

THE COMPARISON OF TWO GRAPHICAL METHODS FOR THE DETERMINATION OF STABILITY CONSTANTS

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The stability of the ternary zinc(II) complexes with acetylacetonate (HA) and heterocyclic bases (quinoline, isoquinoline, acridine) and aromatic amines (1-naphthylamine, 2-aminopyridine) (B) of the ZnA_2B type, formed during extraction of a zinc(II) salt into benzene, were studied. The equilibrium is characterized by a two-phase stability constant (*i.e.* the product of the stability constant and the distribution constant), which has been determined by a two-parameter method. The results obtained by the graphical method proposed in the first communication and by the two-parameter method were compared on extraction systems with pyridine and aniline and on a system with quinoline. The distribution ratio for the zinc(II) salt was measured radiometrically in dependence on the equilibrium concentration of the base in the aqueous phase.

In the first communication¹, extraction equilibria for the formation of ternary zinc complexes with acetylacetonate and pyridine or aniline or their methyl derivatives were studied. The formation of ternary zinc complexes with these substances can be interpreted as addition of one or two molecules of the nitrogen-containing base to the zinc acetylacetonate, the resulting complex being characterized by a higher stability and extractability than the initial chelate. Two types of extraction equilibria have been found.

The first type is successive formation of the complexes with one and two molecules of a pyridine base, the metal distribution ratio increasing with the base equilibrium concentration in the aqueous phase from the value equal to the distribution constant of the initial chelate up to the value of the distribution constant for the dipyridine chelate (the dependence is sigmoid). The other type is direct formation of dianiline chelates, where, however, the distribution constant for the ternary complex cannot be found from the experimental dependence of the distribution ratio on the base concentration.

In the previous work¹, a graphical method for the determination of the stability constants for ternary complexes formed in extraction systems of the first type has been derived and also applied to the second type extraction systems, where, however,

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the experimental data must be handled with the help of a distribution constant obtained by extrapolation. Hence we decided to verify the application range of the graphical method¹, by comparing it with the two-parameter method². For this purpose we selected synergistic extractions of zinc(II) salts with acetylacetonone and nitrogen-containing organic bases into benzene. As the bases, quinoline, isoquinoline, acridine, 1-naphthylamine and 2-aminopyridine were chosen; ternary complexes with zinc(II) acetylacetonate have not been studied with any of these bases. Systems with pyridine and aniline, studied in paper¹, were measured again and are given here for the sake of comparison.

EXPERIMENTAL

Chemicals

Acetylacetonone (Lachema, Brno) and isoquinoline (Úrxovy závody, Valašské Meziříčí) were distilled. The other chemicals (Lachema, Brno) were of *p.a.* purity.

Procedure

The benzene and aqueous phases were prepared by the procedure described earlier¹. The organic bases were dissolved in the benzene phase, together with acetylacetonone. The aqueous phase contained $5 \cdot 10^{-5} \text{M} \cdot 6.5 \text{ZnSO}_4$ with an activity of about $15 \cdot 10^3$ impulses per ml. The overall electrolyte concentration was 0.1M (NaOH — NaClO₄). The distribution constants for quinoline, isoquinoline, 2-aminopyridine and acridine were determined by titration described in the previous work¹. The distribution constant for 1-naphthylamine was determined spectrophotometrically (Spektromom 201, MOM Budapest) at a wavelength of 740 nm. During the determination of the distribution constants of the bases the aqueous phase always contained 0.1M-NaClO₄.

RESULTS AND DISCUSSION

For the study of the synergistic extraction of zinc(II) salts with acetylacetonone and nitrogen-containing bases into benzene, a pH range from 7.4 to 8.4 (8.0 to 8.4 for 2-aminopyridine) was chosen, within which the distribution ratio of zinc during extraction with 0.1M acetylacetonone into benzene is independent of the pH (see Fig. 1 in ref.¹). The distribution of the bases in the two-phase system in this pH range is not affected by their protonation (see the pK_a values in Tables I and II). As the distribution ratio in the synergistic systems does not decrease below the distribution constant value for zinc(II) acetylacetonone ($\log K_D(O) = -0.65$) in the whole range of concentrations of base B (Fig. 1), we assume that the formation of cationic complexes ZnB_i^{2+i} in the aqueous phase does not affect the equilibria for successive formation of complexes of zinc(II) acetylacetonate with one and two molecules of the base under the given experimental conditions. The dependence of the distribution ratio of the zinc(II) salt, D, on the equilibrium concentration of the base in the aqueous phase, [B], for $[\text{Zn}] \rightarrow O$, is given by

