}^{2+}}$: 10^{-4} mol/L (I = 0.1 mol/L KNO_3).

TABLE 2
Extraction Data of the β-Diketones of Table 1

No.	pH	lg K_{ex}
1	4.23	−4.50
2	4.10	−4.20
3	6.60	−9.20
4	4.32	−4.64
5	3.90	−3.80
6	3.55	−3.10

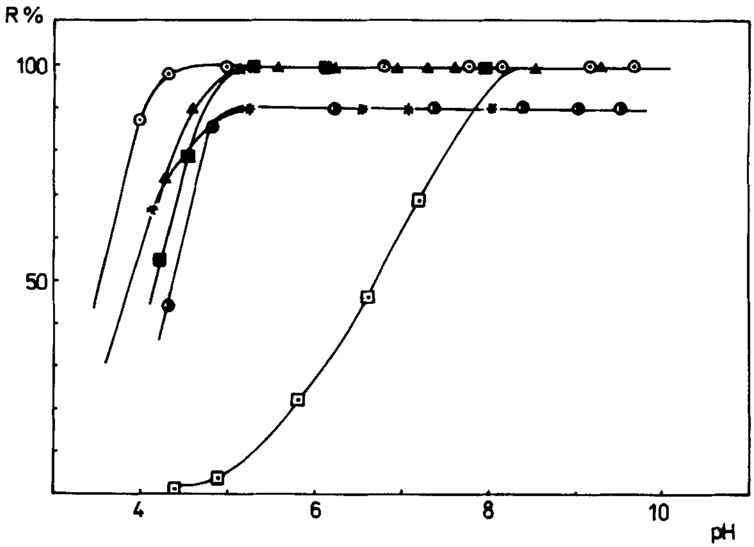


FIG. 3. Extraction of copper from ammoniacal solution, $R = f$ (pH). $c_{Cu^{2+}}$: 10^{-4} mol/L (I = 0.1 mol/L NH_4Cl).

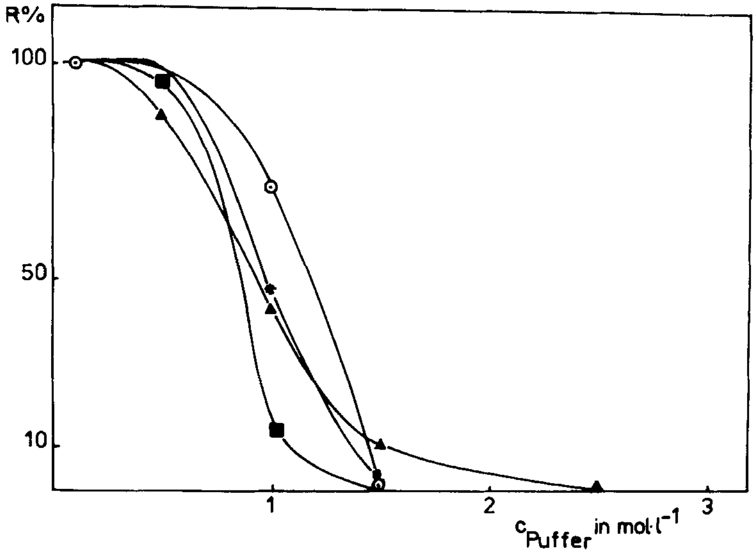


FIG. 4. Extraction of copper from ammoniacal solution. c_{HL}: 10%. c_{Cu}: 3 g/L in NH_3/NH_4Cl-buffer. Solvent: kerosene/toluene (1 + 1).

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