Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Search for Optimum Conditions of Extraction of Transition Metal Complexes with Alkylimidazoles. I. Extraction of the Co(II), Ni(II), and Zn(II) Complexes of 1-Methylimidazole and of the Co(II) and Zn(II) Complexes of 2-Methylimidazole

B. Lenarcik[a]; J. Głowacki[a]; M. Rzepka[a]
[a] INSTITUTE OF CHEMISTRY, PEDAGOGICAL UNIVERSITY, KIELCE, POLAND

To cite this Article Lenarcik, B. , Głowacki, J. and Rzepka, M.(1979) 'Search for Optimum Conditions of Extraction of Transition Metal Complexes with Alkylimidazoles. I. Extraction of the Co(II), Ni(II), and Zn(II) Complexes of 1-Methylimidazole and of the Co(II) and Zn(II) Complexes of 2-Methylimidazole', Separation Science and Technology, 14: 1, 37 — 54

To link to this Article: DOI: 10.1080/01496397908057143

URL: http://dx.doi.org/10.1080/01496397908057143

SEPARATION SCIENCE AND TECHNOLOGY, 14(1), pp. 37–54, 1979

Search for Optimum Conditions of Extraction of Transition Metal Complexes with Alkylimidazoles. I. Extraction of the Co(II), Ni(II), and Zn(II) Complexes of 1-Methylimidazole and of the Co(II) and Zn(II) Complexes of 2-Methylimidazole

---

B. LENARCIK, J. GŁOWACKI, and M. RZEPKA

INSTITUTE OF CHEMISTRY
PEDAGOGICAL UNIVERSITY
KIELCE, POLAND

Abstract

It has been shown that for the Co(II), Zn(II), and Ni(II) complexes of 1-methylimidazole and for the Co(II) and Zn(II) complexes of 2-methylimidazole, the partition coefficient D between the aqueous and organic phases is proportional to the degree of formation α_n of a definite complex. Tetrahedral species have been found to be extracted with the Co(II) and Zn(II) complexes of 2-methylimidazole and with the Zn(II) complexes of 1-methylimidazole.

INTRODUCTION

There has been recent increased interest in the separation of metals in the form of complexes from aqueous solutions by extraction techniques (*1*). In view of the rapid exhaustion of rich metallic ores, progress in the development of extractive metallurgy is to be expected.

It has long been known that the transfer of a metal cation from an aqueous phase to an organic phase is accompanied by its dehydration, reduction of its electric charge, and an increase in the volume of the coordination sphere. These conditions can be satisfied by combining the ions into complexes with the proper ligands (*2*). Consequently, the extraction of a metal is controlled by the stability of its complexes in aqueous phase and by the equilibrium concentration of the free ligand (*3*).

In previous work (*4–7*) we found alkylimidazoles to be able to form complexes of remarkable stability with cations of the first row of the transition metals. Our further studies were aimed at an exploration of the possibility of extracting these complexes from aqueous solutions with organic solvents. We were prompted to carry on these investigations because of the change of the structure of coordination spheres from octahedral to tetrahedral which accompanied the formation of Co(II) and Zn(II) complexes with most alkylimidazoles.

The tetrahedral species contain a smaller number of water molecules in the coordination sphere than do the octahedral ones. Hence the former should pass more readily to the organic phase (*8*).

The object of this work was to investigate the effect of free ligand concentration in aqueous solution on the extraction of the Co(II), Ni(II), and Zn(II) complexes of 1-methyl- and 2-methylimidazoles (1-MI and 2-MI, respectively, throughout). The studies were based on the results of our earlier work (*4*, *6*) on the stability and structure of the methylimidazole complexes of the metals. Some correlations between the free ligand concentration and parameters describing the extraction in thiocyanate systems have been derived by Mańko and Soczewiński (*9–11*).

EXPERIMENTAL

Reagents

Commercially available reagents were used. 1-MI (Merck-Schuchardt), b.p. 199.5 °C, was purified by distillation. 2-MI (Koch-Light Laboratories), m.p. 141 °C, was used as supplied.

Ligand solutions of proper concentration were prepared from carefully dried samples.

Nitric acid (analytical grade reagent obtained from Nitrogen Works, Tarnów), properly diluted, was standardized against Na_2CO_3 or $Na_2B_4O_7 \cdot 10H_2O$.

Solutions of the Co(II), Ni(II), and Zn(II) nitrates (all analytical grade reagents obtained from Nitrogen Works, Chorzów) were prepared from twice crystallized salts.

The metal concentrations were determined by titration with a disodium salt of EDTA solution and checked gravimetrically.

Potassium nitrate (analytical grade reagent, Nitrogen Works, Chorzów) was twice crystallized before use. Its concentration was assessed gravimetrically in the form of K_2SO_4.

As extractants, benzyl alcohol, isoamyl alcohol, cyclohexanol, cyclohexanone, diethyl malonate, ethyl acetylacetate, tributyl phosphate, and other solvents were used. They were purified by distillation before use.

For the pH measurements, ready-to-use buffer solutions of pH 7.00 (type S 1326) and 4.01 (type S 1316), manufactured by Radiometer, Copenhagen, were employed.

Apparatus

The pH measurements were accomplished by means of a PHM-64 digital pH meter (Radiometer, Copenhagen). The measuring cell consisted of a combined GK 2301 C electrode.

Absorption spectra of the Co(II) 2-MI complexes were taken on a Specord UV-VIS recording spectrophotometer (C. Zeiss, Jena) using quartz cuvettes.

Procedure

All measurements were run at 25°C at a fixed (0.5; KNO_3) ionic strength of the aqueous phase. Moreover, in all solutions a constant concentration (0.2 *M*) of methylimidazole nitrate was maintained.

Two kinds of solutions were placed in 25-cm^3 or 50-cm^3 volumetric flasks. One contained a weighed sample of a ligand, nitric acid, metal nitrate, and a proper quantity of KNO_3; the other kinds of solution were prepared in exactly the same manner but did not contain the ligand. By mixing together in proper proportions the acidic solution (not containing the ligand) with a basic solution, 10 to 12 samples with volumes of 10 cm^3 were obtained. These solutions had the same metal concentration and differed only in the free ligand concentration.

