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A Relation between Stability of the Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) Complexes of 3- and 4-Methylpyridines in Solution and Extractability of These Complexes

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Abstract

The extraction of the 3- and 4-methylpyridine complexes of Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) with oxygen-containing solvents has been studied. A correlation has been found between stepwise formation of the complexes and the extent of extraction. The composition of extractable species has been determined.

3-Methylpyridine and 4-methylpyridine have been shown to form complexes of considerable stability with the first-row transition metal cations. These complexes are formed in aqueous solution according to the equation (*1–3*):

$$[M(H_2O)_6]^{2+} + nL \rightleftarrows [ML_n(H_2O)_{6-n}]^{2+} + nH_2O$$

Introduction of methylpyridine molecules to the coordination sphere of a metal undoubtedly increases the probability of passing a complex to the organic phase. Accordingly, one may expect that at a particular number of the methylpyridine molecules bound with the central ion, there should be a solvent available to ensure transition of the metal to the organic phase. Thus the extraction of the metal complexes depends on the concentration of a satisfactory hydrophobic species in aqueous solution. So far, studies on metal ion extraction have been focused on the determination of the

composition of extractable species by the equilibrium displacement (*4–10*), isomolar series (*11–16*), or saturation (*17–22*) methods.

In this article an attempt has been made to determine the composition of extractable species on the basis of a relation between the percent of extraction, E, partition coefficient, D, and stepwise degrees of formation of particular complexes, α_n. The complexes studied were those of 3-methylpyridine and 4-methylpyridine with Cd(II), Cu(II), Ni(II), Zn(II), and Co(II). Analogous investigations with other systems were carried out earlier (*23*).

EXPERIMENTAL

Reagents

3-Methylpyridine and 4-methylpyridine (Fluka AG) were purified by fractional distillation, fractions corresponding to their boiling points being collected. Nitric acid (Z.A., Tarnów, Poland) was standardized against sodium tetraborate decahydrate. Solutions of Co(II), Ni(II), Zn(II), Cu(II), and Cd(II) nitrates were prepared from recrystallized analytical grade reagents (Z. A., Tarnów) and their titre was determined by means of di-Na EDTA. In a similar manner, the KNO_3 (Z. A., Tarnów) solution was prepared, its concentration being determined gravimetrically as K_2SO_4. Acetylacetone, isoamyl alcohol, benzyl alcohol, *n*-hexanol, isobutanol, cyclohexanol, cyclohexanone, and CCl_4 were analytical grade reagents, purified by fractional distillation.

Instrumentation

The pH was measured by a PHM-64 (Radiometer, Copenhagen) digital pH meter using a GK 2301 C combination electrode. Absorption spectra were taken on a Specord UV-VIS (C. Zeiss, Jena) spectrophotometer.

Procedure

A solution of equal concentrations of a metal ion and methylpyridine conjugate acid, and a different concentration of a free base was prepared. To 9 cm^3 of this solution, 9 cm^3 of a solvent was added and the mixture was shaken for a few minutes to speed up attaining equilibrium. After phase separation the pH of the aqueous phase was measured and the metal concentration in it was assayed spectrophotometrically or volumetrically. The change in the volume of the phases was accounted for in calculations. All measurements were carried out at 25 ± 0.1°C at a fixed ionic strength (0.5, KNO_3).

To prevent hydrolysis of the complexes, a high and constant concentration (0.2 *M*) of a methylpyridine nitrate was maintained throughout.

Calculations

The percent of extraction, E, and the partition coefficient, D, were calculated from the metal concentrations in the aqueous phase before and after attaining equilibrium (C°_M and C_M, respectively):

$$E = \frac{C^\circ_M - C_M}{C^\circ_M} 100\%$$

$$D = \frac{C_{M\ org}}{C_M}$$

The equilibrium free ligand concentration in the aqueous phase, [L], was determined on the basis of pH measurements:

$$[L] = \frac{K_a(C_{HNO_3} - [H_3O^+])}{[H_3O^+]}$$

where K_a is the dissociation constant of the conjugate acid of a methylpyridine, C_{HNO_3} is the nitric acid concentration, and $[H_3O^+]$ is the hydronium ion concentration.

