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TECHNICAL NOTE

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

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## ABSTRACT

The extraction of copper from ammoniacal solution was studied with different cyclohexyl-substituted β-diketones. For comparison with LIX 54, the extraction parameters were determined for their dependence on the chain length of the substituent as well as on the influence of pH and the concentrations of copper and ammonia.

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

## INTRODUCTION

LIX 54 (Henkel KGaA) represents a commercially available β-diketone type of extractant which is especially recommended for the extraction of copper from ammoniacal etch solutions (1–3). Beyond this, a series of other applications is reported in the literature (4–7). By GC-MS measurements, LIX 54 was found to exist as a mixture of at least four isomeric 1-phenyl-3-isoheptyl-1,3-propane-diones solved in saturated alkanes (8). For exact physicochemical studies, however, pure compounds are necessary, the properties of which do not depend on the composition of a technical grade starting material. Unfortunately, only *n*-octanoic acid and 2-ethyl-hexanoic acid are available to synthesize such β-diketones. Cyclohexyl-substituted carboxylic acids offer an alternative possibility for the preparation of β-diketones having branched alkyl substituents.

To further former results (9), 1-phenyl-3-cyclohexyl-1,3-propanedione, 1; 1-phenyl-4-cyclohexyl-1,3-butanedione, 2; and 1-phenyl-5-cyclohexyl-1,3-pentanedione, 3, were synthesized and studied as extractants for comparison with LIX 54.

## EXPERIMENTAL

### Extractants and Metal Complexes

The β-diketones were synthesized by following a literature procedure (10) that uses the Claisen condensation of acetophenone with the corresponding phenyl esters in the presence of sodium amide. It was found that phenyl esters give the desired β-diketones with higher yields and better purities than do the corresponding alkyl esters. The purity of the compounds was examined by GC-MS measurements. (GC-MS system: VG 12-250 with a HP gas chromatograph, 40 m capillary column SE 54, temperature program at 70–250°C, and electron ionization at 70 eV.) They were further characterized by $^1$H-NMR (300.13 MHz) and $^{13}$C-NMR spectroscopy (75.47 MHZ) measured in $CDCl_3$ (Bruker ARX 300 spectrometer). The analytical data are presented in Table 1. All compounds were very soluble in kerosene. The copper complexes were prepared by adding an alcoholic copper acetate solution to alcoholic solutions of the ligands (molar ratio 1:2). The resulting solid complexes were recrystallized from alcohol.

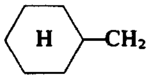
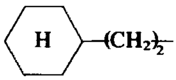
### Extraction Parameters

The experimental conditions for copper extraction were as follows:

| | |
|---|---|
| $c_{Cu^{2+}}$ | *$10^{-4}$ M* |
| $c_{HL}$ | $10^{-2}$ M (solvent: kerosene) |
| Phase ratio | 1/1 (20 mL separation funnels) |
| Temperature | 25°C |
| Extraction cycle | 10 minutes (mechanical shaker) |

pH adjustment was made by adding $HNO_3$ or NaOH prior to extraction. To measure pH, a pH meter MV 86 (Präcitronic, Dresden) with a glass electrode EGA 501 N (Forschungsinstitut Meinsberg) was used. The metal concentrations were determined by atomic absorption spectrometry (AAS 1100 B, Perkin-Elmer). All chemicals were of p.a. quality. The copper stock solution was prepared by diluting a Merck standard solution with

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

| | No. | | |
|---|---|---|---|
| | 1 | 2 | 3 |
| R |  |  |  |
| Symbol | ○ | △ | ● |
| $bp_{(10\ torr)}$/°C | 175–185 | 200 | 195–210 |
| Analytical data | Calculated (found) | Calculated (found) | Calculated (found) |
| C | 78.21 (78.16) | 78.64 (78.61) | 79.02 (79.33) |
| H | 7.89 (7.71) | 8.27 (7.88) | 8.59 (8.69) |
| $^1$H-NMR (δ) | 16.4 (s, OH)<br>6.2 (s, CH—enol)<br>4.08 (s, $CH_2$—keto) | 16.4 (s, OH)<br>6.1 (s, CH—enol)<br>4.0 (s, $CH_2$—keto) | 16.3 (s, OH)<br>6.2 (s, CH—enol)<br>4.03 (s, $CH_2$—keto) |
| $^{13}$C-NMR (δ) | 199.7 ($C_1$—OH)<br>184.1 ($C_3$—OH)<br>94.3 ($C_2$) | 195.4 ($C_1$—OH)<br>183.6 ($C_3$—OH)<br>96.6 ($C_2$) | 197.4 ($C_1$—OH)<br>182.7 ($C_3$—OH)<br>95.7 ($C_2$) |

bidistilled water. The distribution coefficient $D = c_{Cu^{2+}(o)}/c_{Cu^{2+}(w)}$ was calculated from the copper concentration measured in the aqueous phase before and after extraction. For the extraction constant, the equation $-\log K_{ex} = pH_{0.5} + \log c_{HL}$ is valid.

