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

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Liquid–Liquid Extraction of Copper from Ammoniacal Solution with 4-Acylpyrazol-5-ones

W. MICKLER and E. UHLEMANN
INSTITUT FÜR ANORGANISCHE CHEMIE
UNIVERSITÄT POTSDAM
AM NEUEN PALAIS 10, D-0-1571 POTSDAM, GERMANY

ABSTRACT

The extraction of copper from ammoniacal solution with different 4-acylpyrazol-5-ones was studied. Depending on the nature of aliphatic acyl groups, the influence of pH and of the concentrations of ammonia and copper were evaluated. The extraction parameters are given and compared with those of the commercially available extractant LIX 54. The best results were obtained for 1-phenyl-3-methyl-4(2-ethylhexanoyl)-pyrazol-5-one.

Key Words. Liquid–liquid extraction; 4-Acylpyrazol-5-ones; Copper extraction; Ammoniacal solution

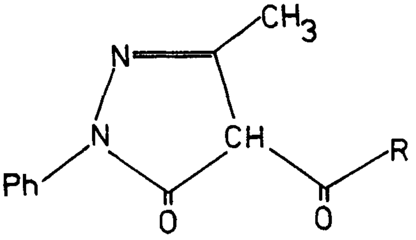
INTRODUCTION

Substituted 4-acylpyrazol-5-ones exhibit favorable extraction qualities, but until now they have not been used as commercial extractants (1). An interesting application is the separation of lanthanides and actinides from acidic solutions with 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one (2–4). The extraction is improved by synergists such as trioctylphosphine oxide (5), triphenylphosphine oxide (6), crown ethers (7), and methyltrioctylammonium chloride (8). In these cases, 1 : 1 adducts are formed and the extraction curve is shifted to lower pH. A mixture of 1-phenyl-3-methyl-4-benzoyl-pyrazol-5-one with trioctylphosphine oxide was also used to extract transition metals (9–11) from acidic solutions. For this purpose bis-pyrazolones were recently recommended (12, 13) as a new type of possible extractants. Because of the expected high hydrophobicity, 1-phenyl-3-methyl-4-stearoyl-pyrazol-5-one was repeatedly chosen as an extractant (14–16). It is suitable to separate alkaline earth impurities from alkali salts (17). A disadvantage of many 4-acylpyrazol-5-ones is the formation of sparingly soluble precipitates in alkaline solutions. To avoid these difficulties, new 4-acylpyrazol-5-ones exhibiting aliphatic acyl groups were synthesized and tested for the extraction of copper from ammoniacal solution. Some preliminary results were reported elsewhere (18).

EXPERIMENTAL

Extractants

The extractants are characterized by the formula



Acyl group	R
Stearoyl-	$H_3C{-}(CH_2)_{16}{-}$
Octadecenoyl-	$H_3C{-}(CH_2)_7{-}CH{=}CH{-}(CH_2)_7{-}$
n-Octanoyl-	$H_3C{-}(CH_2)_6{-}$
2-Ethylhexanoyl-	$H_3C{-}(CH_2)_3{-}CH(C_2H_5){-}$
n-Butanoyl	$H_3C{-}(CH_2)_3{-}$

The syntheses were performed following the method of Jensen (19) by the reaction of 1-phenyl-3-methyl-pyrazol-5-one with the corresponding acid choride. The compounds were purified by distillation *in vacuo* or by recrystallization from alcohol. Their analytical data are presented in Table 1.

TABLE 1

Analytical and Thermal Data of Different 4-Acylpyrazol-5-ones

Symbol	Acyl group	mp (bp) (°C)	Analytical data (calculated/found) (%)		
			C	H	N
○	Stearoyl-	mp 70.5–71.5	76.30/76.6	10.08/10.34	6.36/6.38
△	Octadecenoyl-	bp 200–240	76.65/74.8	9.17/9.75	6.39/6.69
●	*n*-Octanoyl-	mp 76.0–76.5	71.95/72.07	8.07/8.20	9.33/8.88
□	2-Ethylhexanoyl-	bp 178	71.95/71.48	8.07/8.02	9.33/8.88
◪	*n*-Butanoyl-	mp 74.5–75.0	68.82/69.08	6.61/6.58	13.10/12.52

EXTRACTION PARAMETERS

The experimental conditions of the liquid–liquid extraction were:

$c_{Cu^{2+}}$:	10^{-4} mol·L (I = 0.1 mol·L^{-1} KCl/NH_4Cl)
c_{HL}:	10^{-2} mol·L (HL = extractant, solvent kerosene)
Phase ratio:	1:1 (20 mL, separation funnel)
Temperature:	25°C
Extraction cycle:	10 min (mechanical shaker)

The pH adjustment was done by adding HNO_3 or NaOH. For the measurement of 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-3 Carl Zeiss, Jena).