$$D = (K_D(0) + K_1 K_D(1) [B] + K_2 K_D(2) [B]^2) / (1 + K_1 [B] + K_2 [B]^2), \quad (1)$$

where $[B] = c_B / (K_D(B) + 1)$ in the pH region where protonation of the base does not occur, c_B is the overall base concentration in the system, $K_D(B)$ its distribution constant and $K_D(i)$ the distribution constant of the i -th complex, ZnA_2B_i (A is the anion of the acetylacetonone enol-form). K_1 is the equilibrium constant for the addition of i molecules of base B to the acetylacetonate in an aqueous medium

$$K_1 = [ZnA_2B_i] / [ZnA_2] [B]^i. \quad (2)$$

The basis of the graphical method proposed in work¹ is conversion of relationship (1) into a normalized form

FIG. 1

Synergistic Extraction of a Zinc Salt with Acetylacetonone and Nitrogen-Containing Bases into Benzene

$[B]$ is the equilibrium base concentration in the aqueous phase (mol. l^{-1}); 0.100M acetylacetonone, pH 7.80–8.40, 20°C. Curve 1 quinoline, 2 isoquinoline, 3 acridine, 4 1-naphthylamine, 5 2-aminopyridine. With curve 3, the application of the two-parameter method is shown, i.e. the asymptotes and the x -coordinate of their intercept, yielding the $K_D(1) K_1 K_D(0)$ value, see relationship (4).

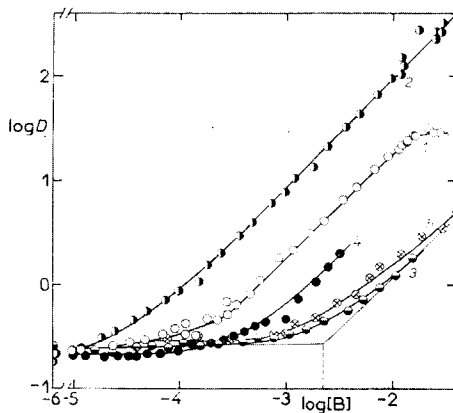


TABLE I

Stability Constants K_1 (ZnA_2, iB) and Distribution Constants $K_D(i)$ for Ternary Complexes of Zinc with Acetylacetonone and Nitrogen-Containing Bases in 0.1M- $NaClO_4$ at $\approx 20^\circ C$

Base	pK_a^a	$\log K_D(B)^b$	$\log K_1$	$\log K_2$	$\log K_D(1)$	$\log K_D(2)$
Pyridine	5.23	0.42 ^c	1.07	1.88	1.07	1.32
			1.34 ^c	2.20 ^c	0.99 ^c	1.43 ^c
Quinoline	4.94	1.94	2.30	4.20	0.90	1.46
Aniline	4.58	1.00 ^c	—	0.80	—	1.66
			—	-0.10 ^c	—	1.70 ^c

^a The dissociation constant of the protonated form of the base at 20°C according to ref.¹⁰;

^b the base distribution constant in the 0.1M- $NaClO_4$ —benzene system; ^c see ref.¹.

$$D' \equiv (D - K_D(0))/K_D(2) = (K_1\Delta_1[B] + K_2\Delta_2[B]^2)/(1 + K_1[B] + K_2[B]^2), \quad (3)$$

where $\Delta_i = (K_D(i) - K_D(0))/K_D(2)$. For small base concentrations, $[B]$, $D \approx K_D(0)$; for large concentrations, $D \approx K_D(2)$. This holds rigorously for the first type of complexation equilibria in work¹, where the $K_D(2)$ value is measurable. With the second type, the $K_D(2)$ value is obtained by extrapolation of the $1/D$ vs $1/[B]$ dependence to zero and hence is subject to an error, the magnitude of which can be assessed by comparing the experimental curve with the theoretical dependence of $\log D$ vs $\log [B]$, calculated from the constants obtained. On further handling of the data with the first type of system, the $\log D'$ dependence on $\log [B]$ is represented by a straight line with unit slope (see Fig. 2, straight lines 3 and 4) and the values of $-\log K_1\Delta_1$ and $-0.5 \log K_2$ are obtained as intercepts on the ordinate at $\log D' = 0$

