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Liquid-Liquid Distribution of 4-Acyl-3-methyl-1-phenyl-5-pyrazolones and Their Zinc Complexes

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The distribution of eight 4-acyl-3-methyl-1-phenyl-5-pyrazolones and their zinc complexes between aqueous and cyclohexane phases was investigated. The acid dissociation constants and partition constants of the extractants were discussed in terms of a substituent effect. It was found that two series of examined reagents in which one has an aromatic substituent at the 4-position of 5-pyrazolone, and the other an aliphatic one give similar extraction constants. Since their acid dissociation constants are essentially the same, a relationship, $\log P_{\mathrm{MA}} = 2\log P_{\mathrm{HA}} + \text{constant}$, is postulated. The extraction constant of a fluorinated reagent which has a considerably small pK_a value is also similar to that of the reagents having aliphatic substituents. Another relationship, $\log \beta_2 = 2\mathrm{p}K_a + \text{constant}$, is postulated.

The solvent extraction system has been widely employed as a convenient separation and concentration method of metal cations, and the extraction mechanism has been investigated in terms of the nature of metal cations, the role of solvents, and the chelation and distribution behavior of ligands.

The previous papers indicate that 4-acyl-5-pyrazolones (Fig. 1), a kind of β-diketones, have several advantages.[1-3] First, metal ions are extractable from acidic media because the pyrazolones are strong acids, and secondly, various kinds of derivatives can be easily synthesized, an important point for the investigation on the extraction mechanism. Obvious substituent effects were observed in the extraction of europium and barium,[1] and in the synergistic extraction of alkaline earths,[2] europium and scandium.[3]

In the present paper, quantitative investigations are made on the distribution of 4-acyl-3-methyl-1-phenyl-5-pyrazolones and the extraction of their zinc complexes.

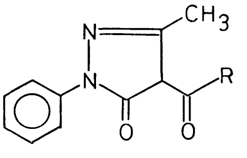

Fig. 1. 4-Acyl-3-methyl-1-phenyl-5-pyrazolones.

Experimental

Reagents. 4-Acyl-3-methyl-1-phenyl-5-pyrazolones were synthesized according to Jensen's method,[4] that is, from 3-methyl-1-phenyl-5-pyrazolone and the corresponding acid chloride or acid anhydride for the fluorinated ligand. The crude compounds were recrystallized from aqueous dioxane or methanol. Analytical data for these reagents are shown in Table 1. Zinc-65 was supplied by New England Nuclear, Boston, Mass. as a hydrochloric acid solution. This solution was once dried up and diluted with perchloric acid. Sodium perchlorate used to adjust the ionic strength (0.1) was recrystallized from water. All the other chemicals were chemically pure or reagent-grade materials.

Table 1. Elemental analysis of the compounds studied

Reagent No.	R	Calcd (Found) (%)			Mp θ_m/°C
		C	H	N	
1	Phenyl	73.37	5.07	10.07	92—92.5
		(73.54	4.99	10.22)	
2	2-Methylphenyl	73.96	5.52	9.58	111—112
		(73.64	5.52	9.33)	
3	3-Methylphenyl	73.96	5.52	9.58	94—95
		(73.72	5.39	9.38)	
4	4-Methylphenyl	73.96	5.52	9.58	100
		(74.01	5.46	9.66)	
5	2-Naphthyl	76.81	4.91	8.53	101
		(76.93	4.96	8.55)	
6	Propyl	68.83	6.60	11.47	45
		(68.78	6.59	11.66)	
7	Heptyl	71.97	8.05	9.33	61
		(72.17	8.09	9.25)	
8	Trifluoromethyl	53.34	3.33	10.36	146
		(53.55	3.30	10.56)	

Distribution of the Reagents. The experiments were performed in a 30 cm^3 glass-stoppered centrifuge tube. A cyclohexane solution containing pyrazolone (0.02 mol dm^{-3}) and an equal volume of the aqueous solution containing sodium perchlorate (0.1 mol dm^{-3}) and sodium acetate (0.01 mol dm^{-3}) as a buffer solution were shaken for 1 h in a thermostated room at 25±1 °C. The hydrogen ion concentration was controlled at a desired value with sodium hydroxide and perchloric acid. After the two layers had been separated centrifugally, the ligand concentration was measured spectrophotometrically. The ligand concentration in the aqueous phase was measured after the dilution with sodium hydroxide solution to complete the dissociation of the ligand. This anionic form which is stable enough for a few days, exhibits strong absorption at 250—300 nm. The sum of the ligand concentration determined in each phase coincided well with the initial concentration. The pH value of the aqueous phase was checked after extraction.