The K_a values for 4-methylpyridine and 3-methylpyridine (5.5×10^{-7} and 1.4×10^{-6}, respectively) were taken from Refs. *2* and *3*. The degrees of formation, α_n, at arbitrary ligand concentrations were calculated from

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

The cumulative stability constants, β_n, were taken from Refs. *2* and *3*.

RESULTS AND DISCUSSION

The results of extraction experiments are shown in Figs. 1–3 in the form of the $D = f(\text{pH})$ plots. In all systems a distinct increase in the partition coefficient values is observed with increasing pH of the aqueous phase. This indicates that the increase in the free base concentration and the formation of successive complexes in aqueous solution increases the probability of extraction of a metal ion.

The extraction can be characterized by the following equation and the corresponding equilibrium constant:

$$[M(H_2O)_6]^{2+} + nHL^+ + 2NO_3^- + xS \rightleftharpoons [ML_nS_x(NO_3)_2] + nH_3O^+$$

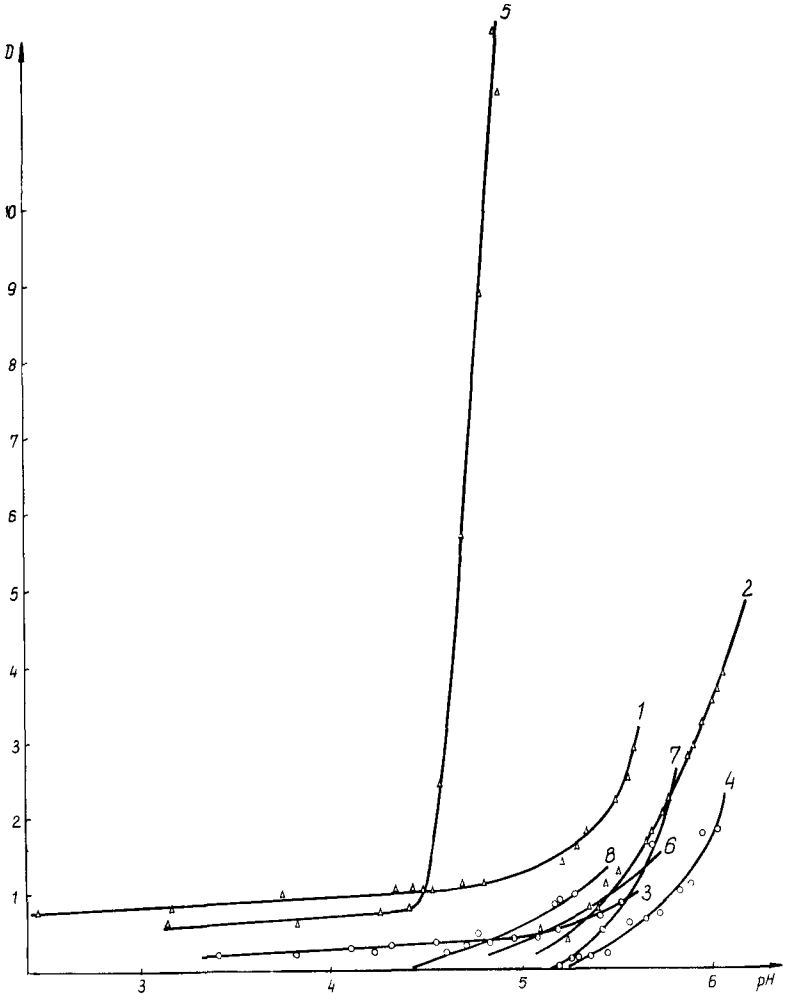

FIG. 1. Plots of the function $D = f(\text{pH})$. 1: Ni(II)–4-methylpyridine (4-pic)–isoamyl alcohol. 2: Ni(II)–4-pic–(isoamyl alcohol + 4-pic). 3: Co(II)–4-pic–isoamyl alcohol. 4: Co(II)–4-pic–(isoamyl alcohol + 4-pic). 5: Co(II)–3-pic–acetylacetone. 6: Ni(II)–3-pic–isobutyl alcohol. 7: Cd(II)–4-pic–isobutanol. 8: Cu(II)–4-pic–isoamyl alcohol.