## RESULTS AND DISCUSSION

The results obtained by NMR measurement show that the studied extractants predominantly exist in the enol structure. Evaluation of the signals of CH protons (δ ≈ 6.2 ppm) and $CH_2$ protons (δ ≈ 4.0 ppm) proves that only about 7% of the keto form is present in the keto–enol equilibrium.

The course of copper extraction under usual conditions is given in Fig. 1 as a plot of the extraction rate $R$ versus pH. The logarithmic plot of log $D$ versus pH is shown in Fig. 2. Based on the slopes of the straight lines of this function, the composition of the extracted species is $CuL_2$. Both figures prove that quantitative extraction of copper takes place only above pH 5 but falls off above pH 11 because of competitive reactions in the aqueous phase. Some extraction data are summarized in Table 2 and compared with those for LIX 54.

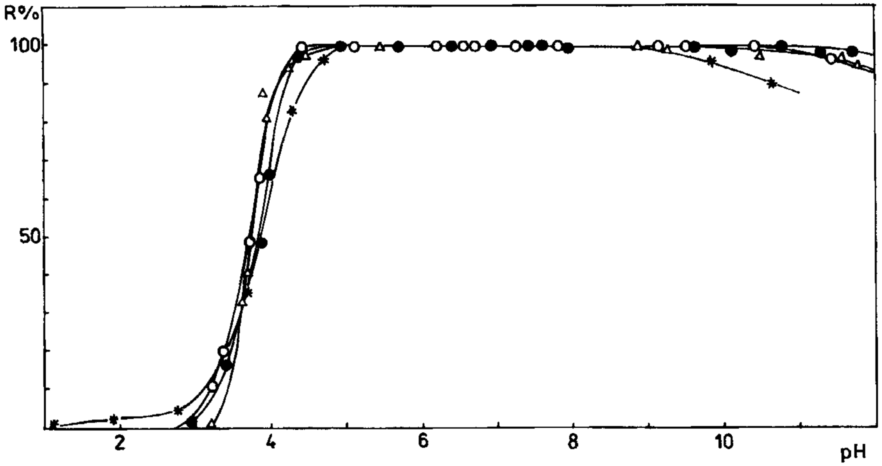
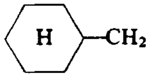
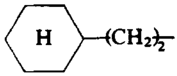


FIG. 1 Extraction of copper(II) with different β-diketones. $c_{Cu^{2+}}$: $10^{-4}$ mol·L$^{-1}$ ($I$ = 0.1 mol·L$^{-1}$ HNO$_3$). $c_{HL}$: $10^{-2}$ mol·L$^{-1}$ (in kerosene). $R = f(\text{pH})$. For the key to the symbols, see Tables 1 and 2.

TABLE 2
Extraction Data of Substituted β-Diketones

| No. | R | Symbol | pH$_{0.5}$ | log $K_{ex}$ |
|---|---|---|---|---|
| 1 |  | ○ | 3.70 | −3.40 |
| 2 |  | △ | 3.75 | −3.50 |
| 3 |  | ● | 3.80 | −3.60 |
| 4 | $i$-$C_7H_{15}$ (LIX 54) | * | 3.90 | −3.80 |