Distribution of Zinc Complexes. A cyclohexane solution containing pyrazolone (0.02 mol dm^{-3}) and an equal volume of the aqueous solution containing Zn^{2+} (1×10^{-6} mol dm^{-3}), radioactive tracer (^{65}Zn), sodium perchlorate (0.1 mol dm^{-3}) and sodium acetate (0.01 mol dm^{-3}) were shaken for 1 h. After the two layers had been separated, 2 cm^3 of each phase was pipetted into a test tube and the radioactivities were counted.

Apparatus. Radioactivities were determined by counting with a Metro Electronics NaI (44.5 mm diam. × 50.8 mm depth) well-type scintillation counter, model PbW-6, connected to a Metro automatic scaler, model SS-1060H. A Shimadzu UV-180 spectrophotometer was used for spectrophotometric measurements, and a Hitachi-Horiba F-7ss pH meter for pH measurements.

Results and Discussion

Data Processing. In a quantitative treatment for the distribution of the reagents, the acid dissociation constant, K_a, and the partition constant, P_{HA}, are defined as follows:

$$K_a = \frac{[H^+][A^-]}{[HA]},$$

$$P_{HA} = \frac{[HA]_o}{[HA]}, \qquad (1)$$

where [HA] and $[A^-]$ are the concentration of the neutral and anionic species of the extracting reagents in the aqueous phase, and the subscript o denotes the species in the organic phase. Thus, the distribution ratio of the reagents, D_{HA}, can be written as,

$$D_{HA} = \frac{[HA]_o}{[HA]+[A^-]},$$

or

$$D_{HA} = \frac{P_{HA}}{1+K_a[H^+]^{-1}}. \qquad (2)$$

When the hydrogen ion concentration is high enough, D_{HA} agrees with P_{HA}, while $\log D_{HA}$ agrees with $\log P_{HA}+pK_a-pH$ for low hydrogen ion concentrations.

The concentration of the anionic form can be described by using the initial ligand concentration, $[HA]_i$, as follows:

$$[HA]_i = [HA]_o + [HA] + [A^-],$$

$$[A^-] = \frac{[HA]_i}{1+[H^+](1+P_{HA})\cdot K_a^{-1}}. \qquad (3)$$

When the divalent metal ion and the distribution ratio of the metal ion are denoted by M^{2+} and D_{MA}, the extraction constant, K_{ex}, can be written as follows:

$$M^{2+} + 2HA \rightleftharpoons MA_{2,o} + 2H^+,$$

$$K_{ex} = \frac{[MA_2]_o[H^+]^2}{[M^{2+}][HA]_o^2}. \qquad (4)$$

The extraction constant can be rewritten by the chelate formation constants, β_2, and the partition constant of the chelates, P_{MA}, as follows:

$$\beta_2 = \frac{[MA_2]}{[M^{2+}][A^-]^2},$$

$$P_{MA} = \frac{[MA_2]_o}{[MA_2]},$$

$$K_{ex} = K_a^2\cdot\beta_2\cdot P_{MA}\cdot P_{HA}^{-2}. \qquad (5)$$

Distribution of the Reagents. Figure 2 shows the distribution behavior of the reagents **1**, **7**, and **8** as a function of pH. The distribution curves are asymptotic to a constant value, $\log P_{HA}$, at high hydrogen ion concentrations, and to a straight line with a slope of −1, *i.e.* the theoretical line (Eq. 2) at low hydrogen ion concentrations. The similar distribution behavior was also observed for other reagents. The results are summarized in Table 2. The acid dissociation constants increase in the order expected from the substituent effect,[1] but are essentially the same except for reagents **2** and **8**. Although the partition constants increase with the carbon number, the influence of increasing the carbon number is not always the same when aromatic substituents are compared with aliphatic ones. For instance, $\log P_{HA}$ for reagent **7** is much larger than for reagent **5**, whose carbon number is larger than that of reagent **7**.