All chemicals were of p.a. quality. The copper stock solution was prepared by dilution of a Merck standard solution with double-distilled 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

$$-\log K_{ex}/n = pH_{0.5} + \log c_{HL}$$

is valid (n = number of liberated protons; $pH_{0.5}$ = pH for log D = 0).

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 in Fig. 2, the composition of the extracted species is evaluated to be CuL_2. The pH dependence of the extraction up to pH 12 is shown in Fig. 1. Surprisingly, all curves of the examinated 4-acylpyrazol-5-ones run through a minimum in the pH 6–7 region. This can be attributed to competition reactions between extraction and copper ion hydrolysis. 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. The characteristic extraction data are given in Table 2. It can be seen that the influence of different 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 identi-

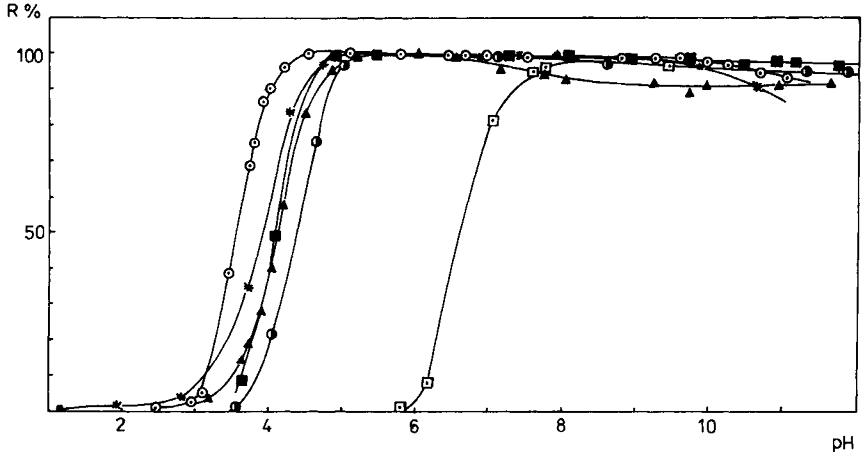


FIG. 1 Extraction of copper(II) with different 4-acylpyrazol-5-ones. $c_{Cu^{2+}}$: 10^{-4} mol·L^{-1} (I = 0.1 mol·L^{-1} KNO_3). c_{HL}: 10^{-2} mol·L^{-1} (in kerosene). $R = f(pH)$. See Table 1 or 2 for the key to the symbols.

cal. However, 4-acylpyrazolon-5-ones are able to extract copper from stronger acidic solutions than β-diketones, such as LIX 54 (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. In general, branched aliphatic chains favor the solubility; similar structures were also found in the commercial extractant LIX 54 (20).

Figures 4 and 5 show the extraction of copper from solutions containing ammonia as an auxiliary complexing reagent. In this case a decrease of the extraction rate caused by copper ion hydrolysis was not observed. By increasing the ammonia concentration, the copper extraction decreases because ammonia works as a competing ligand. Above pH 10, copper extraction is seriously hindered. Moreover, the formation of precipitations and emulsions occurs under these circumstances. In Figs. 6 and 7 a comparison between 1-phenyl-3-methyl-4(2-ethylhexanoyl)-pyrazol-5-one and the technical extractant LIX 54 is given. Starting with moderate copper concentrations to avoid precipitations in the organic phase, the pyrazolone is able to extract copper from stronger ammoniacal solution than LIX 54 does (Fig. 6). In this case the loading of the organic phase is limited to 9.2 g/L copper, whereas for LIX 54 the loading capacity comes up to

