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Liquid-Liquid Extraction of Copper with 4-Acylpyrazol-5-ones

W. Mickler[a]; E. Uhlemann[a]
[a] INSTITUT FÜR ANORGANISCHE CHEMIE UNIVERSITÄT POTSDAM POSTFACH, POTSDAM, GERMANY

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TECHNICAL NOTE

Liquid–Liquid Extraction of Copper with 4-Acylpyrazol-5-ones

W. MICKLER and E. UHLEMANN
INSTITUT FÜR ANORGANISCHE CHEMIE
UNIVERSITÄT POTSDAM
POSTFACH 60 15 53, D-14415 POTSDAM, GERMANY

INTRODUCTION

Substituted 4-acylpyrazol-5-ones exhibit favorable extraction qualities. The application of these compounds to extract copper from ammoniacal solution was recently (1) reported. But some of the extraction curves were changed by mistake while that paper was in press. Therefore, the exact results are given here.

RESULTS AND DISCUSSION

The extraction of copper with selected 4-acylpyrazol-5-ones under the usual conditions is shown in Figs. 1 and 2. From the rise of the log D/pH curve, the composition of the extracted species is evaluated to be CuL_2. In the pH dependence of the extraction (Fig. 1), surprisingly, all curves of the examined 4-acylpyrazol-5-ones run through a minimum in the pH 6–7 region. This can be attributed to competition reactions between the extraction and hydrolysis of copper ions. In the case of short-chain acyl groups, the extraction reaction is fast and therefore hydrolysis is limited. However, the extraction rate decreases as the chain length of the acyl group increases.

To attain good extraction, extensive prolongation of the extraction cycle is necessary. As an example, the dependence on time for the extraction of copper with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-pyrazol-5-one at pH 6.2 is shown in Fig. 3. It can be seen that the influence of different

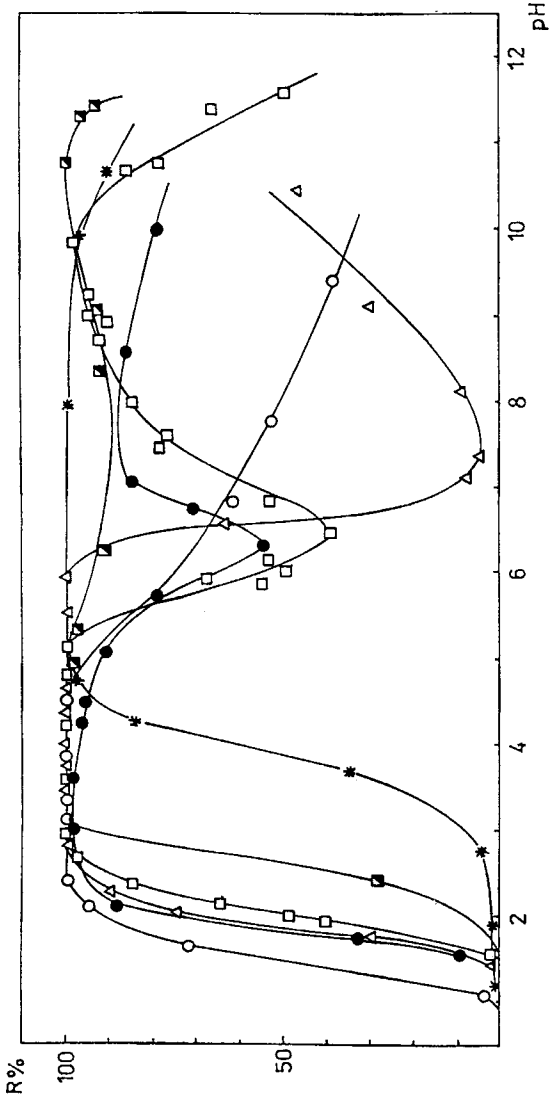

FIG. 1 Extraction of copper(II) with different 1-phenyl-3-methyl-4-acylpyrazol-5-ones. $c_{Cu^{2+}}$: 10^{-1} mol·L^{-1} (I = 0.1 mol·L^{-1} KNO_3). c_{HL}: 10^{-2} mol·L^{-1} (in kerosene). $R = f(pH)$. Acyl groups: (○) stearoyl, (△) octadecenoyl, (●) *n*-octanoyl, (□) 2-ethylhexanoyl, (◪) *n*-propanoyl, (*) LIX 54 (*i*-octanoyl).