Distribution of Zinc Complexes. A plot of $\log D_{MA}$ against $\log [HA]_o$ for reagent **1** is shown in Fig. 3. A slope of 2 indicates that the extracted species is ZnA_2, and no further addition to this extracted form occurs in this ligand concentration range. Furthermore, dependence of $\log D_{MA}$ on pH and $\log [A^-]$

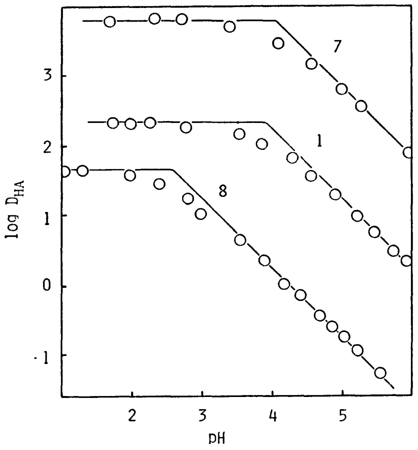

Fig. 2. Distribution of 4-acyl-5-pyrazolones between cyclohexane and water as a function of pH. The numerals show the reagent number in Table 1.

TABLE 2. EXTRACTION PARAMETERS FOR ZINC COMPLEXES

Reagent No.	pK_a	$\log P_{HA}$	$pH_{1/2}$[a)]	$\log K_{ex}$	$\log P_{MA}\cdot\beta_2$	$\log K_a\cdot P_{HA}^{-1}$
1	3.92	2.33	4.37	−5.32	7.18	−6.25
2	3.58	3.12	3.98	−4.56	8.84	−6.70
3	4.09	2.91	4.24	−5.08	8.92	−7.00
4	4.02	2.88	4.35	−5.30	8.50	−6.90
5	4.13	3.40	4.42	−5.44	9.62	−7.53
6	3.97	2.50	4.78	−6.14	6.80	−6.47
7	4.07	3.79	4.68	−5.96	9.76	−7.86
8	2.56	1.67	—	−5.86	2.60	−4.23

a) $[HA]_o = 0.02\ mol\ dm^{-3}$.

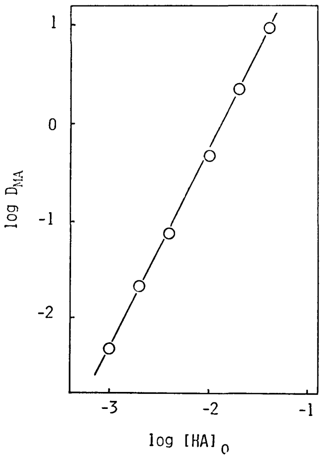

Fig. 3. Influence of the reagent **1** concentration on the extraction of zinc complex at pH 4.60.

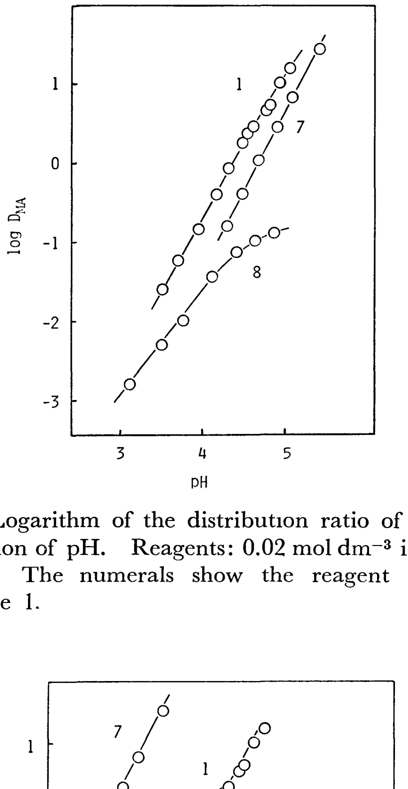

Fig. 4. Logarithm of the distribution ratio of zinc as a function of pH. Reagents: 0.02 mol dm^{-3} in cyclohexane. The numerals show the reagent number in Table 1.