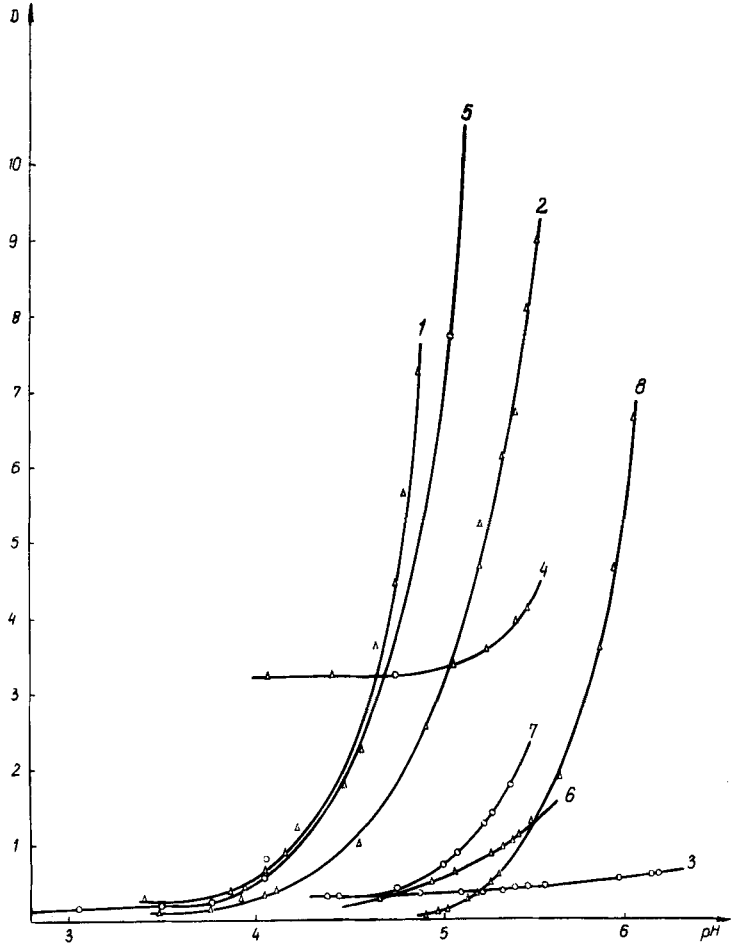

FIG. 2. Plots of the function $D = f(\text{pH})$. 1: Zn(II)–3-methylpyridine (3-pic)–acetylacetone. 2: Zn(II)–3-pic–(acetylacetone + CCl_4, 1:1). 3: Zn(II)–4-pic–isoamyl alcohol. 4: Zn(II)–4-pic–cyclohexanol. 5: Ni(II)–3-pic–(acetylacetone + CCl_4, 1:1). 6: Co(II)–3-pic–isobutanol. 7: Cu(II)–3-pic–isobutanol. 8: Cd(II)–4-pic–cyclohexanol.

