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Studies on Extraction of Transition Metal Complexes of 3,4-Dimethylpyridine and 3,5-Dimethylpyridine with Oxygen-Containing Solvents

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Abstract

On the basis of a correlation between the degrees of formation α_n of successive 3,4-dimethylpyridine and 3,5-dimethylpyridine complexes of Co(II), Ni(II), Zn(II), and Cd(II) in aqueous solution; extraction percent E; and partition coefficients D; the distribution constants P_n of successive complexes passing to the organic phase during extraction have been determined. The measurements were carried out at a fixed ionic strength $I = 0.5$ at 25°C, using solutions of the dimethylpyridines in oxygen-containing solvents.

Alkylpyridines in organic solvents have been recommended in a patent specification (*1*) as effective and selective solutions for the extraction of Co(II), Cu(II), and Zn(II) from aqueous media. The purpose of this cycle of preliminary investigations is to determine factors affecting the extraction of some transition metals with pyridine derivatives. In the first article of this cycle, a correlation was found between the formation degrees of successive 3,5-dimethylpyridine complexes in aqueous solution, $\alpha_n = f([L])$, and percentage extraction of a metal ion, $E = f([L])$ (*2*).

In the second article (*3*) we pointed out, taking as examples 3-methyl- and 4-methylpyridine complexes, that this correlation could be fundamental for the determination of the composition of extractable species. Analogous correlations had been observed earlier during studies on the extraction of alkylimidazole complexes of transition metals (*6, 7*).

The purpose of this study was to determine the composition of the Co(II), Ni(II), Zn(II), Cu(II), and Cd(II) complexes of 3,4-dimethyl- and 3,5-dimethylpyridine extracted with oxygen-containing solvents.

EXPERIMENTAL

Reagents

3,4- and 3,5-Dimethylpyridines (Fluka AG) were purified by fractional distillation. Nitric acid (analytical reagent; Nitrogen Works, Tarnów) was standardized against anhydrous sodium carbonate or borax. The concentration of the metals in solutions of the Co(II), Ni(II), Zn(II), Cd(II), and K(I) nitrates was determined gravimetrically or volumetrically by titration with a di-Na EDTA solution.

The following organic solvents were used: 2-pentanol, 2-butanol, cyclohexanol, cyclohexanone, and mixtures of 2-butanol with benzene and with benzyl alcohol taken in various proportions. All these solvents were additionally purified by fractional distillation.

Instrumentation

The measurements of pH were carried out by means of a PHM-64 digital pH meter (Radiometer, Copenhagen) using a 2301C combination electrode. Absorption spectra of the aqueous and organic phase were taken on a Specord UV-VIS spectrophotometer (Carl Zeiss, Jena). The metal concentration after extraction was assayed colorimetrically using a Spekol (Carl Zeiss) spectrocolorimeter.

Procedure

All measurements were carried out at 25°C at a fixed ionic strength (0.5; KNO_3). The equilibrium concentration of the metals in the aqueous phase was determined colorimetrically by using sodium diethyldithiocarbamate as a complexing reagent. Other particulars concerning the procedure have been reported elsewhere (*3*).

Calculations

The extraction percent E was calculated from the difference between the metal concentration in the aqueous phase before and after the extraction:

$$E = \frac{c_M^0 - c_M}{c_M^0} 100\% \qquad (1)$$

where c_M^0 and c_M are metal concentrations in the aqueous phase before and after extraction, respectively.

The mean ligand concentration at equilibrium [L] was calculated from the pH value of the aqueous phase:

$$[\mathrm{L}] = \frac{K_a[\mathrm{HL}^+]}{[\mathrm{H}_3\mathrm{O}^+]} \tag{2}$$

where K_a is the dissociation constant of the conjugate acid of 3,4- or 3,5-dimethylpyridine, and HL^+ is the concentration of the salt heterocyclic base nitrate in the aqueous phase.

The K_a values of 3.16×10^{-6} and 1.03×10^{-6} for 3,4- and 3,5-dimethylpyridine, respectively, were determined by us earlier (*4*, *5*).

For each system the degree of formation of successive complexes, α_n, was then calculated at arbitrary equilibrium ligand concentrations from

$$\alpha_n = \frac{\beta_n[\mathrm{L}]^n}{\sum_{n=0}^{n=N} \beta_n[\mathrm{L}]^n} \tag{3}$$

The values of cumulative stability constants β_n were taken from Refs. *4* and *5*.

RESULTS AND DISCUSSION

Of the solvents used in this work, 2-butanol, 2-pentanol, and cyclohexanone proved to be effective for the extraction of Ni(II), Co(II), and Cu(II) complexes with 3,4-dimethylpyridine, whereas cyclohexanone was effective for the Cd(II) and Zn(II) complexes with this ligand. Complexes of Zn and Cd are not extracted by 2-butanol. Typical extraction curves for these ligands, $D = f(\mathrm{pH})$, are shown in Figs. 1–3. In all cases, with the exception of the Zn(II)–2-pentanol system, an increase in the pH of the aqueous phase was accompanied by an increase in the partition coefficient value D. This is due to the increase in the free ligand concentration [L] in the aqueous phase as the pH is raised, as shown by Eq. (2). With Zn(II) an increase in the ligand concentration in the aqueous phase presumably results in the formation of complexes which undergo more reluctant solvation, thus remaining in the aqueous phase.

