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TECHNICAL NOTE

# Extraction of Zinc with Long-Chain β-Diketones and 4-Acyl-5-pyrazolones

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## ABSTRACT

The extraction of zinc with long-chain 4-acyl-5-pyrazolones and β-diketones was studied. For comparison with the commercial extractant LIX 54, the extraction parameters were studied for their dependence on pH and on the influence of ammonia and tartrate. Among the examined compounds, 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone shows the best extraction results. Zinc as well as nickel and cadmium can be extracted from tartrate solution. The separation of zinc and cadmium is possible. The extraction is disturbed by the presence of complexing agents such as ammonia or cyanide.

*Key Words.* Liquid–liquid extraction; β-Diketones; LIX 54; 4-Acyl-5-pyrazolones; Extraction, zinc, nickel, and cadmium; Ammoniacal and tartrate solutions

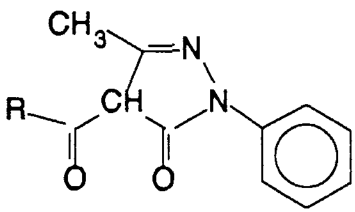
## INTRODUCTION

For the extraction of zinc from acidic solutions, organophosphorous ligands such as DEHPA or CYANEX (1–3) are preferably used. Other suitable extractants are KELEX 100 (4) as well as ACORGA ZNX 50 (5). Beside LIX- and KELEX-type reagents, bis-pyrazolones are recommended to separate zinc from alkaline solution (6–8). 4-Acyl-5-pyrazolones can be regarded as modified β-diketones, but they are able to extract metal ions at lower pH values than open-chain β-diketones. Therefore, they offer the possibility of avoiding the pH region where hydrolysis of the metal ions takes place. In this paper the extraction of zinc with selected 4-acylpyrazolones is studied in comparison with β-diketones containing analogous substituents. As a commercially available β-diketone, LIX 54 (Henkel KGaA) was used. It consists of a mixture of isomeric 1-phenyl-3-isoheptyl-1,3-propanediones (9). The influence of masking agents such as ammonia, tartrate, or cyanide is also checked.

## EXPERIMENTAL

### Extractants

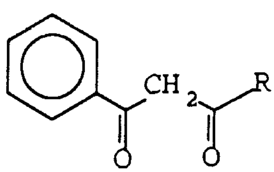
The 4-acyl-5-pyrazolones examined are characterized by the formula




A survey of them is given in Table 1.

The syntheses were performed according the method of Jensen (10) by the reaction of 1-phenyl-3-methyl-5-pyrazolone with the corresponding acid chlorides (11).

The β-diketones studied have the general formula




They are collected in Table 2.

TABLE 1
4-Acylpyrazol-5-ones

| Symbol | 4-Acyl group | R |
|---|---|---|
| ⊙ | -butanoyl | $-(CH_2)_2-CH_3$ |
| ● | -octanoyl | $-(CH_2)_6-CH_3$ |
| ○ | -stearoyl | $-(CH_2)_{16}-CH_3$ |
| □ | -2-ethylhexanoyl | $-CH(C_2H_5)-(CH_2)_3-CH_3$ |
| △ | -octadecenoyl | $-(CH_2)_7-CH{=}CH-(CH_2)_7-CH_3$ |

TABLE 2
β-Diketones

| Symbol | Acyl group | R |
|---|---|---|
| * | *i*-Octanoyl (mixture)- (LIX 54) | *i*-$C_7H_{13}$(mixture) |
| ▲ | 2-Ethylhexanoyl- | $-CH(C_2H_5)-(CH_2)_3-CH_3$ |
| ■ | *n*-Octanoyl- | $-(CH_2)_6-CH_3$ |
| ◑ | Cyclopentyl-propanoyl- | $-(CH_2)_2-C_5H_9$ |
| ⊠ | Cyclohexyl-acetyl- | $-CH_2-C_6H_{11}$ |
| | *For Comparison, the Following Were Synthesized* | |
| ◪ | 1-(*p*-Hexylphenyl)-1,3-butanedione | |
| ⊡ | 1-Phenyl-2-hexyl-1,3-butanedione | |



The syntheses were made by following a procedure of Hauser (11) by Claisen condensation of acetophenone and the corresponding phenyl or ethyl esters in the presence of sodium amide. Analytical data for the compounds summarized in Tables 1 and 2 were given recently (12).