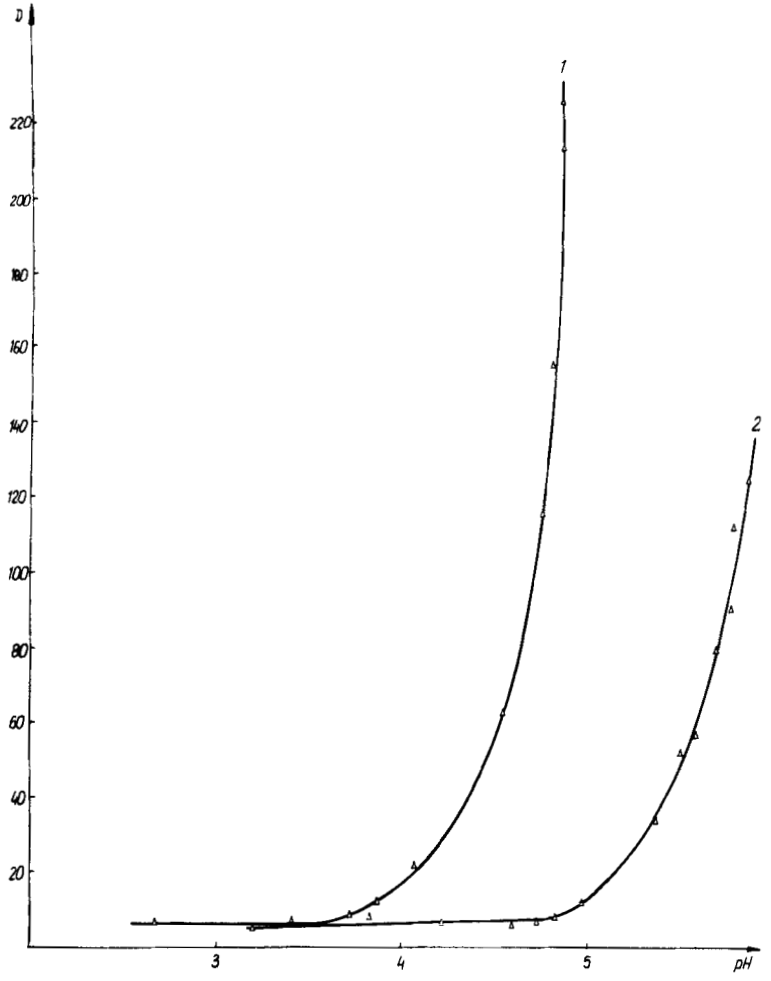

FIG. 3. Plots of the function $D = f(\mathrm{pH})$. 1: Ni(II)–3-methylpyridine (3-pic)–acetylacetone. 2: Cu(II)–3-pic–(acetylacetone + CCl_4).

$$K_{ex} = \frac{[ML_nS_x(NO_3)_2][H_3O^+]^n}{[HL^+]^n[NO_3^-]^2[S]^x[M(H_2O)_6^{2+}]}$$

$$\log K_{ex} = \log D - 2\log[NO_3^-] - x\log[S] - n\log[HL^+] + n\log[H_3O^+]$$

$$\log D = \log K_{ex} + x\log[S] + 2\log[NO_3^-] + n\log[HL^+] + n\,\mathrm{pH}$$

To determine the composition of a complex passing to the organic phase, log D is plotted against pH.

It follows from the above equation that the slope of the straight line is equal to the number of ligand molecules in a complex undergoing extraction. The n values obtained in this manner are listed in Tables 1 and 2. For some systems the n values were not always integers. For instance, the slope for the Co(II)–4-methylpyridine system is equal to 1 with isoamyl alcohol as the extractant and 1.6 for this system extracted with a mixture of isoamyl alcohol and 4-methylpyridine (Fig. 4). Thus, in the latter case more than one complex passes to the organic phase.

To be able to determine the composition of all complexes passing to the organic phase, use has been made of a method of searching for a correlation between the percent of extraction and the degrees of formation of successive complexes, α_n.

The percent of extraction, E, as a function of free ligand concentration in aqueous phase at equilibrium was determined for all systems (Figs. 5–7).

TABLE 1

Composition of Complexes with 4-Picoline Passing to the Organic Phase

Metal	Extractants	tan α	Individual partition coefficients P_n				Composition of extractable complex[a]
			P_1	P_2	P_3	P_4	
Ni	Isoamyl alcohol + 4-picoline	2.5			6.52		$[Ni(4\text{-pic})_3S](NO_3)_2$
Co	Isoamyl alcohol	1	3				$[Co(4\text{-pic})_1S_3](NO_3)_2$
Co	Isoamyl alcohol + 4-picoline	1.6		2.29			$[Co(4\text{-pic})_2S_4](NO_3)_2$
Cu	Isoamyl alcohol	3.8				5.88	$[Cu(4\text{-pic})_4S_2](NO_3)_2$
Zn	Isoamyl alcohol + 4-picoline	1		1.71			$[Zn(4\text{-pic})_2S_4](NO_3)_2$
Cd	Cyclohexanol	3			13.8	8.82	$[Cd(4\text{-pic})_3S_3](NO_3)_2$ $[Cd(4\text{-pic})_4S_2](NO_3)_2$
Cd	Isoamyl alcohol	4.4			8.49	10	$[Cd(4\text{-pic})_3S_3](NO_3)_2$ $[Cd(4\text{-pic})_4S_2](NO_3)_2$

[a]S = molecule of extractant; 4-pic = 4-picoline.