The relationship between D and pH has usually been employed for the determination of the composition of extractable complexes (*3*). Assuming that in the extraction process only one complex passes to the organic phase, the reaction taking place during the extraction can be written as

$$[\mathrm{M(H_2O)_6}]^{2+} + n\mathrm{HL}^+ + 2\mathrm{NO}_3^- + x\mathrm{S} \rightleftharpoons [\mathrm{ML}_n\mathrm{S}_x(\mathrm{NO}_3)_2] + n\mathrm{H}^+ + 6\mathrm{H_2O} \tag{4}$$

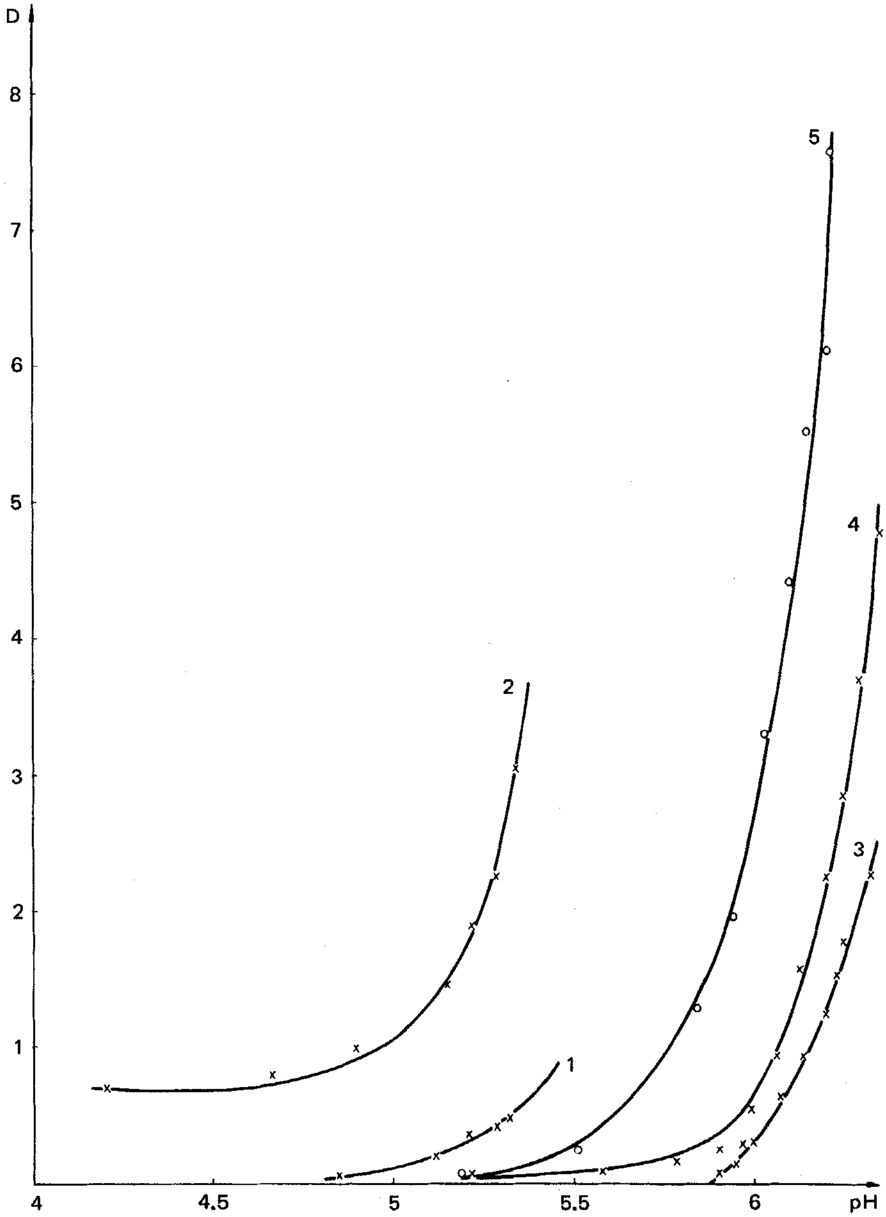

FIG. 1. Plots of the function $D = f(\mathrm{pH})$ for the systems Ni(II)–3,4-dimethylpyridine–2-pentanol (1); Ni(II)–3,4-dimethylpyridine–2-butanol (2); Ni(II)–3,4-dimethylpyridine–cyclohexanone (3); Co(II)–3,4-dimethylpyridine–cyclohexanone (4); Cd(II)–3,4-dimethylpyridine–cyclohexanone (5). [The initial concentration of metal = 0.02 M/dm^3; the ionic strength (KNO_3) = 0.5.]