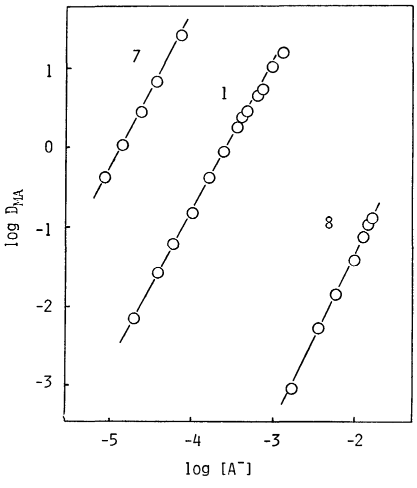

Fig. 5. Logarithm of the distribution ratio of zinc as a function of log [A$^-$]. The numerals show the reagent number in Table 1.

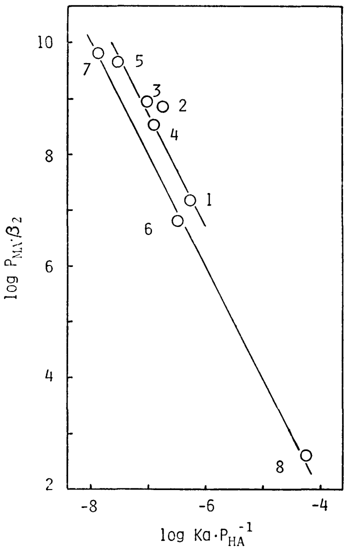

Fig. 6. Correlation between $\log P_{\mathrm{MA}}\cdot\beta_2$ and $\log K_a\cdot P_{\mathrm{HA}}$. The numerals show the reagent number in Table 1.

has also been examined to confirm the availability of Eq. 4 and are shown in Figs. 4 and 5. The values of [A$^-$] can be obtained from Eq. 3. The plots of $\log D_{\mathrm{MA}}$ against pH at a constant $[\mathrm{HA}]_o$ gave straight lines with a slope of 2 for reagents **1** and **7**. The slope for reagent **8** is smaller than 2, for in this pH region log [A$^-$] increases no longer linearly with pH because of its strong acidity and low partition constant (see Table 2). Each plot of $\log D_{\mathrm{MA}}$ against log [A$^-$] shows a straight line with a slope of 2 as seen in Fig. 5. The values of $\log K_{\mathrm{ex}}$ and $\log P_{\mathrm{MA}}\cdot\beta_2$ calculated from Eqs. 4 and 5 are summarized in Table 2 together with $\mathrm{pH}_{1/2}$ (pH value at which 50% of the metal ion was extracted with 0.02 mol dm^{-3} of the reagent) and $\log K_a\cdot P_{\mathrm{HA}}^{-1}$. As shown in Table 2, the values of $\log K_{\mathrm{ex}}$ are close together for reagents **1**—**5** with aromatic substituents, and for reagents **6**—**8** with aliphatic ones. Figure 6 illustrates the plots for the relationship between $\log P_{\mathrm{MA}}\cdot\beta_2$ and $\log K_a\cdot P_{\mathrm{HA}}^{-1}$. Two straight lines with a slope of -2 are obtained for the two groups. The ligands with an aromatic substituent except for reagent **2** have similar values of K_a so that the values of β_2 are expected also to be similar to each other when other influences such as steric hindrance are negligible. On the basis of this assumption a relationship between P_{MA} and P_{HA} can be postulated from Fig. 6 as follows:

$$\log P_{\mathrm{MA}} = 2\log P_{\mathrm{HA}} + \text{constant}. \qquad (6)$$

This relationship is also applicable to the aliphatic substituted group. Equation 6 is valid for the solvent extraction system of a reagent in various solvents[5] and of a solvent with various reagents.[6] Furthermore, reagent **8** which is a considerably strong acid also has a similar $\log K_{\mathrm{ex}}$ value to reagents **6** and **7**. Since complex formation is the exchange reaction of a hydrogen ion for a metal ion, strong acidity may bring low chelation ability. On the basis of this assumption another relationship between K_a and β_2 can be postulated as follows:

$$\log \beta_2 = 2\mathrm{p}K_\mathrm{a} + \text{constant}. \tag{7}$$

Further investigation is required to confirm this relationship. The difference in the values of $\log K_{\mathrm{ex}}$ between aromatic and aliphatic substituted groups may be caused by the stabilization of the complexes based on the aromatic resonance effect.

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