Extraction experiments were carried out as follows. In calibrated test tubes with ground-in stoppers, 10 cm^3 of a solution was placed and its pH measured (pH_1). Then equal volumes of an organic solvent were added. Extractants were selected on the basis of the trial-and-error procedure using the aforementioned oxonium compounds and proper mixtures of the compounds. To speed up the extraction process, the samples were shaken in a laboratory shaking apparatus for 30 min. As soon as equilibrium was established, the change in volume of both phases was noted and the pH of the aqueous phase was measured (pH_2) in order to determine the equilibrium concentration of the ligand, [L].

The initial concentrations of metal were 0.025 and 0.020 *M* for 2-MI and 1-MI, respectively. The metal concentration in the aqueous phase after extraction was determined by titration with a 0.02-*M* EDTA solution, taking into account volume changes which had taken place after mixing the two phases together.

For the Co(II) complexes of 2-MI, absorption spectra of the aqueous and organic phases were taken over the visible range. A 0.5-*M* KNO_3 solution served as reference for the aqueous phase, and the pure extractant was the reference for the organic phase.

RESULTS AND DISCUSSION

The extraction process was quantitatively characterized in terms of the partition coefficient *D*, defined by

$$D = \frac{C_M^{\circ} - C_M}{C_M^{\circ}} \qquad (1)$$

where C_M^0 is the analytical concentration of a metal in aqueous solution prior to extraction and C_M is the metal concentration in the solution after attaining equilibrium.

Preliminary qualitative and quantitative tests showed benzyl alcohol to be the most suitable extractant for 2-MI complexes. Good results with benzyl alcohol were also obtained for the Zn(II)–1-MI system (cf. Fig. 1). With the Cc(II) and Ni(II) complexes of 1-MI, a clear-cut partition of the metals between the two phases was achieved with a 1:1 (v/v) mixture of benzyl alcohol and ethyl acetylacetate (cf. Figs. 2 and 3).

On the basis of the ionization constant of a conjugate acid of a given methylimidazole and pH values measured at equilibrium, we found the free ligand concentration [L] in the aqueous phase from

$$[L] = \frac{K_a C_{[HL]NO_3}}{[H_3O^+]} \qquad (2)$$

where K_a, $C_{[HL]NO_3}$, and $[H_3O^+]$ are the ionization constant, the concentration of the conjugate acid of the ligand, and the hydronium-ion concentration, respectively. For the conjugate acids of 1-MI and 2-MI, the K_a values of 6.5×10^{-8} (*6*) and 8.89×10^{-9} (*4*), respectively, were accepted.

Figures 4–7 and 11 show plots of the partition coefficient against the free ligand concentration in the aqueous phase at equilibrium. To find a correlation between the partition coefficient and the composition and

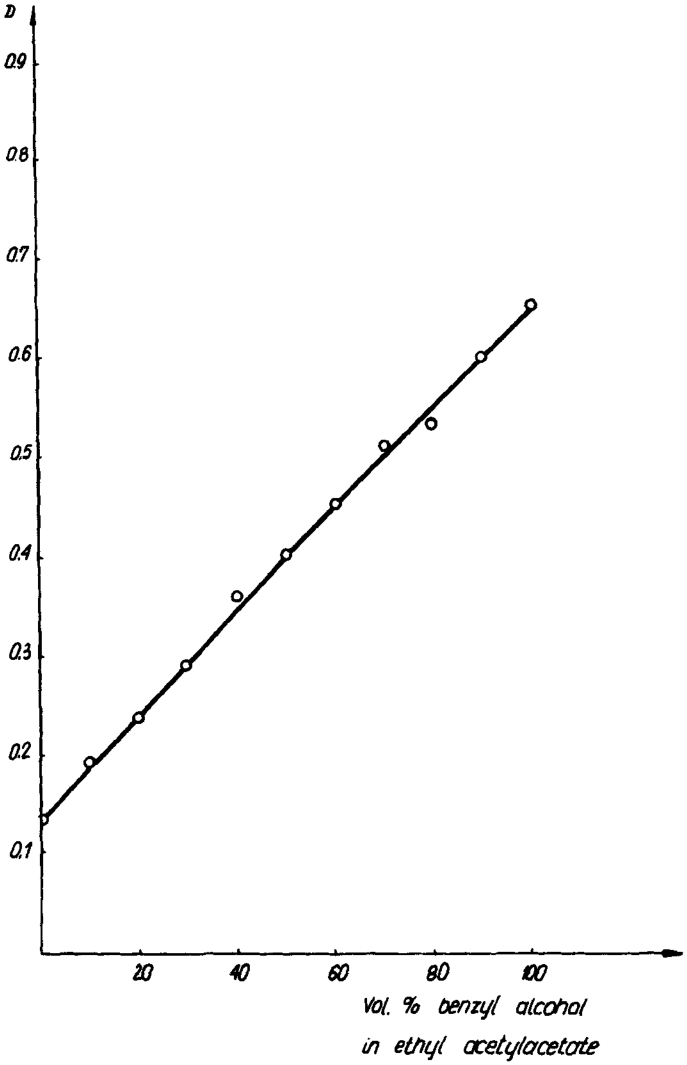

FIG. 1. Partition coefficient, *D*, of the Zn(II) complexes of 1-methylimidazole vs percentage of benzyl alcohol in ethyl acetylacetate (v/v).