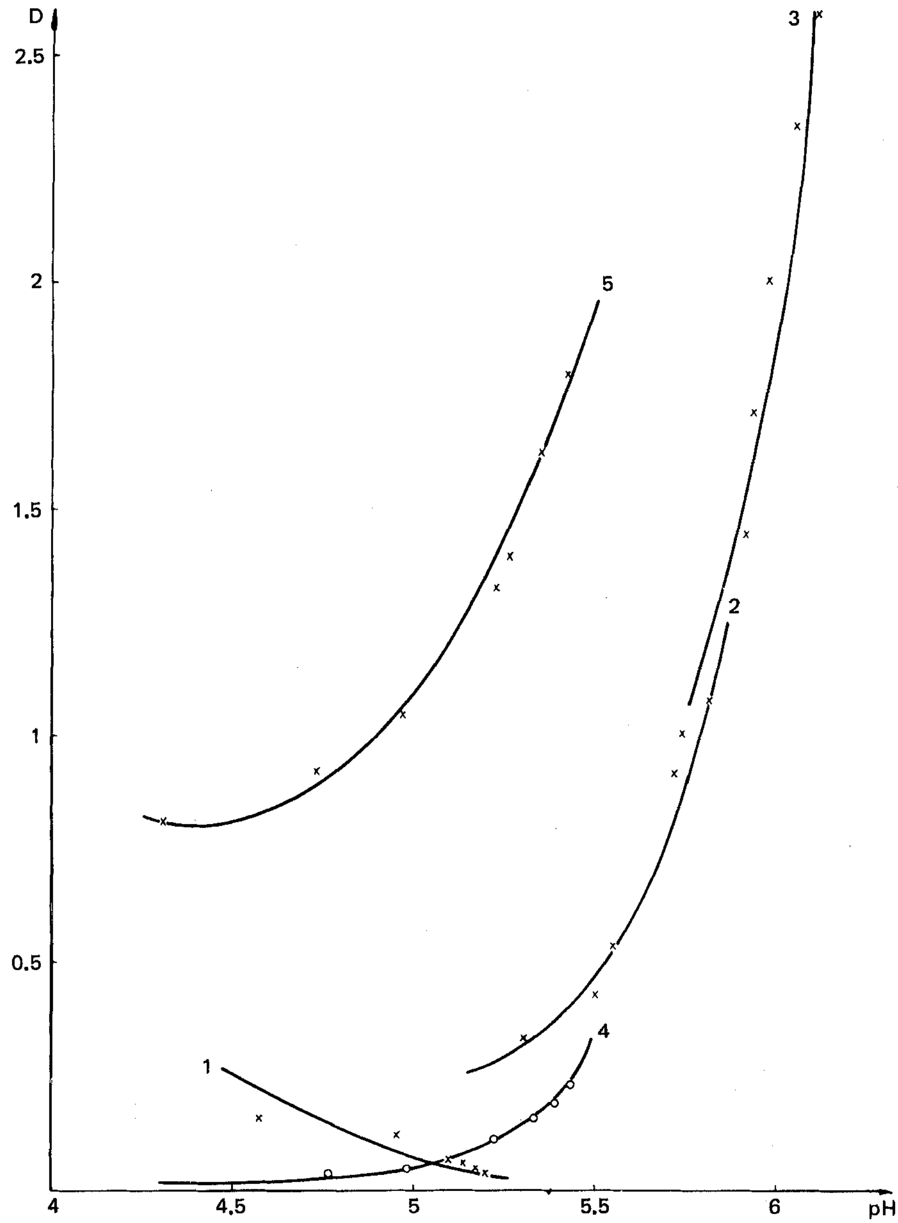

FIG. 2. Plots of the function $D = f(\mathrm{pH})$ for the systems Zn(II)–3,4-dimethylpyridine–2-pentanol (1); Zn(II)–3,4-dimethylpyridine–cyclohexanone (2); Zn(II)–3,4-dimethylpyridine–cyclohexanone + 10% of 3,4-dimethylpyridine solution (3); Co(II)–3,4-dimethylpyridine–2-pentanol (4); Co(II)–3,4-dimethylpyridine–2-butanol (5). [The initial concentration of metal = 0.02 M/dm^3; the ionic strength (KNO_3) = 0.5.]