TABLE 2

Composition of Complexes with 3-Picoline Passing to the Organic Phase

Metal	Extractants	tan α	Individual partition coefficients P_n				Composition of extractable complex[a]
			P_1	P_2	P_3	P_4	
Ni	Isobutanol	0.6		2.76	1.25		$[Ni(3\text{-pic})_2S_4](NO_3)_2$ $[Ni(3\text{-pic})_3S](NO_3)_2$
Ni	Acetylacetone	1.85		1580			$[Ni(3\text{-pic})_2S_4](NO_3)_2$
Ni	Actylacetone +CCl_4, 1:1	1		41.7	2.6		$[Ni(3\text{-pic})_2S_4](NO_3)_2$ $[Ni(3\text{-pic})_3S_3](NO_3)_2$
Co	Isobutanol	1	2.3	1.6			$[Co(3\text{-pic})S_5](NO_3)_2$ $[Co(3\text{-pic})_2S_4](NO_3)_2$
Cu	Isobutanol	1			3.11	4.44	$[Cu(3\text{-pic})_3S_3](NO_3)_2$ $[Cu(3\text{-pic})_4S_2](NO_3)_2$
Cu	Acetylacetone +CCl_4, 1:1	4				250	$[Cu(3\text{-pic})_4S_2](NO_3)_2$
Zn	Acetylacetone	1.25	45.4	182			$[Zn(3\text{-pic})_2S_4](NO_3)_2$ $[Zn(3\text{-pic})S_5](NO_3)_2$
Zn	Acetylacetone +CCl_4, 1:1	1.1	30	5.45	50		$[Zn(3\text{-pic})S_5](NO_3)_2$ $[Zn(3\text{-pic})_2S_4](NO_3)_2$ $[Zn(3\text{-pic})_3S_3](NO_3)_2$

[a]S = molecule of extractant; 3-pic = 3-picoline.

