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

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Abstract

Extraction studies of the Co(II), Ni(II), and Zn(II) complexes of 1-ethyl- and 1-butylimidazole reveal correlations between magnitudes of the extraction process and α_n functions characterizing reactions of stepwise complex formation in aqueous solution. Further, the effect of alkyl substituents in the imidazole ring on extractability of successive complexes has been established. For each of the systems studied, the number of complexes passing to the organic phase has been determined, and appropriate distribution constant values, P_n, have been calculated.

In the first article of this series (*1*), which dealt with extraction of the Co(II), Ni(II), and Zn(II) complexes of 1-methyl- and 2-methylimidazole, the extraction percent, E, of a metal was found to correlate with the degrees of formation of appropriate complexes in solution, α_n. In extension of these studies (*1*, *2*), an attempt has now been made to establish quantitative relationships between magnitudes describing the extraction process and functions characterizing the reaction of stepwise complex formation in solution. Further, the effect of the nature of an alkyl substituent in the imidazole ring on extractability of the successive complexes has been

investigated. As ligands, 1-ethyl- and 1-butylimidazoles have been chosen based on our earlier findings (*3*, *4*) that the compounds formed complexes of remarkable thermodynamic stability. The values of the dissociation constants of conjugate acids of the azoles, K_a, and of stability constants of the complexes, β_n, have been determined previously. Knowledge of these constants provides a prerequisite for the adopted model of extraction of metal complexes with heterocyclic bases.

EXPERIMENTAL

All measurements were run at 25°C and constant ionic strength (0.5) of the aqueous phase, maintained by means of KNO_3 and a ligand nitrate.

Commercially available reagents were used throughout. 1-Ethylimidazole (1-EI; Merck-Schuchardt) and 1-butylimidazole (1-BI; Koch-Light Labs.) were additionally purified by fractionation in vacuo.

The most effective extractants turned out to be 2-methylpropan-1-ol and benzyl alcohol. The alcohols were distilled before use.

The preparation of the remaining reagents as well as particulars concerning the procedures employed were reported in the previous article (*1*).

RESULTS AND DISCUSSION

As previously (*1*), extraction of each metal ion was studied by determining the extraction percent, E, at a varying concentration of the free ligand in solution:

$$E = \frac{C_M^0 - C_M}{C_M^0} \times 100\% \tag{1}$$

where C_M^0 and C_M denote, respectively, the analytical concentration of the metal ion in the aqueous phase before and after reaching partition equilibrium.

The free ligand concentration at equilibrium, [L], was found by measuring the pH of the aqueous phase and was calculated from

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

where K_a is the dissociation constant and $C_{[HL]NO_3}$ is the concentration of a conjugate acid of the ligand. The K_a values for the conjugate acids of 1-EI and 1-BI are 6.5×10^{-8} (*3*) and 6.0×10^{-8} (*4*), respectively.

The α_n value was calculated from the expression

$$\alpha_n = \frac{\beta_n[L]^n}{\sum_{n=0}^{n=N} \beta_n[L]^n} \quad (3)$$

where β_n denotes the cumulative stability constants of the successive complexes and N is the highest coordination number of the central ion (*5*). The values of the dissociation constants of conjugate acids and those of β_n have been taken from Refs. *3* and *4*.

In Figs. 1 to 3 the function $E = f([L])$ for the 1-EI complexes of Co(II), Ni(II), and Zn(II) is shown along with the function describing the steps in the formation of appropriate complexes, $\alpha_n = f([L])$. Figures 4 and 5 show analogous functions for the 1-BI complexes of the metals.

This form of presentation of the results allows determination of the extraction percent at any free ligand concentration in the aqueous phase and estimation of which of the complexes formed in the aqueous phase pass to the organic phase.