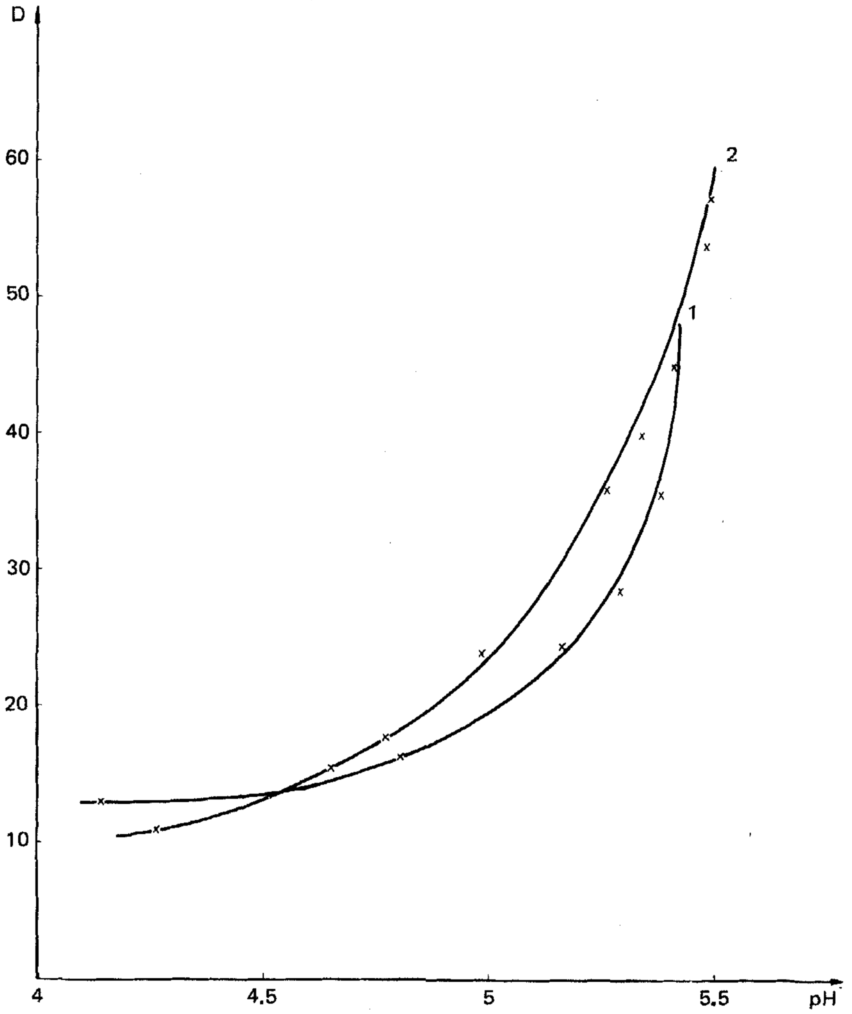

FIG. 3. Plots of the function $D = f(\mathrm{pH})$ for the systems Cu(II)–3,4-dimethylpyridine–2-pentanol (1); Cu(II)–3,4-dimethylpyridine–2-butanol (2). [The initial concentration of metal = 0.02 M/dm^3; the ionic strength (KNO_3) = 0.5.]

The equilibrium constant for this reaction is thus

$$K = \frac{[ML_nS_x(NO_3)_2][H^+]^n}{[HL^+]^n[NO_3^-]^2[S]^x[M(H_2O)_6^{2+}]} \tag{5}$$

Assuming that

$$D = \frac{[\mathrm{ML}_n\mathrm{S}_x(\mathrm{NO}_3)_2]_{\mathrm{org}}}{[\mathrm{M}(\mathrm{H}_2\mathrm{O})_6^{2+}]_{\mathrm{aq}}} \tag{6}$$

We obtain

$$\log D = n\mathrm{pH} + \log K + x \log[\mathrm{S}] + 2 \log[\mathrm{NO}_3^-] + n\,[\mathrm{HL}^+] \tag{7}$$

Equation (7) was used to determine the composition of complexes passing to the organic phase. By plotting log D against pH, straight lines are obtained whose slopes correspond to the number of the ligand molecules attached to the metal ion being extracted. Other concentration values in Eq. (7) are constant.

Numerical values of slopes are listed in Tables 1 and 2.

The extraction was also characterized by a plot of the percentage extraction E against the free ligand concentration (Figs. 4–9). In these figures plots of the degrees of formation of successive complexes α_n against

TABLE 1

Individual Distribution Constants of Successive Metal Complexes with 3,4-Dimethylpyridine

		Individual distribution constants					
Metal	Solvent	P_1	P_2	P_3	P_4	P_5	tg_α
Cd(II)	Cyclohexanone				6.06		2.2
Cu(II)	2-Pentanol					55.5	1
Cu(II)	2-Butanol					66.6	0.73
Zn(II)	2-Pentanol			0.22			
Zn(II)	Cyclohexanone			0.91			1
Zn(II)	10% solution of 3,4-dimethylpyridine in cyclohexanone			13.3			2
Co(II)	2-Pentanol			0.63			1.5
Co(II)	2-Butanol			5.0			0.7
Co(II)	Cyclohexanone			0.83			2.66
Ni(II)	2-Pentanol				1.5		2
Ni(II)	2-Butanol				7.14		1.95
Ni(II)	Cyclohexanone				29.4		3.9

TABLE 2

Individual Distribution Constants of Successive Metal Complexes with 3,5-Dimethylpyridine

		Individual distribution constants				
Metal	Solvent	P_1	P_2	P_3	P_4	tg_a
Ni(II)	2-Pentanol		1.3	1.6		2.6
Ni(II)	10% solution of 3,5-dimethylpyridine in 2-pentanol		1.25	8.33		3.2
Ni(II)	Cyclohexanol		3.64	6.25		1.3
Co(II)	10% solution of 3,5-dimethylpyridine in 2-pentanol		0.91	4.0		0.7
Co(II)	Cyclohexanol		Straight line			0.2
Cu(II)	2-Pentanol				33.3	3.6
Cu(II)	2-Butanol			2.0	5.0	2.8
Zn(II)	2-Pentanol		5.25	40		3.0
Zn(II)	10% solution of 3,5-dimethylpyridine in 2-pentanol		0.5	52.6		2.6
Zn(II)	Cyclohexanol			140		3.0

the same variable are also shown. These extraction curves exhibit certain correlations with plots describing definite complexes in the aqueous phase. For instance, in the Zn(II)–3,4-dimethylpyridine–cyclohexanone system the shape of the extraction curve resembles that of α_3 (Fig. 4). A dissimilar shape of the curve is observed in the system Zn(II)–3,4-dimethylpyridine–2-pentanol where the E values decrease with increasing ligand concentration, and the shape resembles that of α_0. In this case the extraction process is determined by the reaction of the aquocomplex $[Zn(H_2O)_6]^{2+}$ with a molecule of 2-butanol. When the concentration of 3,4-dimethylpyridine is growing, the concentration of $[Zn(H_2O)_6]^{2+}$ decreases and the percent of extraction E also decreases, and the extraction curve is almost parallel to the free ligand concentration axis (Fig. 5).