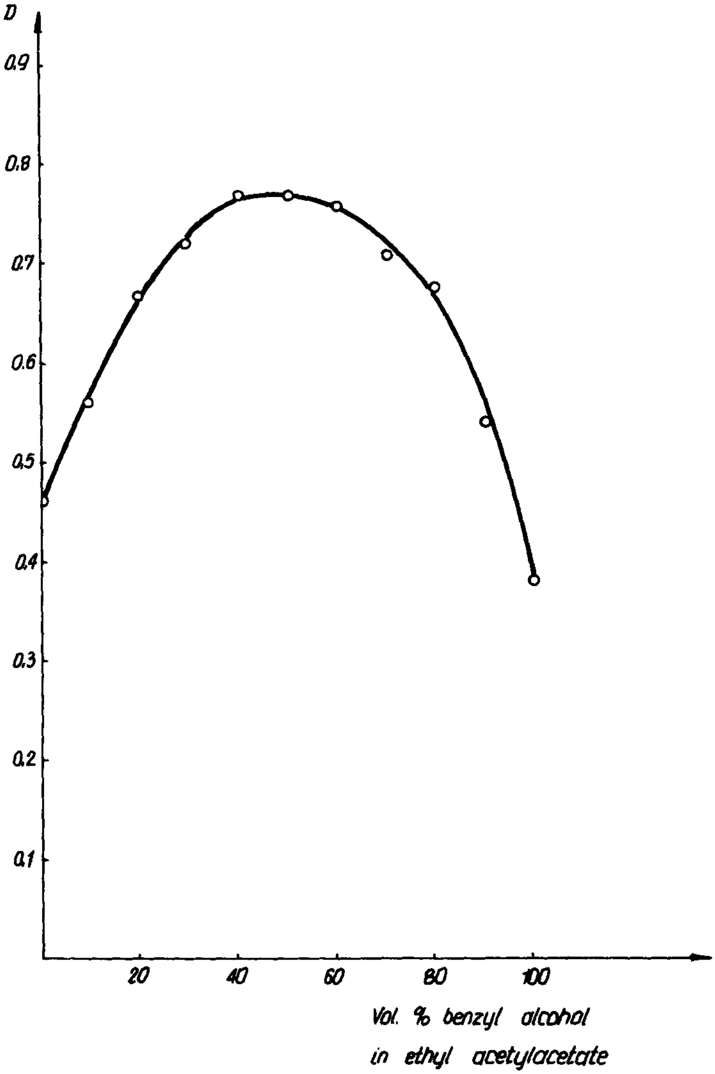

FIG. 2. Partition coefficient, *D*, of the Co(II) complexes of 1-methylimidazole vs percentage of benzyl alcohol in ethyl acetylacetate (v/v).

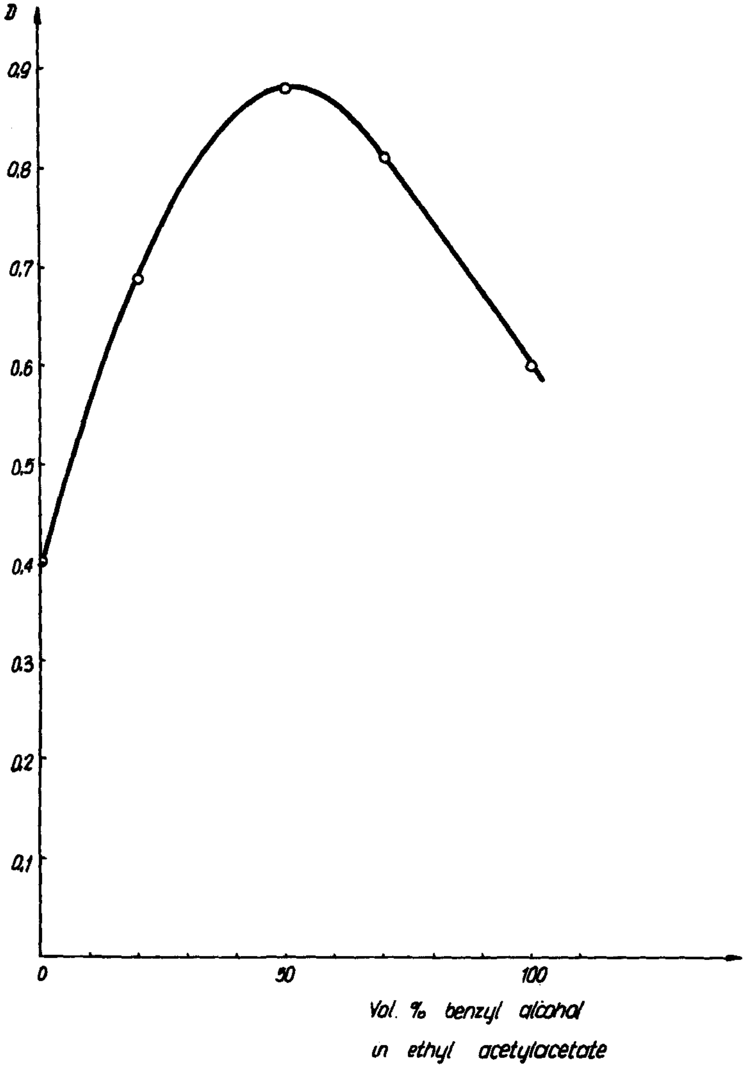

FIG. 3. Partition coefficient, *D*, of the Ni(II) complexes of 1-methylimidazole vs percentage of benzyl alcohol in ethyl acetylacetate (v/v).

stability of complexes occurring in the aqueous phase, the degrees of formation α_n of individual complexes were calculated for each system. The α_n is related to the free ligand concentration at equilibrium by

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

where β_n are cumulative stability constants of successive complexes, and N stands for the maximum coordination number of the central ion.

The α_n values, calculated on the basis of stability constants β_n reported in Refs. *4* and *6* at arbitrary free ligand concentrations, are shown in Figs. 4–7 and 11 to illustrate a dependence between D and [L]. The shape of the function $D = f([\mathrm{L}])$ closely resembles curves showing variations in the degree of formation of some complexes with increasing free ligand concentration. The analogy suggests that the extraction of a metal ion into the organic phase depends on the degree of formation of a definite complex or of a few complexes.