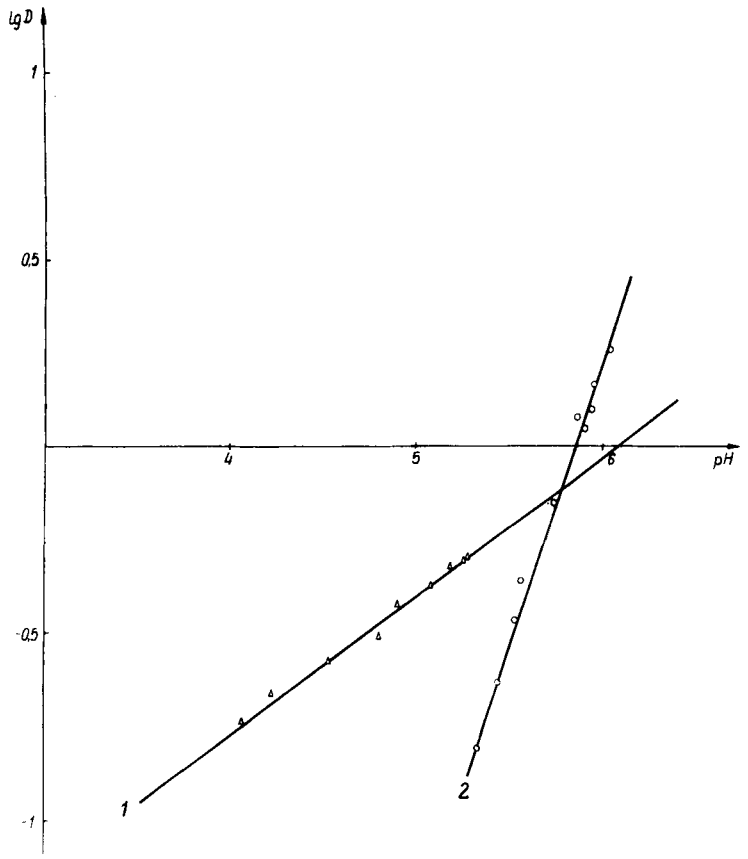

FIG. 4. Plots of the function $\log D = f(\mathrm{pH})$. 1: Co(II)–4-methylpyridine (4-pic)–isoamyl alcohol. 2: Co(II)–4-pic–(isoamyl alcohol + 4-pic).

In Figs. 5–7 the function $\alpha_n = f([\mathrm{L}])$ characterizes the degree of formation of particular metal complexes with the two bases. There is a similarity in the shape and position of the $E = f([\mathrm{L}])$ and $\alpha_n = f([\mathrm{L}])$ curves. For instance, the extraction curve of the Cu(II)–4-methylpyridine system with isoamyl alcohol is similar to the α_4 curve (Fig. 5). The extraction curve of the Co(II)–4-methylpyridine system with isoamyl alcohol resembles that of α_2 (Fig. 6), while the Co(II)–3-methylpyridine–isobutanol curve resembles that of α_1 (Fig. 7). Dissimilar extraction curves were obtained for the systems Ni(II)–3-methylpyridine–acetylacetone (acac) and Cu(II)–3-methylpyridine–acac, where the percent of extraction is as high as 98–99.5%. This might be due to the strong electron-donor nature of the solvent, which exhibits so strong a tendency to penetrate into the co-

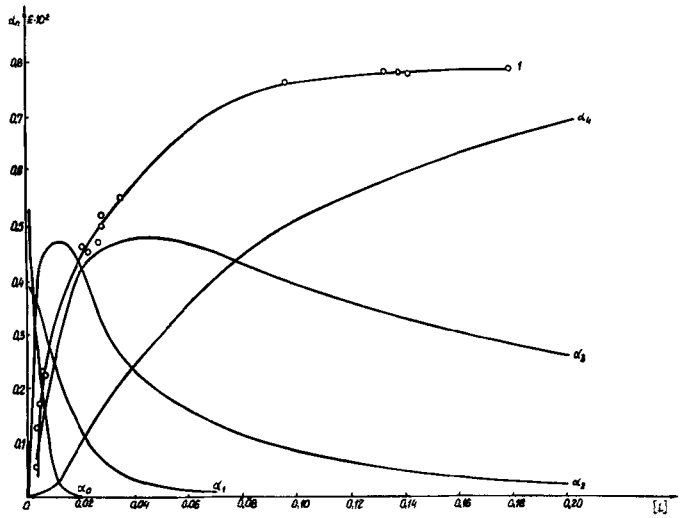

FIG. 5. Plots of the functions $\alpha_n = f([L])$ and $E = f([L])$ for the Cu(II) complexes of 4-methylpyridine extracted with isoamyl alcohol: α_0, α_1, α_2, α_3, and α_4 are successive degrees of complex formation.