The correlation between the extraction curves and those representing the degree of formation of complexes α_n is sometimes obscure (Figs. 7–9). Obviously, it depends on the number of metal complexes being extracted, their degree of solvation, and distribution constant values of particular complexes. To determine the composition and number of the metal complexes passing to the organic phase in each of the systems studied, we employed the method previously used to study the extraction of transition

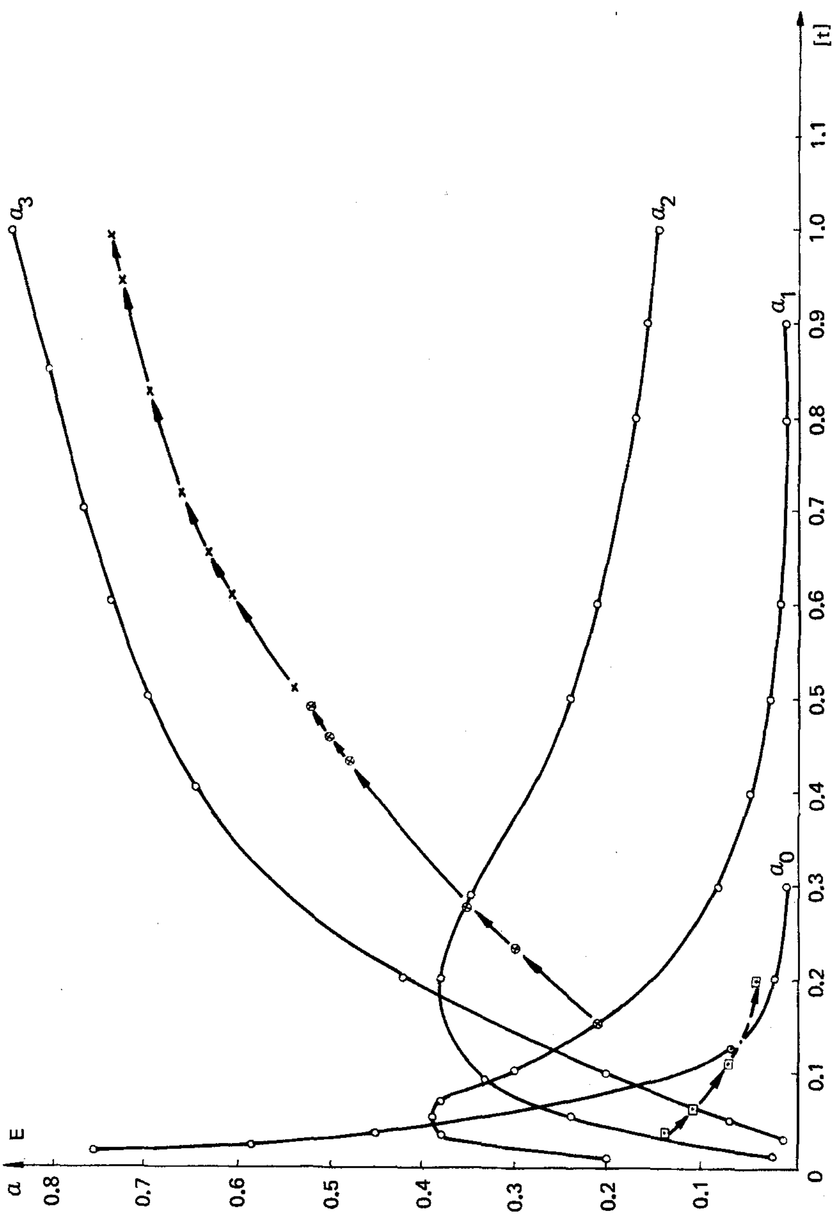

FIG. 4. $E = f([L])$ in the system Zn(II)–3,4-dimethylpyridine together with the degrees of formation α_n of successive complexes. 2-Pentanol (⊡); cyclohexanone (⊗); cyclohexanone + 10% solution of 3,4-dimethylpyridine (×).

