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Solvent Extraction of Metal Chelates

II. An Investigation on some 1-Phenyl-3-methyl-4-acyl-pyrazolones-5

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The apparent mean complexity constants of various 1-phenyl-3-methyl-4-acyl-pyrazolones-5 with Be^{2+}, Mn^{2+}, Zn^{2+}, Pb^{2+}, UO_2^{2+}, La^{3+} and Th^{4+} in a chloroform-water system are compared and discussed.

A linear relationship between the logarithm of the distribution coefficient of an uncharged metal chelate and the logarithm of the distribution coefficient of the undissociated chelating agent is proposed, the slope of the line being characteristic of the metal ion in question.

The compounds investigated are compared with the more common extractive chelating agents with regard to capacity and separation possibilities in a chloroform-water system, and show promise as valuable reagents for analytical and radiochemical separations.

Among the extractive chelating agents the β-diketones, as a group, range among the most useful. Compounds such as acetylacetone and thenoyltrifluoroacetone are to be regarded as standard chemicals in laboratories performing analytical or radiochemical work.

Several investigations on the extractive properties of different chelating agents have been published previously [1,2].

In this paper the results of an investigation on a class of β-diketones, the 1-phenyl-3-methyl-4-acyl-pyrazolones-5, in a chloroform-water system will be reported.

The 1-phenyl-3-methyl-4-acyl-pyrazolones are readily accessible compounds [3]. Furthermore their physico-chemical constants such as acid dissociation constants, distribution coefficients *etc.* can be varied within a wide range by proper substitution in the molecules. Hence this class of compounds seems to serve well as a basis for a closer study of the influence of the physical and chemical properties of a chelating agent on its extractive and chelating behaviour.

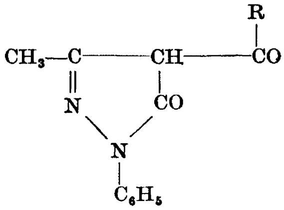

Fig. 1.

RESULTS AND DISCUSSION

The metal ion extractions have been investigated by means of a titration procedure [4], which has been described previously. By this method the chelating agent is characterized by a $pK_{a,E}$ value, which is the apparent pK_a value shown by an acid in the two-phase system under consideration. When only the undissociated acid HA is expected to distribute between the two phases with a distribution coefficient K_d, the following relation was shown to be valid [4,5].

$$pK_{a,E} = pK_a + \log\ (1 + K_d) \tag{1}$$

where pK_a is the value of the acid dissociation constant in aqueous solution.

The chelating agent, metal ion, solvent systems are characterized by either the pH_{50} of 50 % extraction of the metal ion under consideration or by an apparent mean complexity constant K_{av}[4].

As K_{av} is a real constant of the system whereas pH_{50} depends on the actual concentrations involved, the former will be used to characterize the extractive behaviour of a specified metal ion in the system under consideration.

In the case where the uncharged species MA_N is the only one extracted with a distribution coefficient λ and a complexity product β_N, the following relation has been shown to be valid [4].

$$\log\ K_{av} = \frac{1}{N}\ \log\ \beta_N\ (1 + \lambda) \tag{2}$$

where it is assumed that N is the maximum coordination number of the metal ion for the ligand.

By changing the pK_a value of a chelating agent by a proper substitution we generally also change the K_d value of a compound. Conversely it might be possible to change the K_d value of a compound without influencing the pK_a value to any larger degree.

In the acetyl-, propionyl-, butyryl-, valeryl- and capronyl substituted pyrazolones we have such a set of compounds where we expect the pK_a values to remain almost constant throughout the series.

In Fig. 2 is shown a plot of log K_{av} against $pK_{a,E}$ for these compounds and different metal ions. The points corresponding to a specified metal ion are seen to satisfy a linear relationship.