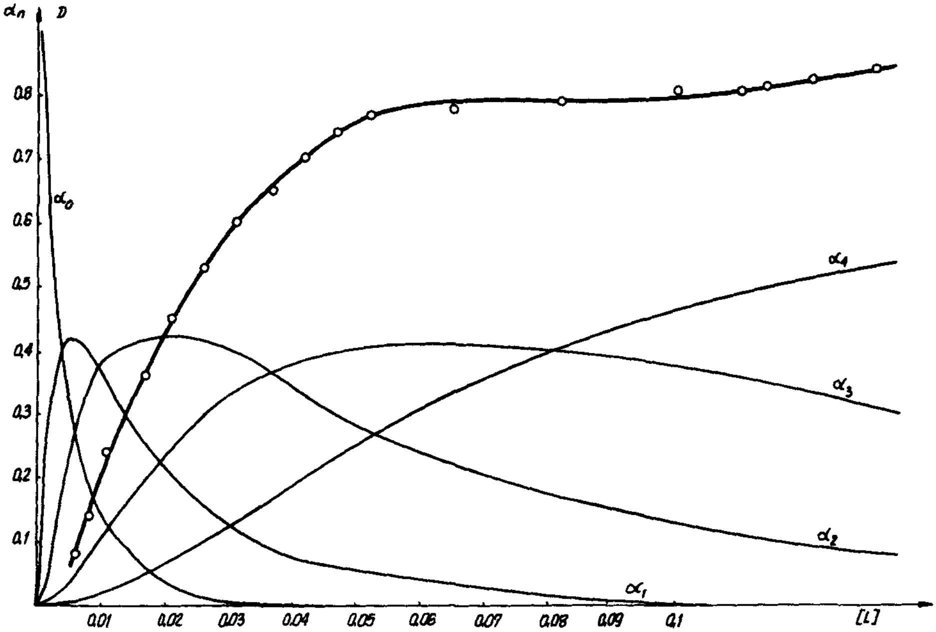

FIG. 4. Partition coefficient, D, for the Co(II) complexes of 1-methylimidazole extracted with benzyl alcohol, together with formation degrees, α_n, of individual complexes vs the free ligand concentration, [L].

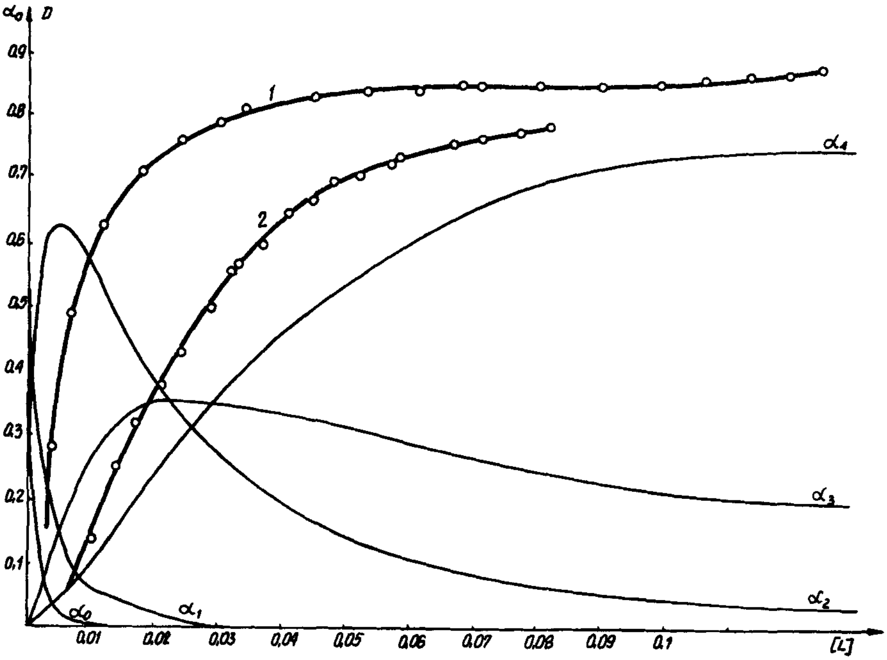

FIG. 5. Partition coefficient, D, for the Ni(II) complexes of 1-methylimidazole extracted with a 50% (v/v) solution of ethyl acetylacetate in benzyl alcohol (Curve 1) and with benzyl alcohol alone (Curve 2), together with formation degrees, α_n, of individual complexes vs the free ligand concentration, [L].

The extraction curve for the Co(II)–1-MI system (Fig. 4) bears a certain similarity to graphs of α_3 and α_4, and is situated above them. This suggests that during extraction, ion pairs containing nitrate anions move to the organic phase and the complex cation contains three or four molecules of 1-MI. These are probably mixed six-coordinate complexes containing both the 1-MI ligands and the extractant molecules, most probably those of ethyl acetylacetate. Such a model of extraction is supported by the similarity of colors of the complexes in both phases.

Figure 5 illustrates the extraction of Ni(II) with ethyl acetylacetate and benzyl alcohol (Curve 1) and with benzyl alcohol alone (Curve 2). The latter curve closely resembles the graph of the function α_4, thus revealing that most probably the $[Ni(1\text{-}MI)_4S_2](NO_3)_2$ species passes to the organic phase (S stands for extractant molecule). With a stronger electron-donating extractant (benzyl alcohol–ethyl acetylacetate mixture), two complexes in the form of ion pairs pass to the organic phase, namely