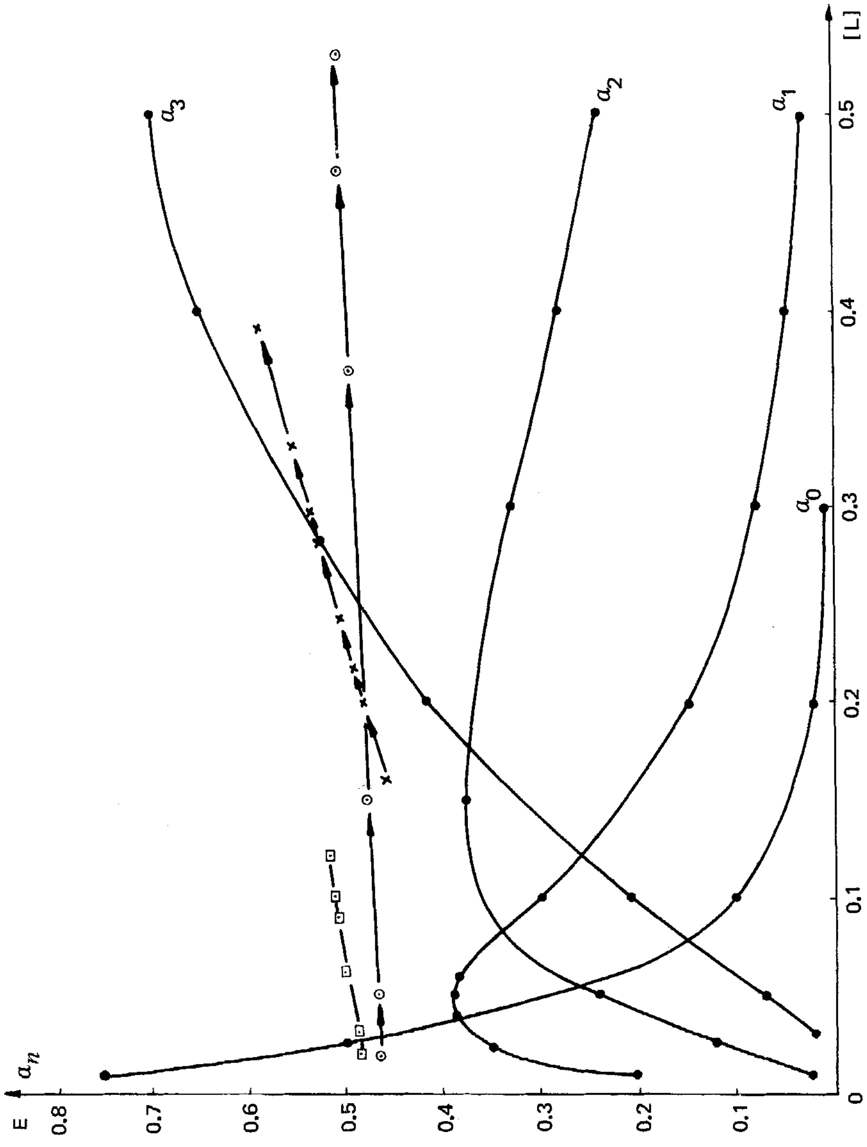

FIG. 5. $E = f([L])$ in the system Zn(II)–3,4-dimethylpyridine together with the degrees of formation α_n of successive complexes. Benzyl alcohol (×); 2-butanol (⊡); 2-butanol + benzene (1:1) (⊙).

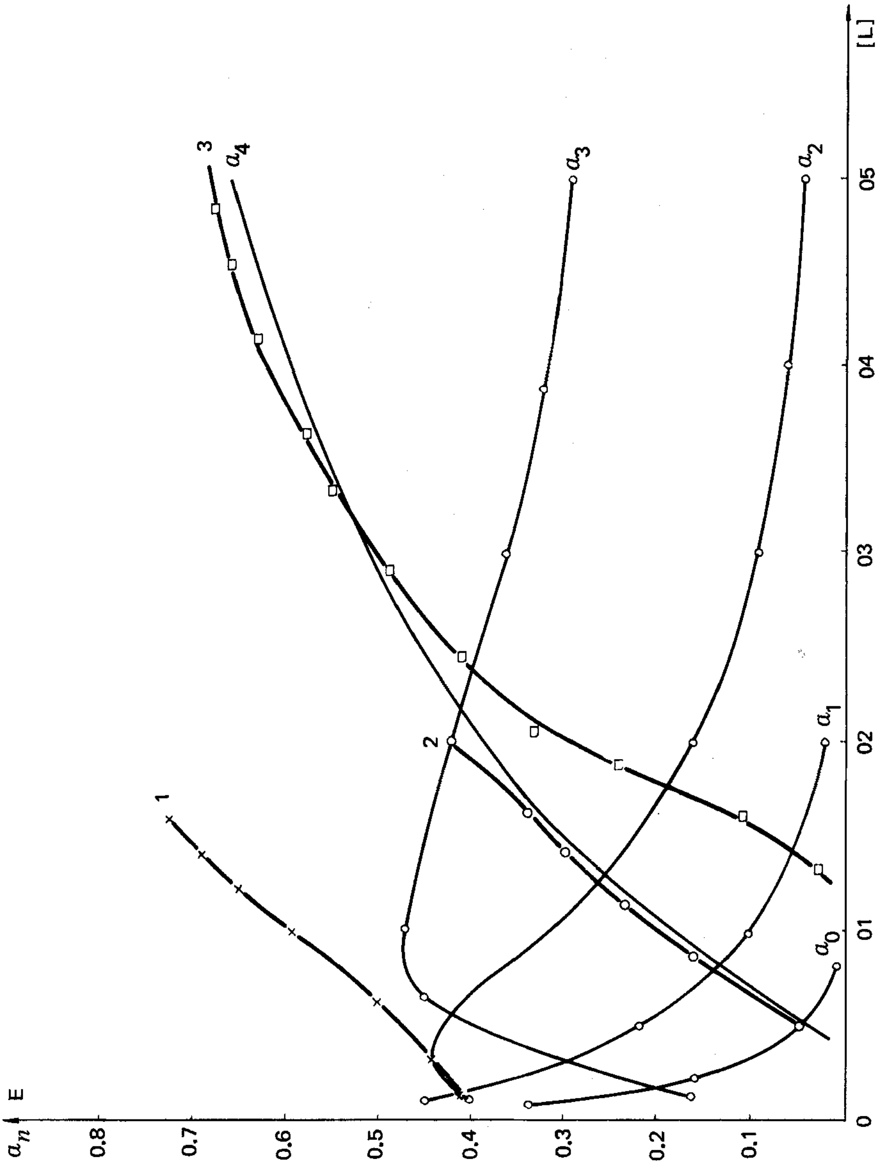

FIG. 6. $E = f([L])$ in the system Ni(II)–3,4-dimethylpyridine together with the degrees of formation α_n of successive complexes. Cyclohexanone (□); 2-butanol (×); 2-pentanol (○).