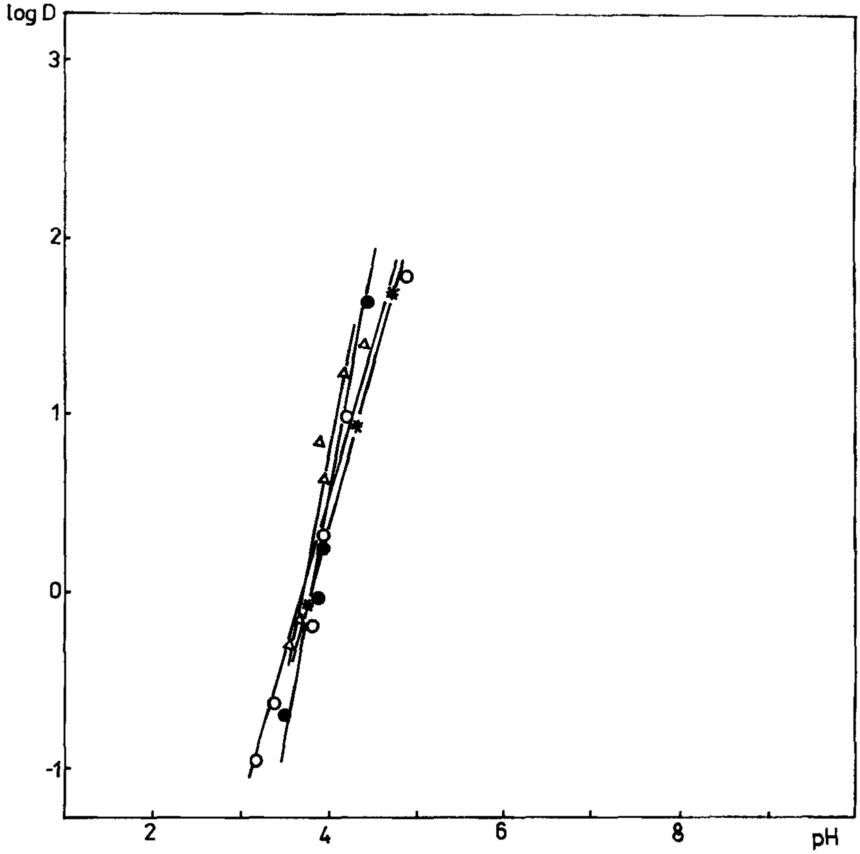
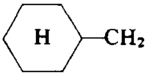
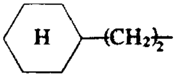


FIG. 2 Extraction of copper(II) with different β-diketones (parameters as in Fig. 1). log $D = f(\mathrm{pH})$. For the key to the symbols, see Tables 1 and 2.

It can be seen that all compounds show very similar behaviors. Deviations previously reported for 1-phenyl-4-cyclohexylbutane-1,3-dione (9) could not be confirmed. The weak influence of substituents on the extraction behavior of the β-diketones studied here can be explained by the identical chelate structures and the similar hydrophobicities of the extractants.

Nevertheless, a small dependence of $\mathrm{pH}_{0.5}$ and log $K_{ex}$ on the chain length of the cyclohexyl alkyl group is observed. Copper extraction is limited by the solubility of the extractants and their copper complexes in an organic solvent. These copper complexes are crystalline compounds

TABLE 3
Analytical Data of the Examined Copper Chelates

| Ligand | R | Solubility in kerosene (mol/L) | mp (°C) | Analytical data (%) Calculated | (Found) |
|---|---|---|---|---|---|
| 1 |  | $3.64 \times 10^{-3}$ | 212 | C 68.99<br>H 6.58 | (68.71)<br>(6.59) |
| 2 |  | $2.36 \times 10^{-3}$ | 167 | C 69.85<br>H 6.98 | (69.54)<br>(7.05) |
| 3 |  | $6.62 \times 10^{-2}$ | 112 | C 70.61<br>H 7.34 | (70.78)<br>(6.58) |

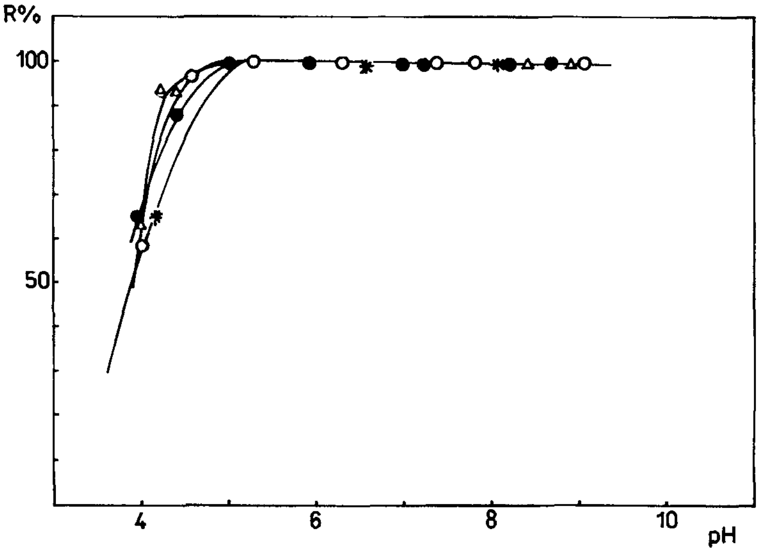


FIG. 3 Extraction of copper(II) with different β-diketones from ammoniacal solution. $c_{Cu^{2+}}$: $10^{-4}$ mol·L$^{-1}$ ($I$ = 0.1 mol·L$^{-1}$ $NH_4Cl$). $c_{HL}$: $10^{-2}$ mol·L$^{-1}$ (in kerosene). $R = f(pH)$. For the key to the symbols, see Tables 1 and 2.