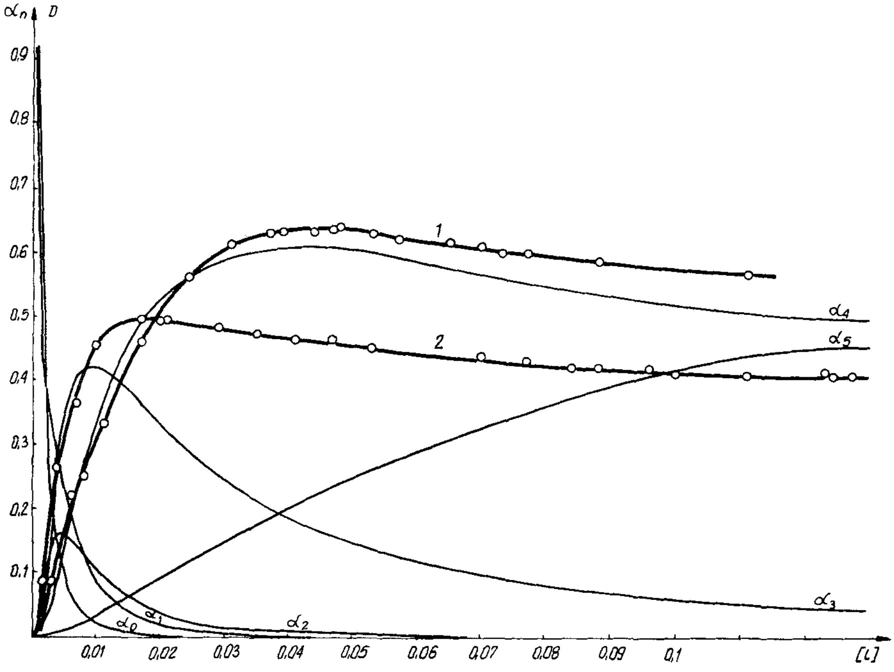

FIG. 6. Partition coefficient, D, for the Zn(II) complexes of 1-methylimidazole extracted with benzyl alcohol (Curve 1) and with a 50% (v/v) solution of ethyl acetylacetate in benzyl alcohol (Curve 2), together with formation degrees, α_n, of individual complexes vs the free ligand concentration, [L].

$[Ni(1\text{-}MI)_3S_3]^{2+}$ and $[Ni(1\text{-}MI)_4S_2]^{2+}$. The position of the $D = f([L])$ graph of benzyl alcohol above the one for $\alpha_4 = f([L])$ suggests that the third complex is partially extracted.

An interesting phenomenon is seen in Fig. 6. Here Curve 1, corresponding to extraction of the Zn(II) complexes with benzyl alcohol, lies above that showing the extraction with the benzyl alcohol–ethyl acetylacetate mixture. The curve for the extraction with benzyl alcohol almost overlaps the graph of α_4. This means that the fourth complex, $[Zn(1\text{-}MI)_4S_2](NO_3)_2$, passes mostly to the organic layer. On the basis of the results reported in Ref. *6*, one can identify the complex as tetrahedral and nonsolvated with the solvent molecules. Owing to stronger electron-donor properties, the benzyl alcohol–ethyl acetylacetate mixture probably extracts the second and the third complexes by attaching to two or one solvent molecule, respectively. The two compounds most probably provide tetrahedral complexes.

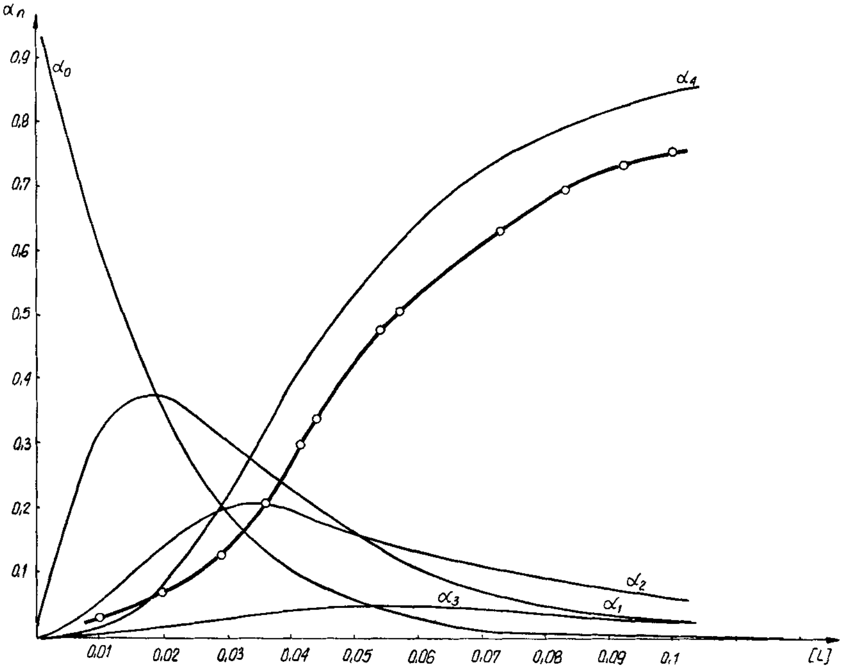

FIG. 7. Partition coefficient, D, of the Co(II) complexes of 2-methylimidazole (extraction with benzyl alcohol), together with formation degrees, α_n, of individual complexes vs the free ligand concentration, [L].

With 2-MI, only the extraction of the Co(II) and Zn(II) complexes could be studied because Ni(II) does not form sufficiently stable species with the ligand (*4*).

Figure 7 shows a close resemblance between the extraction curve and that of the degree of formation of the fourth complex $\alpha_4 = f([\mathrm{L}])$. The mutual position of the curves implies that only a part of complexes containing four 2-MI molecules moves unsolvated to benzyl alcohol. To support this assumption, we investigated the absorption spectra of the aqueous solution prior to extraction and of the aqueous and organic phases after reaching equilibrium (Figs. 8–10). The spectra shown in Fig. 8 suggest that prior to extraction, an equilibrium is set up between tetrahedral and octahedral Co(II) complexes:

$$[\mathrm{Co(2\text{-}MI)_4(H_2O)_2}]^{2+} \rightleftharpoons [\mathrm{Co(2\text{-}MI)_4}]^{2+} + 2\mathrm{H_2O}$$