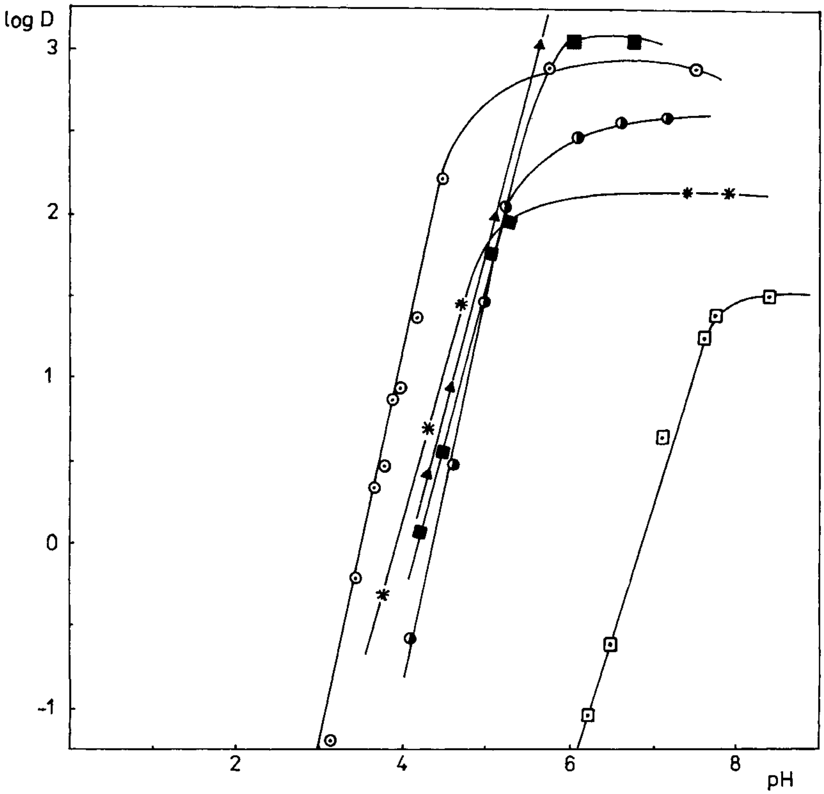


FIG. 2 Extraction of copper(II) with different 4-acylpyrazol-5-ones. $\lg D = f(\mathrm{pH})$. Parameters as in Fig. 1. See Table 1 or 2 for the key to the symbols.

TABLE 2
Extraction Data of 4-Acylpyrazol-5-ones in Comparison with LIX 54

Symbol	Acyl group	$pH_{0.5}$	log K_{ex}	Solubility of the extractant in kerosene ($mol \cdot L^{-1}$)
○	Stearoyl-	1.40	1.20	4.168×10^{-2}
△	Octadecenoyl-	1.90	0.20	Infinitely soluble
●	*n*-Octanoyl-	1.85	0.30	0.105
□	2-Ethylhexanoyl-	2.05	−0.10	Infinitely soluble
*	*i*-Octanoyl- (LIX 54)	3.90	−3.80	

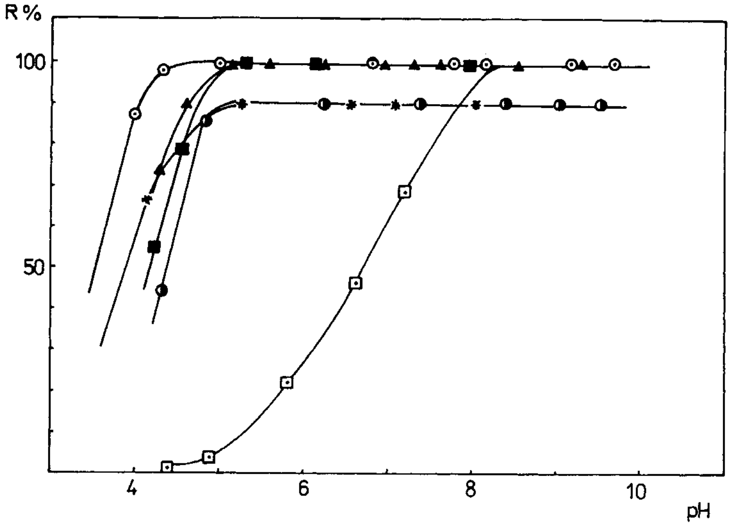


FIG. 3 Extraction of copper(II) with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-pyrazol-5-one. pH 6.2. $R = f(t)$. See Table 1 or 2 for the key to the symbols.

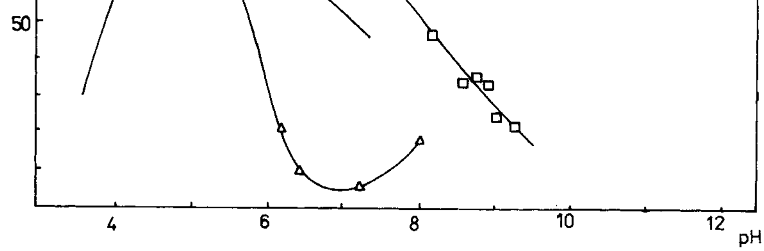


FIG. 4 Extraction of copper(II) from ammoniacal solution. $c_{Cu^{2+}}$: 10^{-4} mol·L^{-1} ($I = 0.1$ mol·L^{-1} NH_4Cl). c_{HL}: 10^{-2} mol·L^{-1} (in kerosene). $R = f(pH)$. See Table 1 or 2 for the key to the symbols.