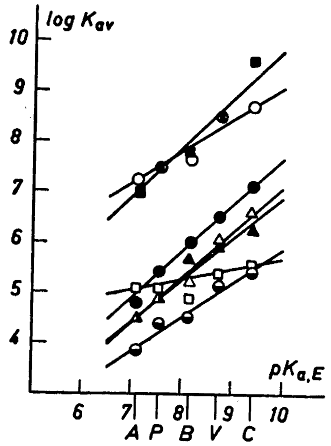

Fig. 2. The apparent mean complexity constants of the 4-acetyl (propionyl, butyryl, valeryl, capronyl) substituted pyrazolones (A, P, B, V, C) with different metal ions in a chloroform-water system plotted against the apparent p$K_{a,E}$ values of the chelating agents in this system.

■Th^{4+}, ○UO_2^{2+}, ●Pb^{2+}, △Zn^{2+}, ▲La^{3+}, □Be^{2+}, ◓Mn^{2+}

As is well established [6] a relationship between $\frac{1}{N}\log\beta_N$ and pK_a for a series of related compounds can be expressed as:

$$\frac{1}{N}\log\beta_N = r\mathrm{p}K_a + q \qquad (3)$$

This equation implies that for pK_a constant β_N will also be constant, and the plot in Fig. 2 should then be expected to represent a relationship between the distribution coefficients K_d and λ.

A linear relationship between the logarithm of the distribution coefficients as

$$\frac{1}{N}\log(1+\lambda) = s\log(1+K_d) + t \qquad (4)$$

when combined with (3) leads to (5)

$$\frac{1}{N}\log\beta_N(1+\lambda) = \log K_{av} = s\mathrm{p}K_{a,E} + (r-s)\,\mathrm{p}K_a + (q+t) \qquad (5)$$

expressing the above observed linear relationship between log K_{av} and p$K_{a,E}$ when pK_a is assumed constant.

The behaviour of each metal ion in the above described systems may therefore be regarded as characterized by the combined action of eqns (3) and (4), and hence on the constants r, q, s, and t.

The magnitudes of s and t might be expected to depend much on the choice of organic solvent whereas r and q can be regarded as independent of this choice.

It is seen that the values of s in the order of magnitude of 0.85 to 1.00 are most common. For the uranyl and manganese ions values 0.60 to 0.65 are found and for the beryllium ion a value as low as 0.20.

That s and r are generally of different magnitude is exemplified in Fig. 3 which shows available data of log K_{av} for the beryllium ion and uranyl ion plotted against p$K_{a,E}$ for variously substituted pyrazolones. The change in

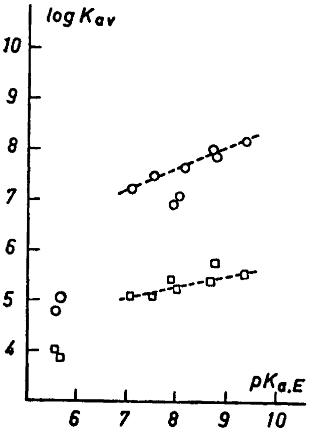

Fig. 3. The apparent mean complexity constants for variously substituted pyrazolones with the uranyl ion (O) and the beryllium ion (□) in a chloroform-water system plotted against the apparent $pK_{a,E}$ values of the chelating agents in this system. Data in Table 1.

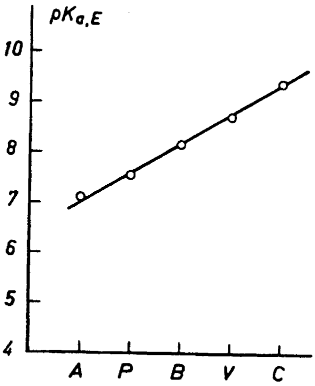

Fig. 4. The apparent $pK_{a,E}$ values of 4-acetyl (propionyl, butyryl, valeryl, capronyl) substituted pyrazolones (A, P, B, V, C) in chloroform plotted as a function of substitution.

$pK_{a,E}$ must be attributed to changes in either pK_a, K_d or in both. The plot contains the data used in the construction of Fig. 2, shown to lie on the dashed lines. In Fig. 3 no simple straight line relationship, apart from this, can be found.