Only the tetrahedral species pass to the organic phase, as is indicated by

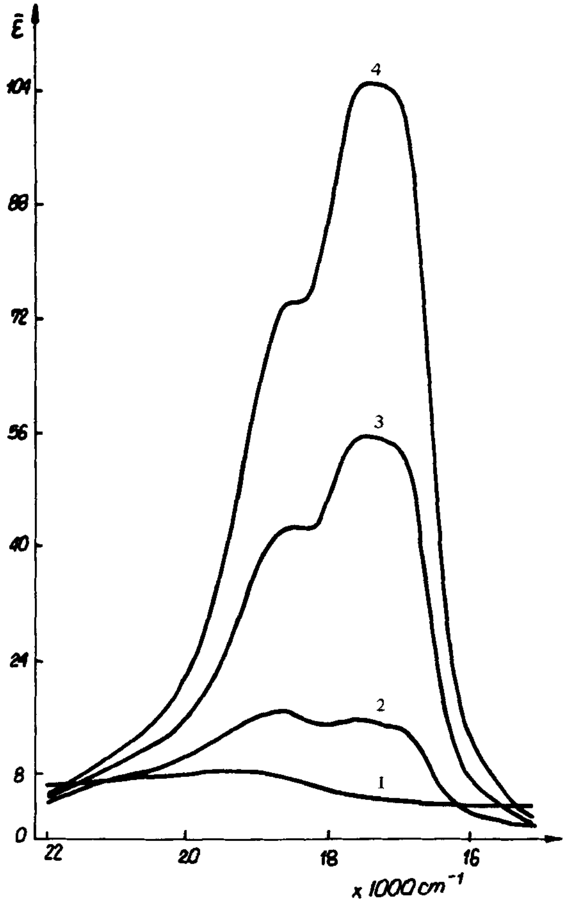

FIG. 8. Absorption spectra of the Co(II) complexes of 2-methylimidazole in the aqueous phase prior to extraction $Co(NO_3)_2$ concentration 25.0 mmole/dm^3. The ligand concentrations in Solutions 1, 2, 3, and 4 are 0.0, 150, 165, and 180 mmole/dm^3, respectively.

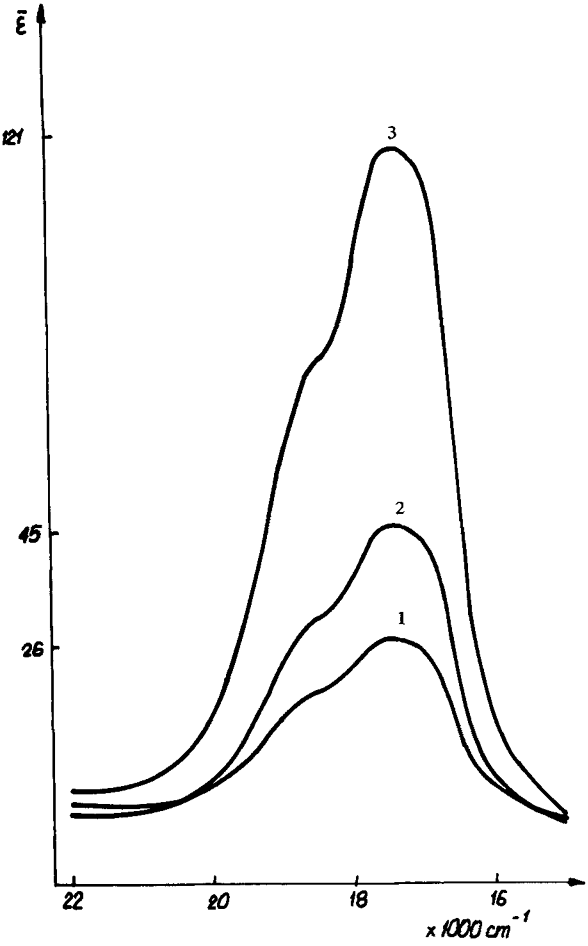

FIG. 9. Absorption spectra of the Co(II) complexes of 2-methylimidazole in the organic phase after extraction. The concentrations of the central ion in Solutions 1, 2, and 3 are 23.15, 22.5, and 19.7 mmole/dm^3, respectively.

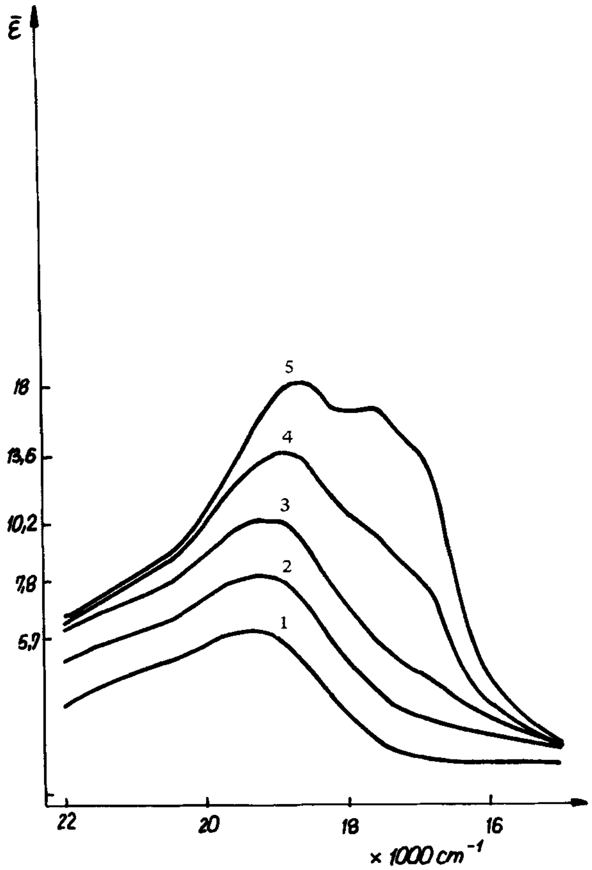

FIG. 10. Absorption spectra of the Co(II) complexes of 2-methylimidazole in the aqueous phase after extraction. The central ion concentrations in Solutions 1, 2, 3, 4, and 5 are 24.5, 24.3, 23.5, 22.0, and 20.0 mmole/dm^3, respectively.