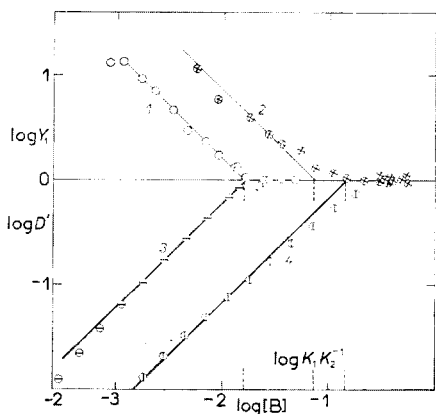


FIG. 2

The Determination of Fraction K_1/K_2 by Two Graphical Methods

K_1 is defined by relation (2). The two-parameter method²: $Y_1 = K_D(2)/D$, where $K_D(2)$ is the distribution constant of ZnA_2B_2 . The asymptotes of the curves for dependences $\log Y_1 = \log(1 + K_1/K_2[B])$ on $\log [B]$: 1 quinoline, 2 pyridine. Method according to ref.¹: D' is given by relation (3), 3 quinoline, 4 pyridine. The experimental values for quinoline are taken from Fig. 1; extraction with pyridine was carried out under the same experimental conditions.

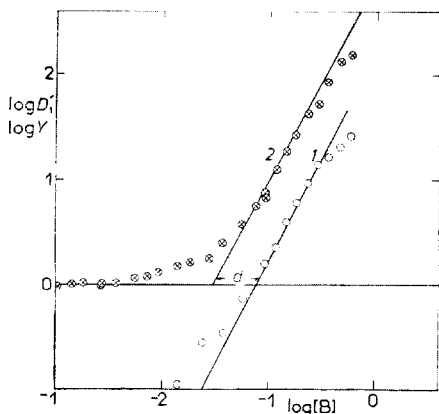


FIG. 3

Comparison of the Graphical Methods for Aniline

Straight line 1 is the dependence, $\log D'_1 \equiv \log D' \cdot K_D(2)$ on $\log [B]$, for $K_D(2)$ see Table I. For D' see relation (3). Straight line 2 is the asymptote to dependence $\log Y = \log D/K_D(0)$ on $\log [B]$, where $K_D(0)$ is the distribution constant for ZnA_2 . $d = 0.5 \cdot \log [K_D(2) K_2/K_D(0)] - 0.5 \log [K_D(2) K_2] = -0.5 \log K_D(0)$.

or $\log D' = -0.30$, respectively. Since the relationship, $K_1\Delta_1 = K_2/K_1$, is valid, the values, K_1 , K_2 and $K_D(1)$ and $K_D(2)$, can be determined. The second equilibrium type, which directly yields a complex with two base molecules, is characterized by a slope of the $\log D'$ vs $\log [B]$ dependence equal to two (Fig. 3, straight line 1). The $-0.5 \log K_2$ value can then be found as the intercept for ordinate $\log D' = 0$. The addition constants, K_1 and K_2 , obtained by this method are comparable with the constants obtained potentiometrically or polarographically in aqueous solution, even for different initial complexes, provided that the central metal is in the same oxidation state with the same local symmetry of the ligand arrangement³. The results given in Table I can thus be compared *e.g.* with the stability constants of mono- and dipyrindinozinc(II) complexes, $Zn(py)_i^{2+}$, determined by Gaur and Sharma⁴ polarographically in 0.1M-KNO₃ at a temperature of $30 \pm 0.01^\circ C$ as $\log K_1 = 0.90$ and $\log K_2 = 1.53$.

The two-parameter method of Dyrssen² was developed for extraction systems in which only a single complex is present in one of the two phases. With the first type of system, existence of complex ZnA_2B can be assumed in the organic phase for small concentrations of $[B]$ (see Fig. 8 in work¹, curve 3) and only complex ZnA_2B_2 exists at large concentrations of $[B]$. With the second type of equilibrium, complex ZnA_2B_2 exists in the organic phase in the whole concentration range of $[B]$, corresponding to the increase in the distribution ratio. Hence, an identical relationship is obtained with the two systems for small values of $[B]$

$$Y \equiv D/K_D(0) = 1 + [B]^i \cdot K_D(i) K_i/K_D(0), \quad (4)$$

where $i = 1$ for the first type and $i = 2$ for the second equilibrium type, and the value of $-\log [K_D(i) K_i/K_D(0)]^{1/i}$ can be found as the x -coordinate for the intercept of the asymptotes to the curve of the $\log Y$ vs $\log [B]$ dependence. For large values of $[B]$, an analogous expression holds for the first type

$$Y_1 \equiv K_D(2)/D = 1 + K_1K_2^{-1}[B]^{-1}, \quad (5)$$

TABLE II

Two-Phase Stability Constants $K_D(1)K_1$ for Adducts of Zinc(II) Acetylacetonate with Nitrogen-Containing Bases in the 0.1M-NaClO₄-Benzene System at $\approx 20^\circ C$