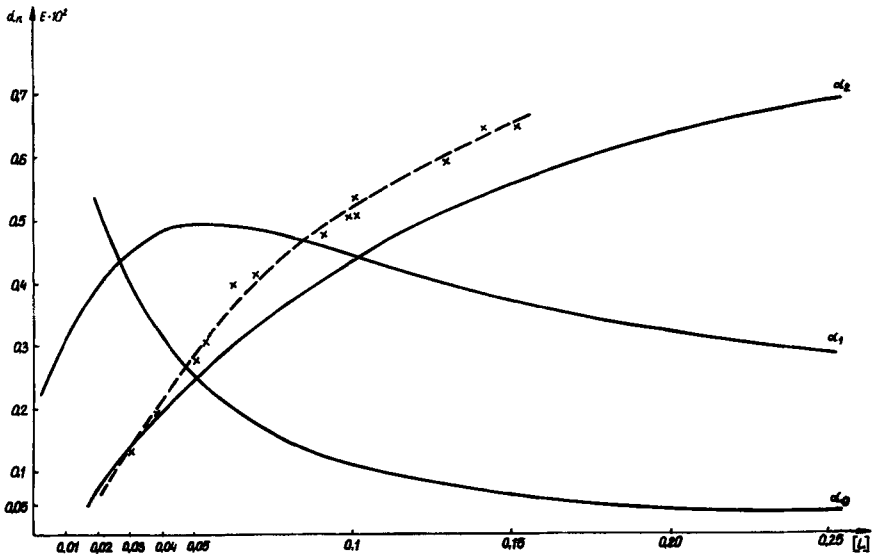

FIG. 6. Plots of the functions $\alpha_n = f([L])$ and $E = f([L])$ for the Co(II) complexes of 4-methylpyridine extracted with isoamyl alcohol: α_0, α_1 and α_2 are successive degrees of complex formation.

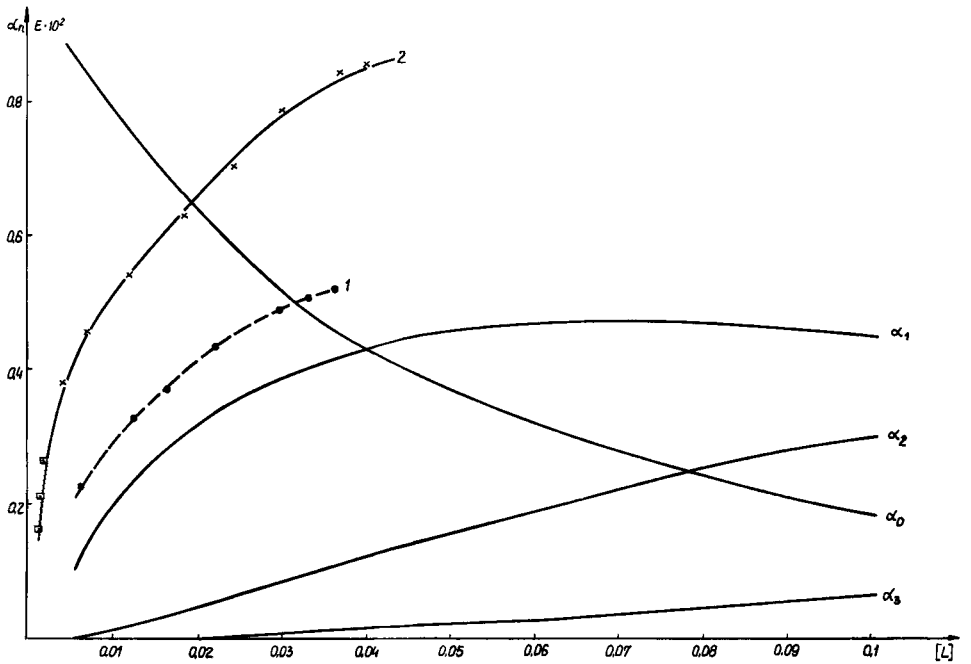

FIG. 7. Plots of the functions $\alpha_n = f([L])$ and $E = f([L])$ for the Co(II) complexes of 3-methylpyridine extracted with isobutanol (1) and a 1:1 acetylacetone–CCl_4 mixture (2): α_0, α_1, α_2, and α_3 are successive degrees of complex formation.

ordination sphere of a metal that is can displace pyridine ligands in systems with lower stability constants of the complexes. In such cases the straight line runs almost parallel to the free ligand concentration axis and does not correlate with any of the α_n curves.

Experiments with acetylacetone diluted with CCl_4 were also carried out. The use of CCl_4 did not affect significantly the percent of extraction.