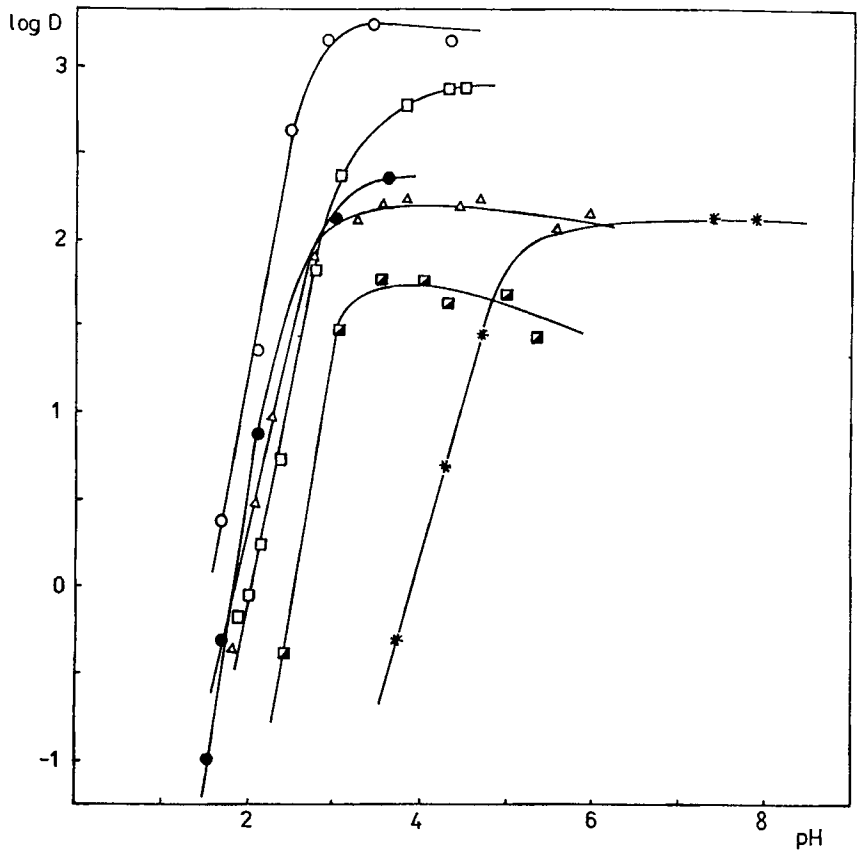

FIG. 2 Extraction of copper(II) with different 1-phenyl-3-methyl-4-acylpyrazol-5-ones. log $D = f(\text{pH})$. See Fig. 1 for the parameters and symbols.

acyl groups on the extraction behavior of 4-acylpyrazol-5-ones is small because the hydrophobicities of all the compounds are similar and the chelate structures are identical. 4-Acylpyrazol-5-ones are able to extract copper from stronger acidic solutions than β-diketones, such as LIX 54 do (Fig. 1). On the other hand, the extraction rate is limited by the solubility of the copper complex formed in the organic phase. From this point of view, LIX 54 excels all the 4-acylpyrazol-5-ones studied in this paper. Corresponding to the solubility of its copper chelate, 4-(2-ethylhexanoyl)-pyrazol-5-one is the best extractant of the series.

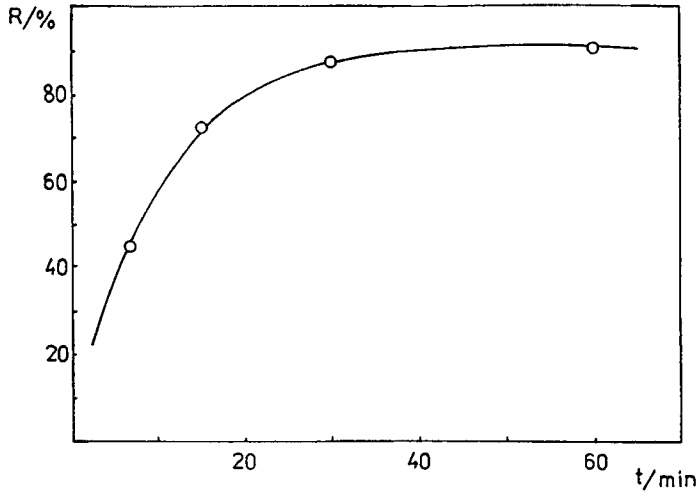

FIG. 3 Extraction of copper(II) with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-pyrazol-5-one. pH 6.2. $R = f(t)$.

In general, branched aliphatic chains favor the solubility; similar structures were also found in the commercial extractant LIX 54.

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