To the author it seems to be too optimistic to expect the validity of eqn (5) to be strictly conserved in changing pK_a and K_d at will. No sharp definition of what is meant by "closely related compounds", can be set up. Many factors, such as steric hindrance, *etc.*, which may alter the complexity constants cannot be included in an equation like (5). Therefore an expression of general validity cannot be expected to be found.

It might be of interest to show the effect of substitution on the distribution coefficient K_d of a chelating agent.

In Fig. 4 is shown a plot of $pK_{a,E}$ in going from acetyl substitution on the pyrazolone through propionyl, butyryl, valeryl to capronyl substitution. A linear relationship is obvious. The slight alternating effect shown might be significant. As is to be expected, an increase of the aliphatic sidechain parallels an increase in lipophilic character of the chelating agent, and hence increases its distribution coefficient between an organic phase and water.

The data used in the construction of Figs. 2, 3 and 4 are collected in Table 1.

The empty places in the table indicate cases where the capacity of the systems has been exceeded by the concentrations used. This means that precipitations of chelates occurred during the titration, and hence no K_{av} values could be determined. The concentrations of chelating agents were 0.05 M, and those of the metal salts *ca.* 0.005 M, in the titration experiments [4]. With metals,

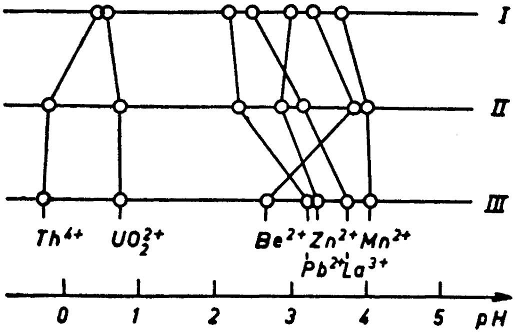

Fig. 5. The pH values of 50 % extraction of tracer amounts of different metals by 1 M solutions of 4-butyryl-1-phenyl-3-methyl-pyrazolone-5 (I) and 4-capronyl-1-phenyl-3-methyl-pyrazolone-5 (II) in chloroform are compared with those for thenoyltrifluoroacetone (III).

which form slightly soluble hydroxides, these were often precipitated when alkaline conditions were reached during the titration. These precipitations did not interfere with the determinations of the K_{av} values, as the pH changes of importance for this determination occurred in acid media.

For each system the pH_{50} of 50 % extraction of tracer amounts of the metal by 1 M solutions of the chelating agent in chloroform can be calculated by means of the following relation [1,4]

$$pH_{50} = pK_{a,E} - \frac{1}{N} \log \beta_N \ (1 + \lambda) \qquad (6)$$

This pH_{50} value is identical with the constant $\frac{1}{N}$ log K used by Dyrssen to characterize the metal ion, chelate, solvent systems.

Inspection of Table 1 shows that, except for the beryllium ion, no large change in the pH_{50} is observed when varying the substituents in the 1-phenyl-3-methyl-pyrazolone-5 nucleus. Data for thenoyltrifluoroacetone (TTA) in chloroform, determined by the titration procedure, have been included in the table.

In Fig. 5 the pH_{50} values determined from eqn (6) for the butyryl- and capronyl-derivatives are compared with those of TTA.

CONCLUSIONS

It has been the aim of the present investigation to separate and clarify some of the various factors involved in metal ion extractions by chelating agents. The ultimate goal of such an investigation is to find chelating agents with properties which make them suitable for a large scale application, *e. g.* in the reprocessing of spent reactor fuels.

Chelating agents might be found which serve well in the laboratory where losses of chemicals and attainments of equilibria play a smaller role than in a large scale application, where a compound for those reasons might be useless.

Table 1.