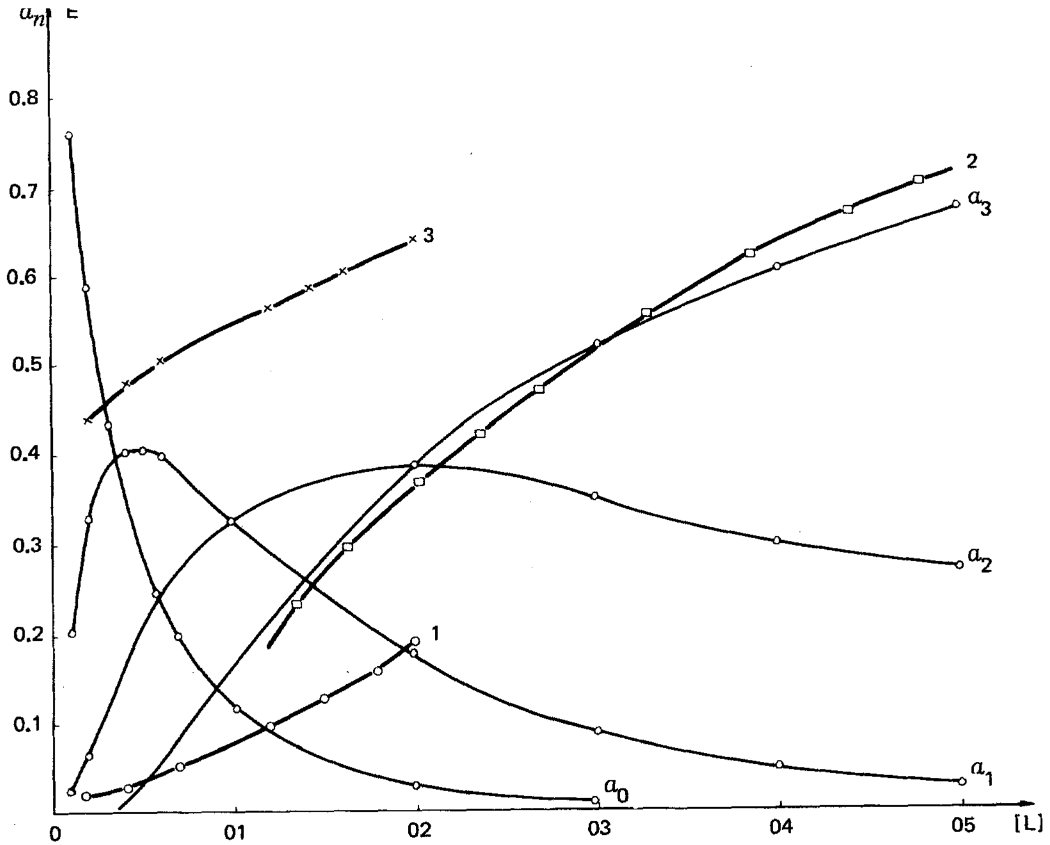

FIG. 7. $E = f([L])$ in the system Co(II)–3,4-dimethylpyridine together with the degrees of formation α_n of successive complexes. 2-Butanol (×); 2-pentanol (○); cyclohexanol (□).

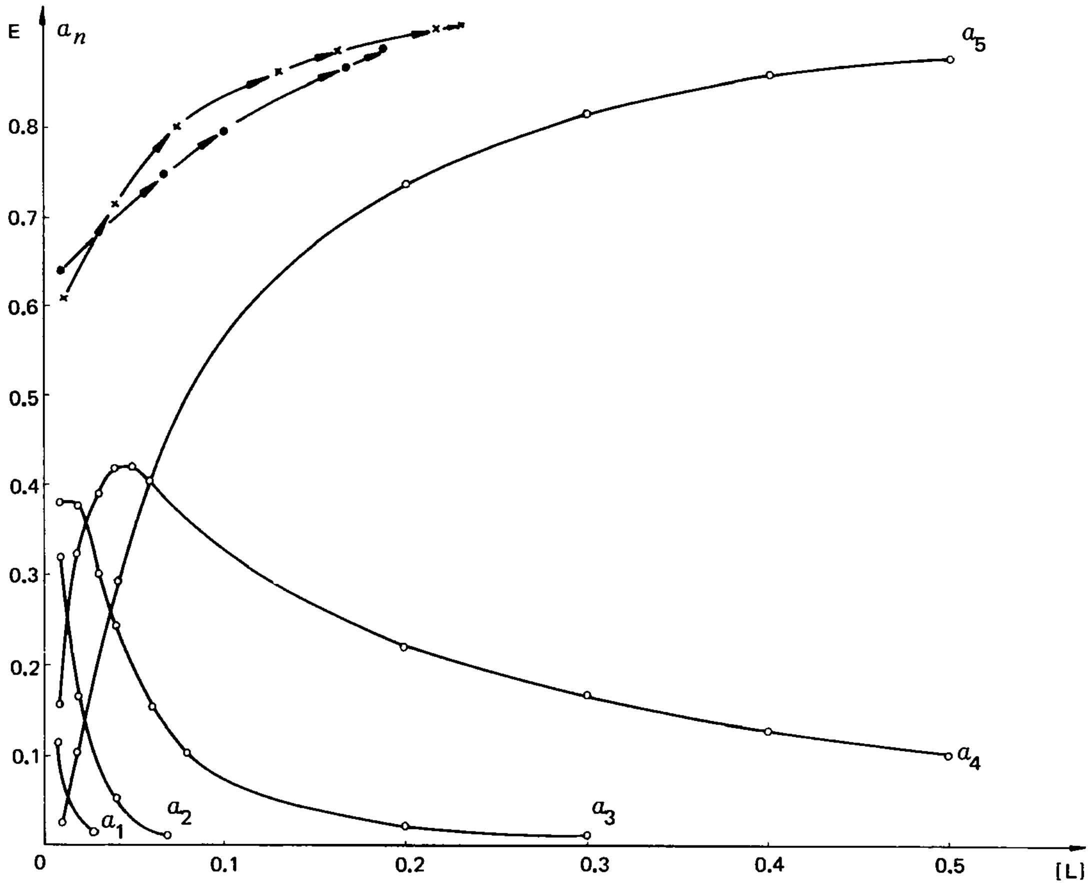

FIG. 8. $E = f([L])$ in the system Cu(II)–3,4-dimethylpyridine together with the degrees of formation α_n of individual complexes. 2-Pentanol (●); 2-butanol (×).