## Extraction Studies

The experimental conditions of the liquid–liquid extraction are given in Table 3.

The pH adjustment was done by adding $HNO_3$ or NaOH. For the measurement, 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 zinc stock solution was prepared by diluting a Merck standard solution by adding bidistilled water.

The distribution coefficient $D = c_{Zn^{2+}(o)}/c_{Zn^{2+}(w)}$ was calculated from the zinc concentration determined in the aqueous phase before and

TABLE 3
Experimental Conditions of the Liquid–Liquid Extraction

| | |
|---|---|
| $c_{Zn^{2+}}$: | $10^{-5}$ mol·L$^{-1}$ ($I$ = 0.1 mol·L$^{-1}$; $KNO_3$) |
| $c_{HL}$: | $10^{-3}$ mol·L$^{-1}$ (solvent: kerosene) |
| Phase ratio: | 1 + 1 (20 mL separatory funnel) |
| Temperature: | 25°C |
| Extraction cycle: | 10 min (mechanical shaker) |

after the extraction. For the extraction constant $K_{ex}$, the equation $-\log K_{ex}/n = pH_{0.5} + \log c_{HL}$ is valid.

Stripping experiments were done with sulfuric acid (30%). The equilibration time was 20 minutes. Stripping was also used for the control of zinc transfer into the organic phase during the extraction process.

## RESULTS AND DISCUSSION

The extraction of zinc with 4-acyl-5-pyrazolones is shown in Fig. 1; the results for β-diketones are given in Fig. 2. The corresponding log $D$/pH diagrams are presented in Fig. 3. From the slopes of the straight lines, the composition of the extracted species proves to be $ZnL_2$. The extraction parameters are summarized in Tables 4 and 5.

As expected, zinc is extracted at a lower pH with 4-acylpyrazolones than with the corresponding β-diketones. The reason is the higher acidity of the pyrazolones. Among different substituents, the 2-ethylhexanoyl group shows the most favorable results. Apparently $C_8$ groups especially, having such a branched structure produces good solubility of the extractant and of the metal chelates formed. Substitution of β-diketones in the 2-position causes a drastic decrease of extraction because chelate formation is sterically hindered. A disturbance of extraction occurs through the



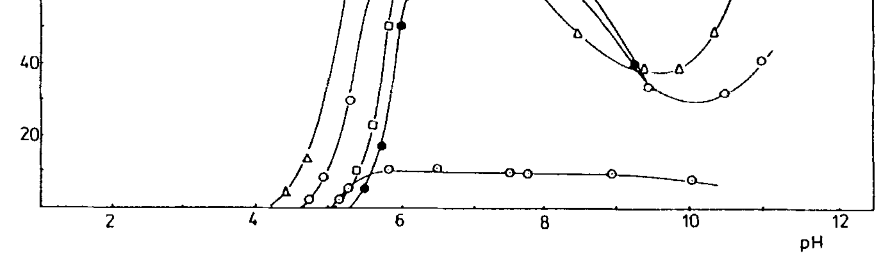



FIG. 1 Extraction of zinc(II) with different 4-acyl-5-pyrazolones. $R = f(\text{pH})$. $c_{Zn^{2+}} = 10^{-5}$ mol·L$^{-1}$ ($I$ = 0.1 mol·L$^{-1}$ $KNO_3$). $c_{HL} = 10^{-3}$ mol·L$^{-1}$ (solvent: kerosene). For symbols see Table 1.