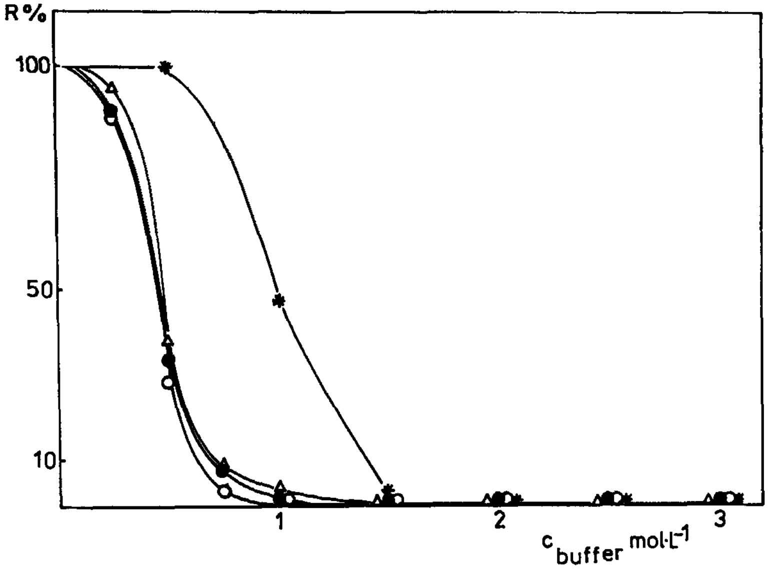


FIG. 4 Extraction of copper(II) with different β-diketones from ammoniacal solution (parameters as in Fig. 3). $R = f(c_{buffer})$. For the key to the symbols, see Tables 1 and 2.

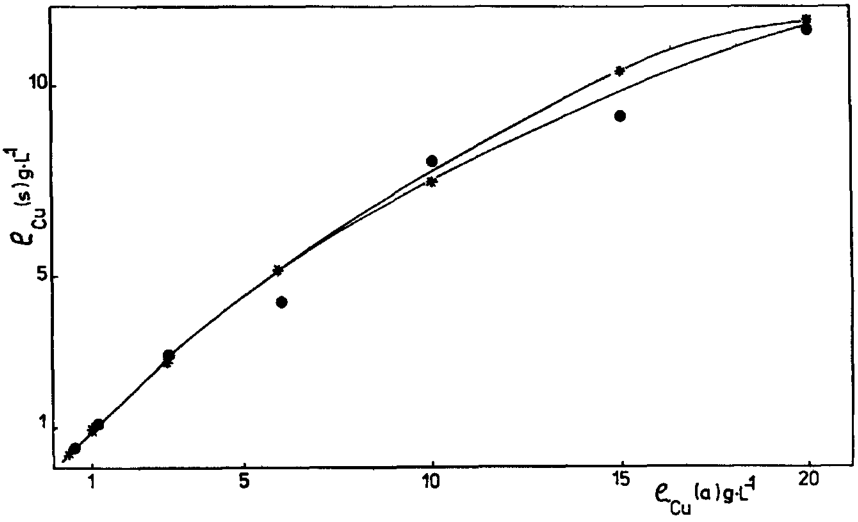


FIG. 5 Extraction isotherms of copper(II) extraction from ammoniacal solution. $\rho_{Cu^{2+}}$: 3.0 g·L$^{-1}$ (in $NH_3/NH_4Cl$ buffer solution). $c_{buffer}$: 1.0 mol·L$^{-1}$. $w_{HL}$: 10% by volume (kerosene/toluene 1 + 1). Extraction cycle: 10 minutes. For the key to the symbols, see Table 2.

which are easily prepared from alcoholic solutions of the ligands and copper acetate. Some analytical details, including the solubility of the compounds in kerosene, are given by Table 3.

The extraction of copper from ammoniacal solution is shown in Figs. 3 and 4. It can be seen in Fig. 3 that extraction is not hindered by low concentrations of ammonia up to pH 10 whereas a drastic increase in ammonia concentration leads to a steep decline of the extraction curve (Fig. 4). In this case ammonia is efficient as a competitive ligand which tends to form copper ammine complexes in the aqueous phase. LIX 54 shows the same behavior but apparently its copper complexes are somewhat more stable to ammonia than are the complexes of cyclohexyl-substituted β-diketones.

A direct comparison between LIX 54 and 1-phenyl-5-cyclohexyl-1,3-pentanedione is made in Fig. 5 which shows the extraction isotherms of both extractants for copper. The extractants are very similar.

The maximum loading of the organic phase amounts to 11 $g \cdot L^{-1}$ copper under the conditions selected. Higher concentrations of copper cause precipitation at the phase boundary as a consequence of the limited solubility of the copper complexes.

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