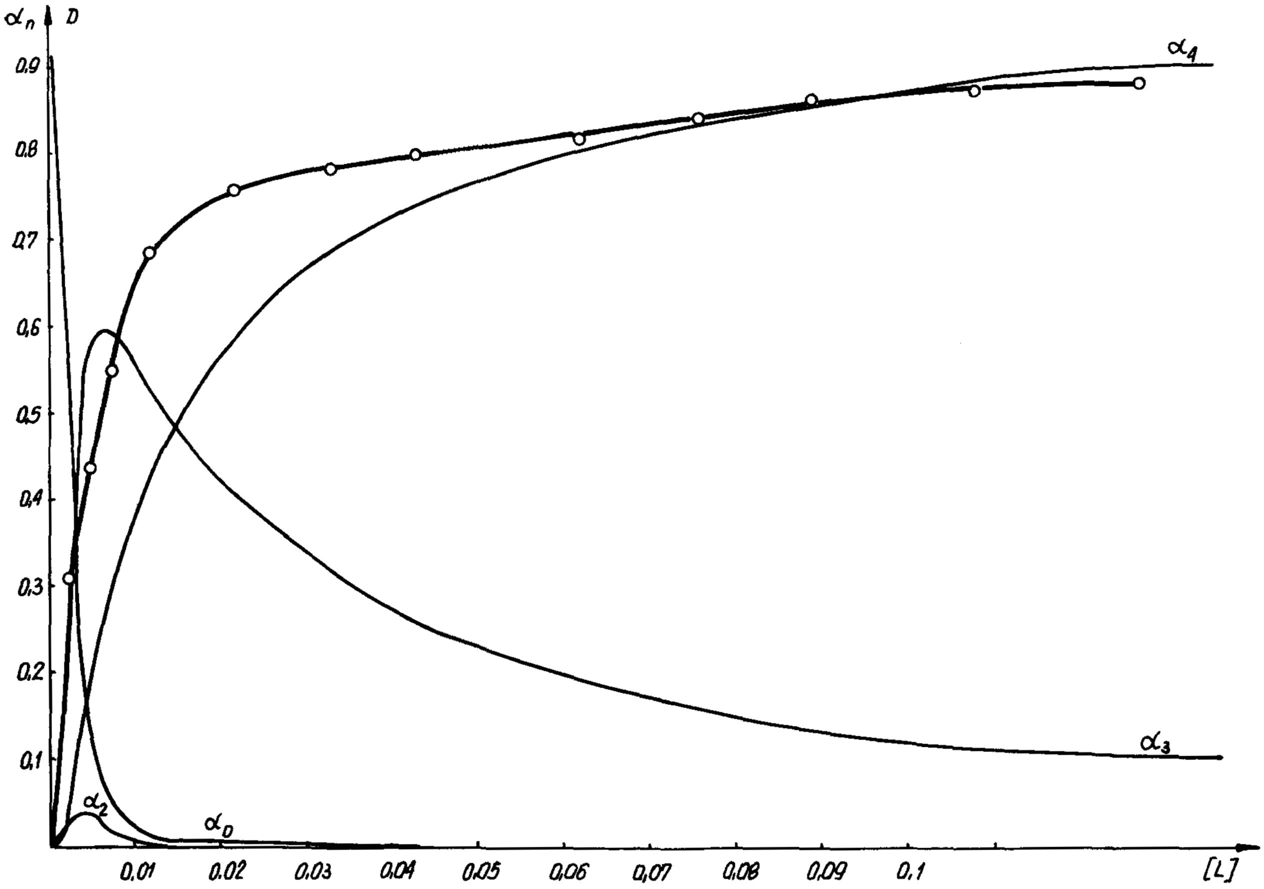

FIG. 11. Partition coefficient, D, of the Zn(II) complexes of 2-methylimidazole (extraction with benzyl alcohol), together with formation degrees, α_n, of individual complexes vs the free ligand concentration, [L].