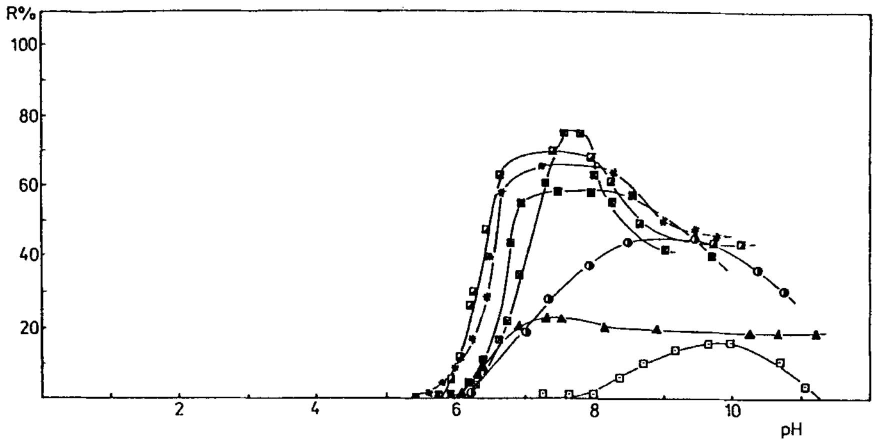



FIG. 2 Extraction of zinc(II) with different β-diketones. $R = f(\text{pH})$. Parameters as in Fig. 1. For symbols see Table 2.

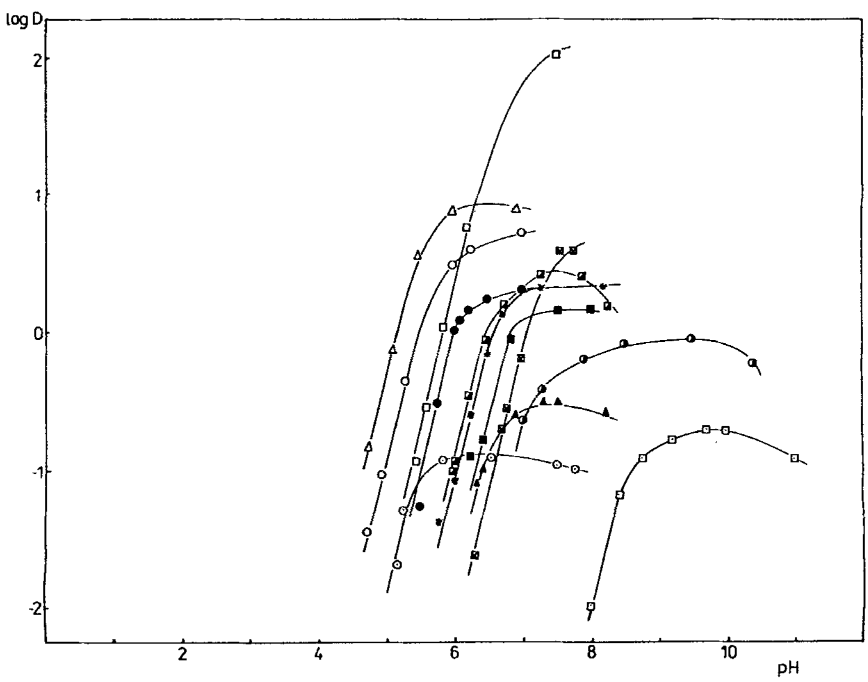



FIG. 3 Extraction of zinc(II). lg $D = f(\text{pH})$. For symbols see Tables 1 and 2. Parameters as in Fig. 1.

TABLE 4
Extraction Data of 4-Acyl-5-pyrazolones
(for symbols, see Table 1)

| Symbol | $pH_{1/2}$ | lg $K_{ex}$ |
|---|---|---|
| ● | 6.00 | −6.00 |
| ○ | 5.45 | −4.90 |
| □ | 5.80 | −5.60 |
| △ | 5.15 | −4.30 |

TABLE 5
Extraction Data of 1,3-Diketones
(for symbols, see Table 2)

| Symbol | $pH_{1/2}$ | lg $K_{ex}$ |
|---|---|---|
| * | 6.55 | −7.10 |
| ■ | 6.80 | −7.60 |
| ⊠ | 7.05 | −8.10 |
| ◪ | 6.45 | −6.90 |