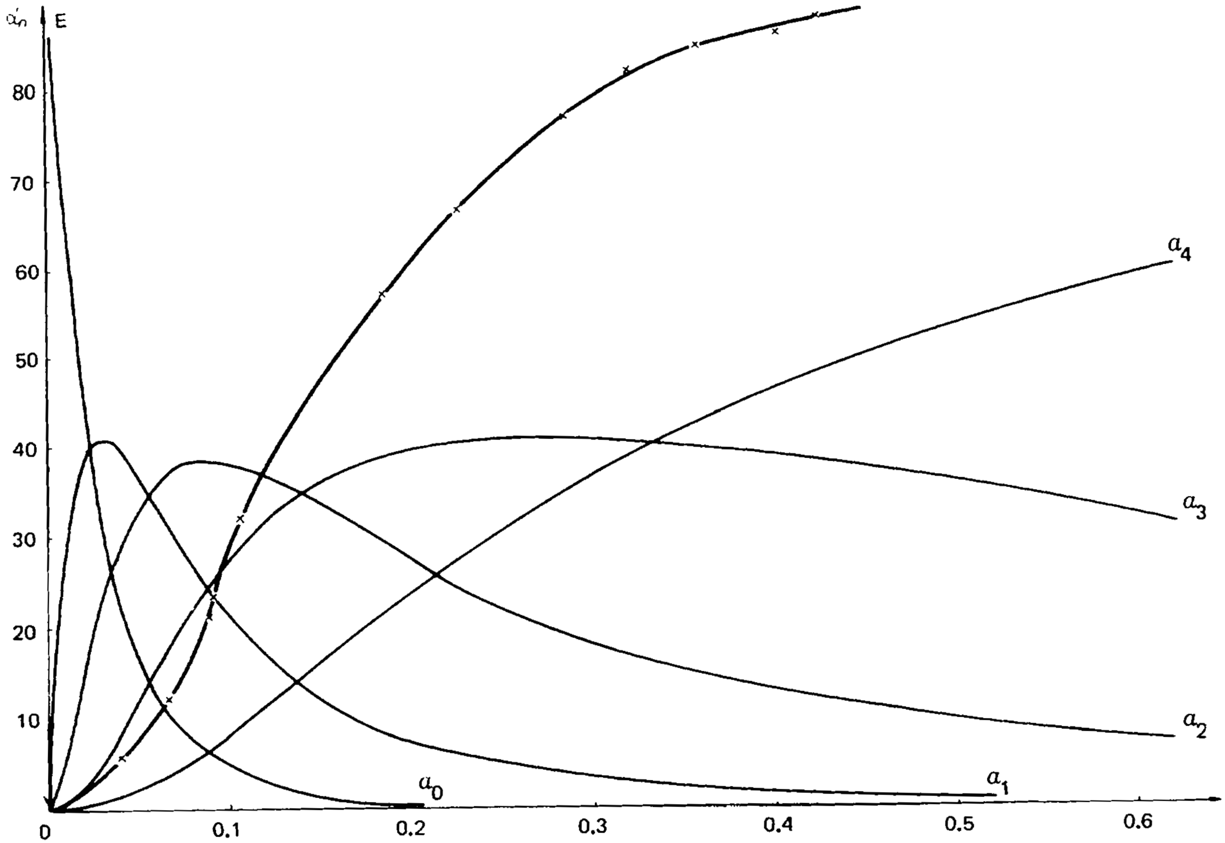

FIG. 9. $E = f([L])$ in the system Cd(II)–3,4-dimethylpyridine–cyclohexanone together with the degrees of formation of individual complexes.

metal complexes with imidazole (*6*, *7*) and pyridine (*2*, *3*) derivatives. The individual distribution constants of successive complexes P_n are determined by this method graphically from the relationship between D and α_n. The reliability of the P_n values obtained in this way was subsequently checked by calculation of the extraction curves $E = f([L])$ using these values. The P_n values were considered reliable when both curves, i.e., the experimental and the theoretical ones, overlapped. The results characterizing the extraction of the 3,4- and 3,5-dimethylpyridine complexes are shown in Tables 1 and 2.

The data of Table 1 show that of the Co(II) and Zn(II) complexes with 3,4-dimethylpyridine, only those containing three molecules of the ligand are extracted. In the case of the Ni(II) and Cd(II) complexes, the ML_4 species are extracted, whereas with Cu(II) the ML_5 ones are extracted. Absorption spectra of the aqueous and organic phases revealed that all these complexes are six coordinate. One can thus assume that the remaining sites of the coordination sphere are occupied by the solvent molecules.

Analogous data concerning the extraction of the 3,5-dimethylpyridine complexes are summarized in Table 2. With this ligand, two complexes, ML_2 and ML_3, are usually extracted, with the exception of Cu(II), where the ML_3 or ML_4 species pass to the organic phase. As was observed previously (*3*) in the Ni(II)–3,5-dimethylpyridine system, a configurational octahedron square equilibrium takes place which depends on the ligand concentration. The Co(II) and Cu(II) complexes are six coordinate. It can thus be assumed that the remaining coordination sites are occupied by the solvent molecules.

To sum up, the following general conclusion can be drawn: The description of the extraction of metal complexes by means of individual distribution constants is more adequate than the characterization of a system by means of the slope of the $\log D = f(\mathrm{pH})$ line (*8*–*10*).

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