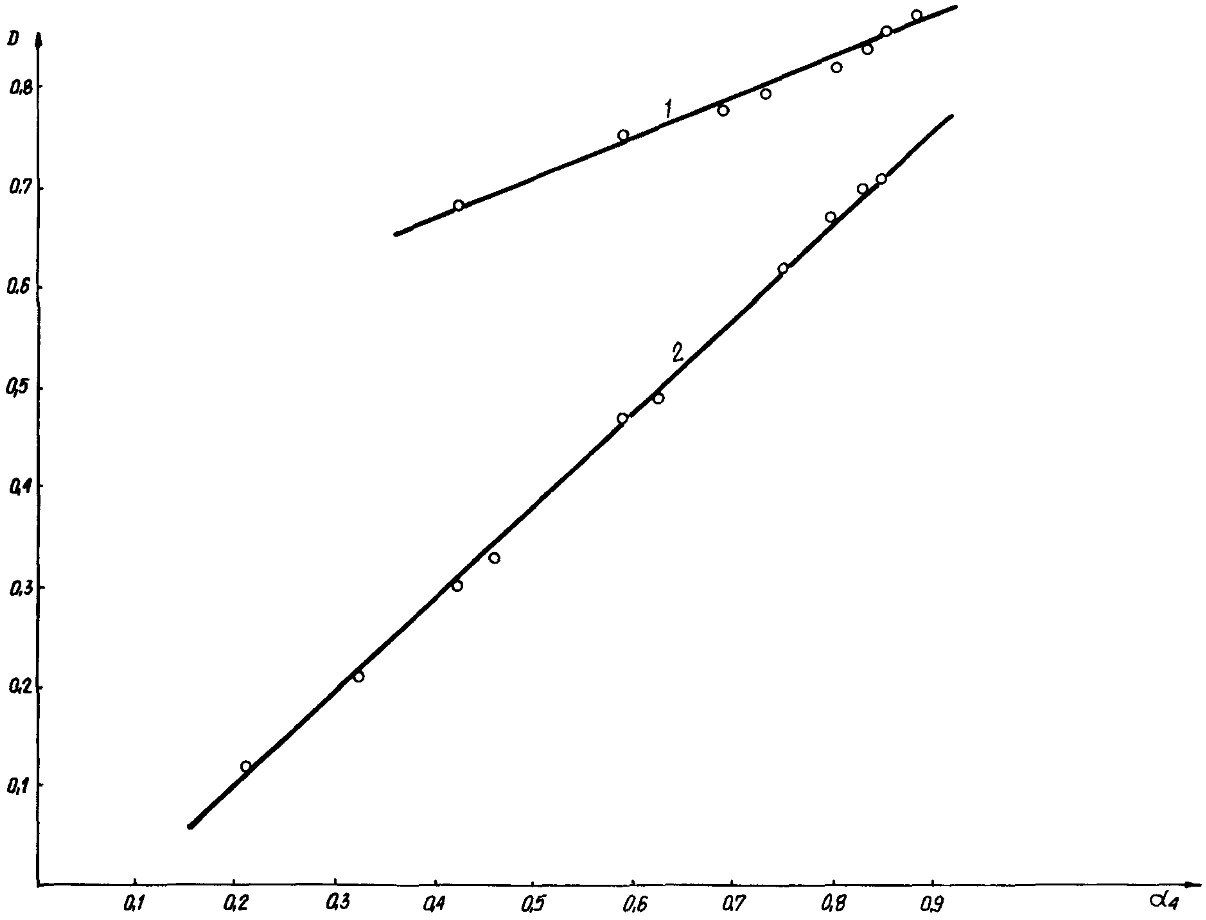

FIG. 12. The dependence between D and α_4 for the Zn(II) (Curve 1) and Co(II) (Curve 2) complexes of 2-methylimidazole.

the shape and position of absorption bands in Fig. 9. The six-coordinate species, $[Co(2\text{-}MI)_n(H_2O)_{6-n})^{2+}$ (Fig. 10), remain mostly in the aqueous phase after extraction. An equally interesting mechanism of extraction has been observed in the Zn(II)–2-MI system (Fig. 11). In this case the curve illustrating extraction at lower free ligand concentrations is situated above the graph of α_4. At a higher 2-MI concentration in the aqueous phase ($[L] > 0.06\ m$), the curves almost overlap. This suggests that at lower 2-MI concentrations the third complex along with the $[ZnL_4]^{2+}$ complex is extracted. According to results reported in Ref. *4*, the complexes are probably tetrahedral.

To verify the above interpretation of the extraction process, we studied the dependence of the partition coefficient and the degree of formation of a complex for which the $\alpha_n = f([L])$ curve shows similarity to the graph of the function $D = f([L])$. The graphs of the function $D = f(\alpha_n)$ are presented in Fig. 12. They show that the partition coefficient is linearly related to the degree of formation of a complex whose $\alpha_n = f([L])$ graph has a shape and position similar to the extraction curve. This permits an unambiguous decision about which of the complexes being formed in the systems passes to the organic phase.

Table 1 lists the most probable composition of complexes extracted with an organic solvent in the form of ion pairs.

TABLE 1

Composition of Complexes Passing to the Organic Phase

Ligand	Metal	Extractant	Composition of extractable complex[a]
1-Methylimidazole (1-MI)	Co(II)	Benzyl alcohol + ethyl acetylacetate	$[Co(1\text{-}MI)_3S_3](NO_3)_2$ $[Co(1\text{-}MI)_4S_2](NO_3)_2$
	Ni(II)	Benzyl alcohol	$[Ni(1\text{-}MI)_4S_2](NO_3)_2$
		Benzyl alcohol + ethyl acetylacetate	$[Ni(1\text{-}MI)_4S_2](NO_3)_2$ $[Ni(1\text{-}MI)_3S_3](NO_3)_2$
	Zn(II)	Benzyl alcohol	$[Zn(1\text{-}MI)_4S_2](NO_3)_2$
		Benzyl alcohol + ethyl acetylacetate	$[Zn(1\text{-}MI)_2S_2](NO_3)_2$ $[Zn(1\text{-}MI)_3S](NO_3)_2$
2-Methylimidazole (2-MI)	Co(II)	Benzyl alcohol	$[Co(2\text{-}MI)_4](NO_3)_2$
	Zn(II)	Benzyl alcohol	$[Zn(2\text{-}MI)_4](NO_3)_2$ $[Zn(2\text{-}MI)_3S](NO_3)_2$

[a] S stands for extractant molecule.

CONCLUSIONS

(1) The 1-MI and 2-MI complexes are extracted in the form of ion pairs, e.g., $[Co(1\text{-}MI)_4](NO_3)_2$.

(2) The extraction process is controlled by the degree of formation of that complex for which there is the highest probability of passing to the organic phase.

(3) The course of extraction as a function of the free ligand concentration in solution can be predicted based on the stability constants of the complexes being formed.

(4) Tetrahedral complexes pass more readily to the organic phase than do octahedral ones. Use can be made of this finding for the selective extraction of zinc from solutions containing other metal ions.

REFERENCES

1. B. Jezowska-Trzebiatowska, S. Kopacz, and T. Mikulski, *Pierwiastki Rzadkie*, Część 1. Występowanie i Technologia. PWN Warszawa 1976.

2. *Khimiya Extrakcii, Dokl. Mezhd. Konf.*, Göteborg, Sweden, August 27–September 1, 1966, Atomizdat, Moskva, 1971.

3. F. Rossotti and H. Rossotti, *The Determination of Stability Constants.*, New York, 1961.

4. B. Lenarcik, J. Kulig, and P. Laidler, *Rocz. Chem.*, *48*, 1151 (1974).

5. B. Lenarcik, B. Barszcz, and J. Kulig, *Ibid.*, *51*, 1315 (1977).

6. B. Lenarcik and B. Barszcz, *Ibid.*, *51*, 1849 (1977).

7. B. Lenarcik and K. Oblak, *Ibid.*, *51*, 2079 (1977).

8. W. Libuś, *Ibid.*, *33*, 931 (1959).

9. R. Mańko and E. Soczewiński, *Ibid.*, *47*, 1265 (1973).

10. R. Mańko and E. Soczewiński, *Ibid.*, *47*, 13 (1973).

11. R. Mańko and E. Soczewiński, *Ibid.*, *46*, 2263 (1972).

Received by editor May 30, 1978