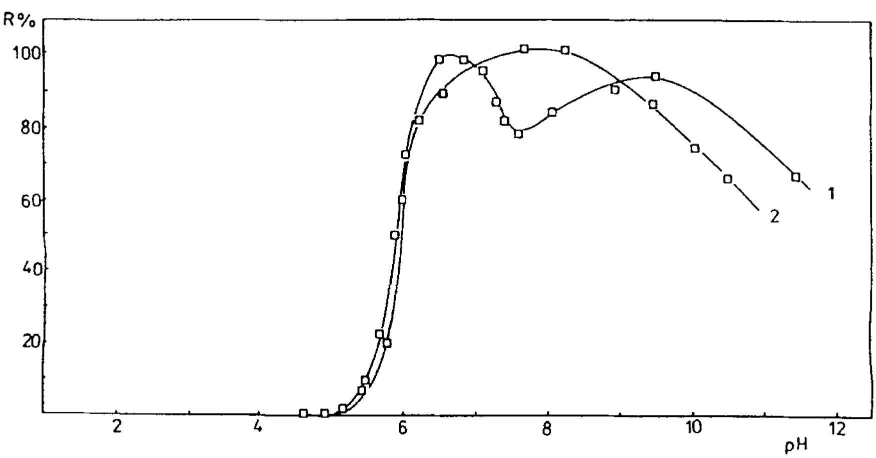



FIG. 4 Extraction of zinc(II) with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone. $R = f(\text{pH})$. Curve 1: $c_{Zn^{2+}} = 10^{-5}$ mol·L$^{-1}$ ($I = 0.1$ mol·L$^{-1}$ $KNO_3$). Curve 2: $c_{Zn^{2+}} = 10^{-5}$ mol·L$^{-1}$ ($I = 0.1$ mol·L$^{-1}$ $KNO_3$), $c_{Tartrat} = 10^{-4}$ mol·L$^{-1}$.

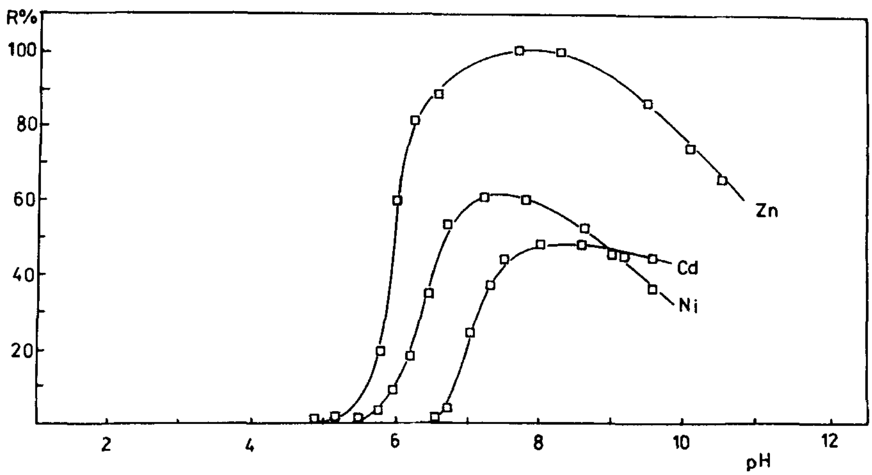



FIG. 5 Extraction of zinc(II), nickel(II), and cadmium(II) with 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone. $c_{M^{2+}} = 10^{-5}$ mol·L$^{-1}$ ($I$ = 0.1 mol·L$^{-1}$ $KNO_3$). $c_{Tartrat} = 10^{-4}$ mol·L$^{-1}$. $c_{HL} = 10^{-3}$ mol·L$^{-1}$ (in kerosene).



formation of polyoxocations by the hydrolysis of zinc ions. The extraction curve runs through a minimum in this region which, in a similar way, was also observed in the extraction of copper (13). Hydrolysis seems to be quicker than extraction, but it can be suppressed by adding tartrate as a masking agent. This behavior is represented in Fig. 4 were 1-phenyl-3-methyl-4-(2-ethylhexanoyl)-5-pyrazolone was used as an extractant. Moreover, this extractant is capable of extracting zinc even from alkaline solution (Fig. 1) whereas the extraction rates generally decrease because of the formation of more stable hydroxo complexes in the aqueous phase. In the same way, cyanide ions prevent zinc extraction. In ammoniacal solution (ammonia/ammonium chloride buffers), the extraction rates are limited to only 20%.

Metal ion hydrolysis also hinders the extraction of nickel and cadmium with 4-acylpyrazolones. Reproducible conditions are only possible by adding tartrate as an auxiliary ligand. The extraction of zinc, nickel, and cadmium from tartrate medium is given by Fig. 5. Corresponding to former results, the sequence of extraction is in the order Zn > Ni > Cd (14). The differences between zinc and cadmium can be used for separation processes, whereas no separation is possible in the case of nickel.

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