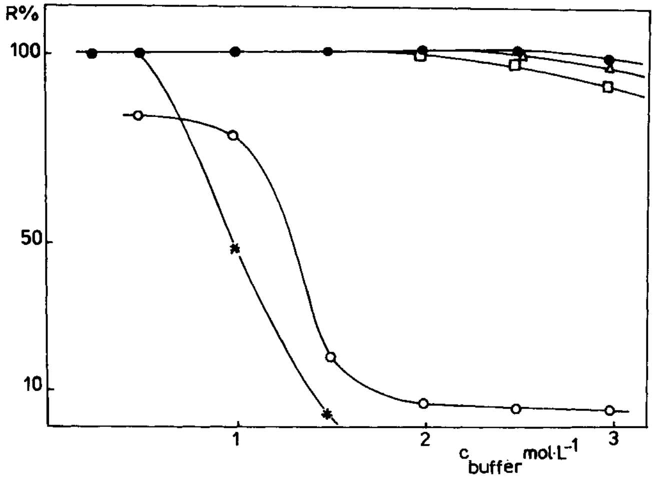


FIG. 5 Extraction of copper(II) from ammoniacal solution. c_{Cu}: 3.0 g·L^{-1} (in NH_3/NH_4Cl buffer solution). c_{buffer}: 1.0 mol·L^{-1}. c_{HL}: 10% by volume (kerosene/toluene 1 + 1). See Table 1 or 2 for the key to the symbols.

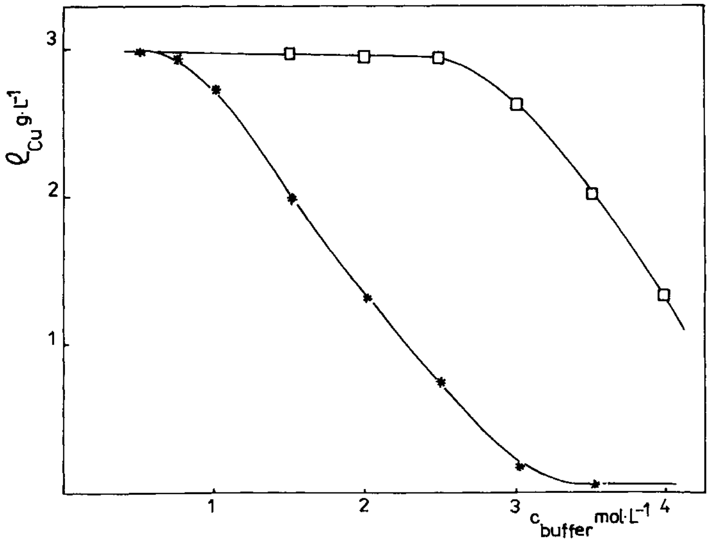


FIG. 6 Extraction of copper(II) from ammoniacal solution. c_{Cu} (organic phase = $f(c_{\text{buffer}})$. Parameters as in Fig. 5. Extraction cycle: 10 minutes. See Table 1 or 2 for the key to the symbols.

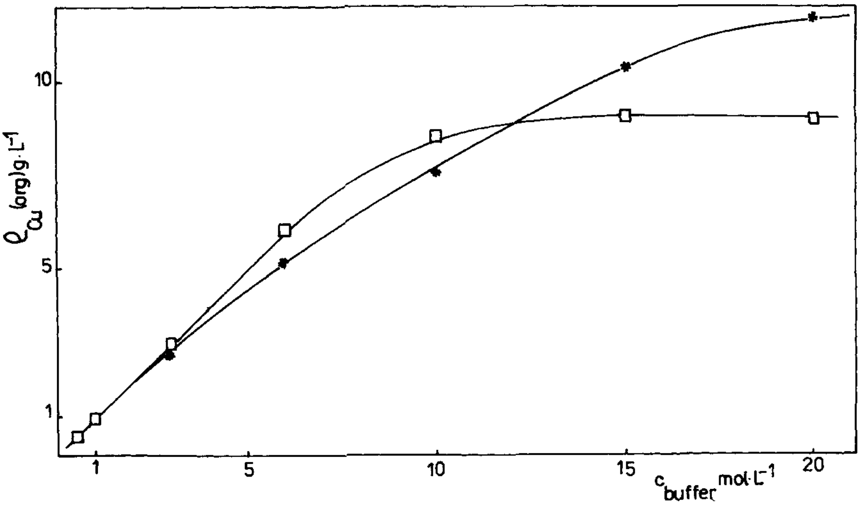


FIG. 7 Extraction isotherm of copper(II) extraction from ammoniacal solution. Parameters as in FIG. 5. See Table 1 or 2 for the key to the symbols.

11.85 g/L copper (Fig. 7). The reasons for this behavior are apparently the different solubilities of the copper complexes.

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