Constant	Py	Quin	i-Quin	Acr	NA	AP
pK_a (sec ¹⁰)	5.23	4.94	5.40	5.60	3.92	6.86
$\log K_D(B)$	0.42 ^a	1.94	1.92	1.49	2.49	-0.48 ^b
$\log K_D(1)K_1$	2.50	3.30	3.93	1.95	2.82	2.35 ^b

^a See ref. ¹; ^b see ref. ⁹; Py pyridine, Quin quinoline, i-Quin isoquinoline, Acr acridine, NA 1-naphthylamine, AP 2-aminopyridine.

TABLE III
Comparison of the Stability Constants in the Benzene Phase ($\log \beta_1$) for the Adducts of Zinc(II) Chelates with Nitrogen-Containing Bases

Chelate	Py	Quin	i-Quin	2-MePy	3-MePy
Acetylacetonate	3.57	5.89	6.30	3.95 ^b	4.62 ^b
Salicylaldoximate	4.26 ^a	3.74 ^a	4.08 ^b	4.14 ^a	4.60 ^a
Cupferronate	3.54 ^b	—	—	—	—

^a See ref.⁵; ^b according to ref.¹; Py pyridine, Quin quinoline, i-Quin isoquinoline, 2-MePy 2-methylpyridine, 3-MePy 3-methylpyridine.

so that the x -coordinate of the intercept of the asymptotes yields the value of $\log K_2 K_1^{-1}$ (Fig. 2, straight lines 1 and 2). The K_2/K_1 values obtained by the two graphical methods are located within the calculated¹ standard deviations for $\log K_2$ (± 0.30 to ± 0.50). Direct addition of two base molecules to the chelate can be observed only with aniline among the newly studied systems (Fig. 3). From the difference in the values of segments d in Fig. 3, a $\log K_D(0)$ value 0.15 lower than the experimental value is obtained; this is relatively good agreement.

The extraction equilibria with isoquinoline, acridine, 1-naphthylamine and 2-aminopyridine are characterized by $\log D$ vs $\log [B]$ dependences (Fig. 1), whose shapes indicate that only complexes ZnA_2B exist in the organic phase. Hence it is useful to use the two-parameter method with this type of system for the determination of the $K_D(1) K_1$ value, the so-called two-phase stability constant. The constants obtained are given in Table II. The two-parameter method does not enable separation of the terms in product $K_D(i) K_i$, but enables obtaining of two-phase stability constants directly from the experimental curves (Fig. 1, curve 3), since the $\log Y$ value corresponds to the $\log D$ value less $\log K_D(0)$.

Rao and Dubey⁵ studied the formation of complexes of zinc(II) salicylaldoximate with a single molecule of an organic base and applied the two-parameter method for the calculation of the stability constants in the organic phase, which are related to our values by

$$\begin{aligned} \log \beta_1 &= \log [ZnA_2B]_{org} [B]_{org} / [ZnA_2]_{org} = \\ &= \log K_D(1) K_1 / K_D(0) + \log K_D(B), \end{aligned} \quad (6)$$

where subscript org denotes that the particular quantity is related to the organic phase. As the stabilities of various metal complexes with a nitrogen-containing base are determined solely by the strength of the metal-to-nitrogen bonds, as shown by

Fridman⁶, the formation constants of complexes can be compared when equally-dentate ligands are involved and the chelate rings have the same dimensions. This is confirmed by comparison of the results obtained in paper⁵ with our results for the same bases, given in Table III. The larger differences with quinoline and isoquinoline are probably caused by the use of concentration-dependent $K_D(B)$ values, taken by Rao and Dubey from ref.⁷.

Kirksey, Hambright and Storm⁸ determined the stability constants for mono-adducts of zinc(II) tetraphenylporphyrine with pyridine bases in benzene, using spectrophotometric titration. The order of the stability constants, 4-methylpyridine > 3-methylpyridine > pyridine > 2-methylpyridine, found by the authors is in agreement with our order of the stability constants for the monoadducts of zinc(II) acetylacetonate in the organic phase (Table III).

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