Substituent R	$pK_{a,E}$	$\frac{1}{N} \log \beta_N (1 + \lambda)$						
		$Th^{4}+$	$UO^{3}+$	$La^{3}+$	$Pb^{2}+$	$Zn^{2}+$	$Mn^{2}+$	$Be^{2}+$
Acetyl	7.10 ±0.1	7.00 ±0.2	7.25 ±0.2	4.50 ±0.15	4.80 ±0.15	4.50 ±0.15	3.85 ±0.15	5.1 ±0.15
Propionyl	7.55 ±0.1	7.50 ±0.2	7.50 ±0.2	4.90 ±0.15	5.42 ±0.15	4.90 ±0.15	4.40 ±0.15	5.1 ±0.15
Butyryl	8.17 ±0.1	7.75 ±0.2	7.65 ±0.2	5.70 ±0.15	6.00 ±0.15	5.20 ±0.15	4.50 ±0.15	4.9 ±0.15
Valeryl	8.74 ±0.1	8.5 ±0.2	8.5 ±0.2	5.9 ±0.15	6.5 ±0.15	6.1 ±0.15	5.15 ±0.15	5.4 ±0.15
Capronyl	9.4 ±0.1	9.65 ±0.2	8.7 ±0.2	6.25 ±0.15	7.1 ±0.15	6.6 ±0.15	5.4 ±0.15	5.55 ±0.15
Ethoxy-carbonyl	7.95 ±0.1	not meas.	6.95 ±0.2	5.45 ±0.15	5.65 ±0.15	—	—	5.45 ±0.15
Chloro-acetyl	5.7 ±0.1	5.65 −0.2	5.05 ±0.2	3.42 ±0.15	4.1 ±0.15	—	—	3.84 ±0.15
Trifluoro-acetyl	5.6 ±0.15	not meas.	4.8 0.2	not meas.	not meas.	not meas.	not meas.	4.0 ±0.15
Benzoyl	8.1 ±0.1	7.7 ±0.2	7.1 ±0.2	5.65 ±0.15	6.25 ±0.15	—	—	5.25 ±0.15
p-Bromo-benzoyl	8.80 ±0.1	8.50 ±0.2	7.9 ±0.2	6.5 ±0.15	7.2 ±0.15	—	—	5.25 ±0.15
p-Nitro-benzoyl	7.6 ±0.1	—	—	—	—	—	—	—
Thenoyltri-fluoroacetone	8.45 ±0.1	8.75 ±0.2	7.75 ±0.2	4.7 ±0.15	5.25 ±0.15	5.1 ±0.15	4.4 ±0.15	5.6 ±0.15

Many polyvalent metal ions show a large degree of hydrolysis even in rather acid solutions, so a chelating agent capable of extraction of these metals from strongly acid solutions would seem to be desirable, as then problems of adsorption and colloid formation could be avoided. Fortunately the polyvalent metal ions are also prone to complex formation so they will possibly combine with a chelating agent even if it is slightly dissociated, *i. e.* in acid solution.

By increasing the acid strength of a chelating agent a correspondingly larger concentration of the complexing anion can be obtained in acid solutions. But, as is well established, the increase in acid strength of an acid, within a series of closely related compounds, parallels a decrease in the metal ion affinity of the anion. The net result of a variation of pK_a in a series of chelating agents might therefore well be only a slight change in the pH_{50} of a metal ion when going from one compound to the other. This has in fact been shown to be the case for the compounds discussed in this paper.

With regard to the separation possibilities, inspection of Fig. 5 shows, that in some cases the acylated pyrazolones are inferior; in other cases superior to

TTA. On the average the capronyl substituted pyrazolone seems to offer even better separation possibilities than TTA for the metal ions investigated.

As the capacities of the systems investigated are rather large, and the separation possibilities adequate for many purposes, the compounds show promise as extractive chelating agents, for analytical and radiochemical work.

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REFERENCES

1. Dyrssen, D. *Svensk Kem. Tidskr.* **68** (1956) 212.
2. Morrison, G. H. and Freiser, H. *Solvent Extraction in Analytical Chemistry.* John Wiley and Sons. New York 1957.
3. Skytte Jensen, B. *Acta Chem. Scand.* **13** (1959) 1668.
4. Skytte Jensen, B. *Acta Chem. Scand.* **13** (1959) 1347.
5. Dyrssen, D. *Svensk Kem. Tidskr.* **64** (1952) 213.
6. Martell, A. E. and Calvin, M. *Chemistry of the Metal Chelate Compounds,* Prentice Hall Inc. New York 1953.

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