As was demonstrated in the previous article (*23*), those systems in which the extraction depends on several successive complexes can be described by the function $D = f(\alpha_n)$, as the partition coefficient depends in this case on the degrees of formation of particular complexes and the individual partition coefficients P_n:

$$D = P_n\alpha_n + P_{n+1}\alpha_{n+1} + P_{n+2}\alpha_{n+2} + \cdots$$

The subscript n denotes the first complex passing to the organic phase. This can easily be identified from the $D = f(\alpha_n)$ plot, since according to the above equation the straight line in this case should pass through the

origin of the coordinates. Its slope permits the P_n value to be determined simultaneously. The second constant, P_{n+1}, can be found graphically from the relation

$$D' = D - P_n\alpha_n = f(\alpha_{n+1})$$

In a similar manner the remaining P_n coefficients characterizing all extractable complexes can be determined.

The reliability of the P_n values was checked by substituting them in

$$E = \frac{D}{1 + D} = \frac{P_n\alpha_n + P_{n+1}\alpha_{n+1} + \cdots}{1 + P_n\alpha_n + P_{n+1}\alpha_{n+1} + \cdots}$$

The set of P_n values was considered to be reliable when the E values calculated from this equation located themselves on the experimental extraction curve. The P_n constants determining the extraction in all the systems studied are listed in Tables 1 and 2. In those extraction systems in which only one particular complex is extracted (one P_n value), the slope of the $\log D = f(\text{pH})$ curve is equal to the subscript of P_n. For instance, in the Co(II)–4-methylpyridine–isoamyl alcohol system the slope is equal to 1 and the minimum number of the extractable complex is just 1 ($P_1 = 3$). Accordingly, both of these approaches show that a complex containing one ligand molecule is being extracted. In the case where a system is described by a set of P_n values, thus indicating that several complexes are extracted simultaneously, the results obtained by the two approaches are divergent. In this case the slope is a fractional value. Hence one can state that the equilibrium displacement method enables one to determine the number of ligand molecules bound with the central ion only in those cases where a particular single complex is being extracted rather than a group of complexes.

To determine the structure of the coordination sphere of the extractable complexes, absorption spectra of the aqueous and organic phases were taken. For the Ni(II)–3-methylpyridine complexes extracted with acetylacetone and an acetylacetone–CCl_4 mixture, spectra typical for octahedral Ni(II) complexes were obtained (*24*).

More interesting features have been found in the spectra of the aqueous and organic phases including the Ni(II)–3-methylpyridine–isobutanol and Ni(II)–4-methylpyridine–isoamyl alcohol systems. Maxima due to octahedral species were observed in the spectra of aqueous phases, whereas the organic phase absorbed strongly over the range 19,000–20,000 cm^{-1}. The increased absorption in this region can be due to the occurrence of a tetra-coordinate Ni(II) complex (*25*).

Accordingly, both hexa-coordinate and tetra-coordinate complexes coexist in the organic phase. On the other hand, spectra of the Co(II)

complexes with the two ligands exhibit absorption bands typical for octahedral species.

To sum up, the composition of the complexes passing to the organic phase can be predicted owing to the correlation between the partition coefficients and the degrees of formation of successive complexes complemented by optical data (Tables 1 and 2). The results of this work can be of practical importance. For instance, during extraction with isobutanol, only the Cu(II), Ni(II), and Co(II) complexes of 3-methylpyridine are extracted to a percent of 30–60%, while the Zn(II) complexes are not extracted. On the other hand, isobutanol turned out to be a suitable solvent for the extraction of Zn(II) with 4-methylpyridine $E = 76$–80%. Further, the Ni(II), Co(II), Cu(II), and to some extent also the Cd(II) and Zn(II) complexes of 4-methylpyridine are fairly well extractable with isoamyl alcohol. This permits the separation of the complexes of these metals with the two isomeric methylpyridines by extraction with isoamyl alcohol.

CONCLUSIONS

(1) A correlation between the partition coefficient, D, and the degrees of formation of successive complexes, α_n, enables the number and composition of extractable complexes to be determined.

(2) This approach appears to be more versatile than the equilibrium displacement method, as it permits the determination of the composition of a series of extractable complexes.

(3) In the majority of the systems studied, octahedral complexes are extracted, whereas with Ni(II) the coordination number decreases from 6 to 4 during extraction.

(4) Different extents of extraction found during experiments with two extractants enable separation of the complexes by partitioning.

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