Figures 1 to 3 show that the plots of $E = f([L])$ for extraction with 2-methylpropan-1-ol exhibit a good correlation with a curve describing the degree of formation of the fourth complex. It is concluded that primarily a complex containing four 1-EI ligands passes to the organic phase. This statement does not rule out the possibility of extraction of lower complexes (third and second), especially with the Ni(II) and Co(II) species.

With benzyl alcohol as extractant, E for systems with a given ligand attains considerably higher values compared with 2-methylpropan-1-ol. The shape of the extraction curve resembles the one for α_4, in particular with the Co(II) species.

In systems comprising metal ions and 1-BI, the correlation between the E and α_n functions is poorer. However, the similarity of the $E = f([L])$ and $\alpha_n = f([L])$ plots allows conclusions to be drawn about the composition of the extractable species. In particular, the second and the third complexes are most probably extracted from Co(II) solutions whereas the third and the fourth complex are extracted from the Ni(II) and Zn(II) solutions, respectively. Unlike the 1-EI systems, extraction of the 1-BI metal complexes is practically independent of the nature of the extractant used.

In order to establish more precisely which species formed in the aqueous phase is being extracted, an attempt was made to determine the graphical distribution constants of particular complexes, P_n (*6*). The total con-

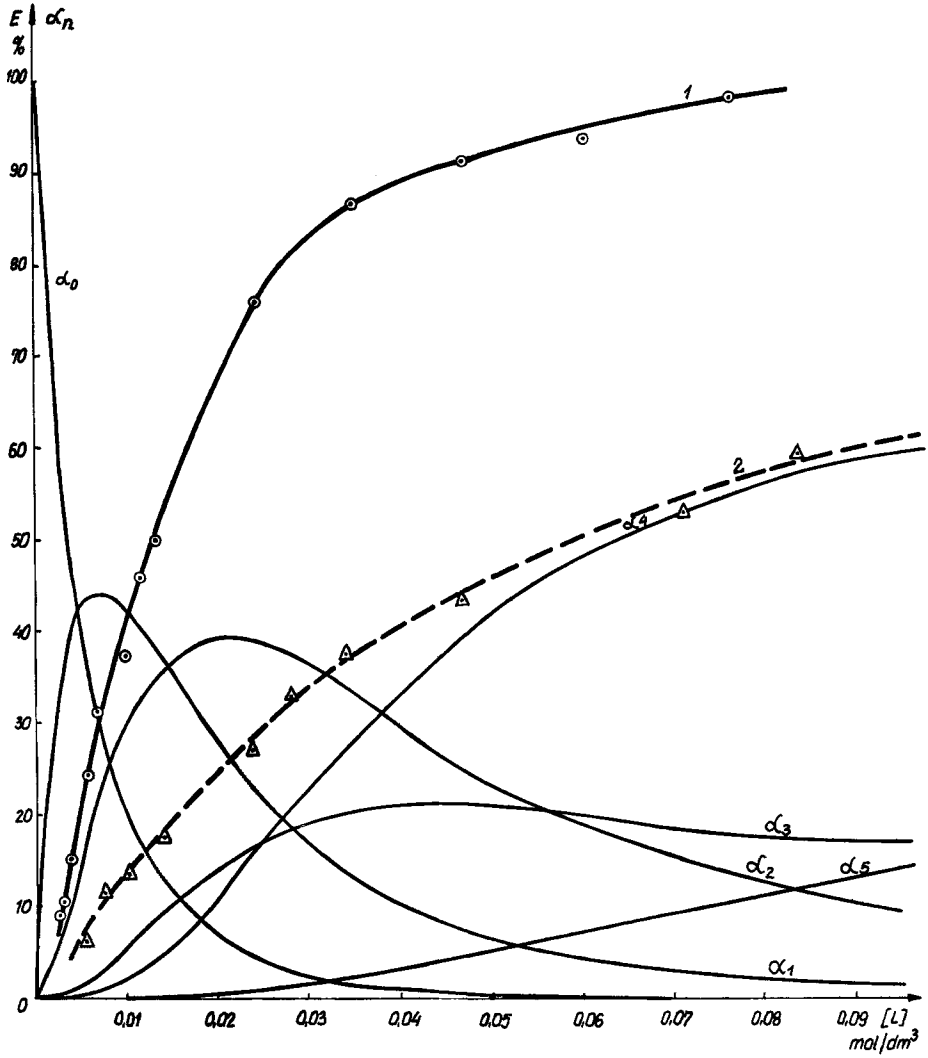

FIG. 1. Extraction percent of Co(II)–1-ethylimidazole complexes with benzyl alcohol (Curve 1) and with 2-methylpropan-1-ol (Curve 2) compared with the degrees of formation of particular complexes.

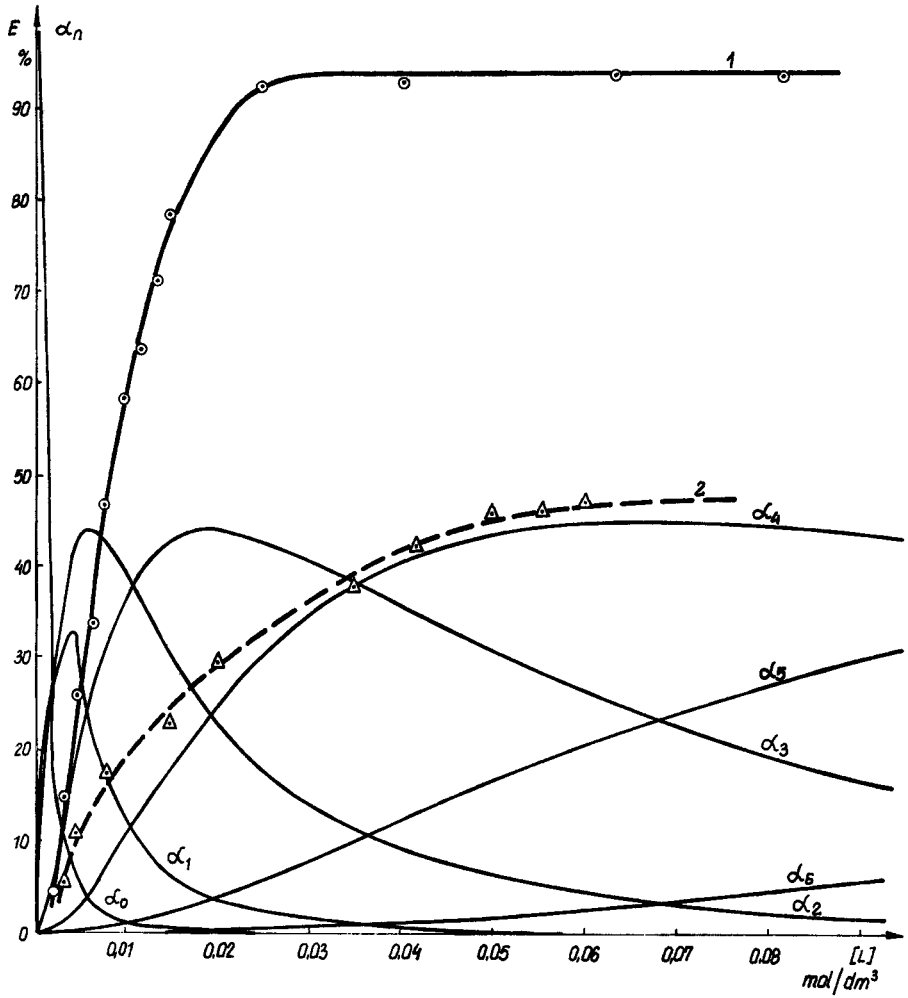

Fig. 2. Extraction percent of Ni(II)–1-ethylimidazole complexes with benzyl alcohol (Curve 1) and with 2-methylpropan-1-ol (Curve 2) compared with the degrees of formation of particular complexes.

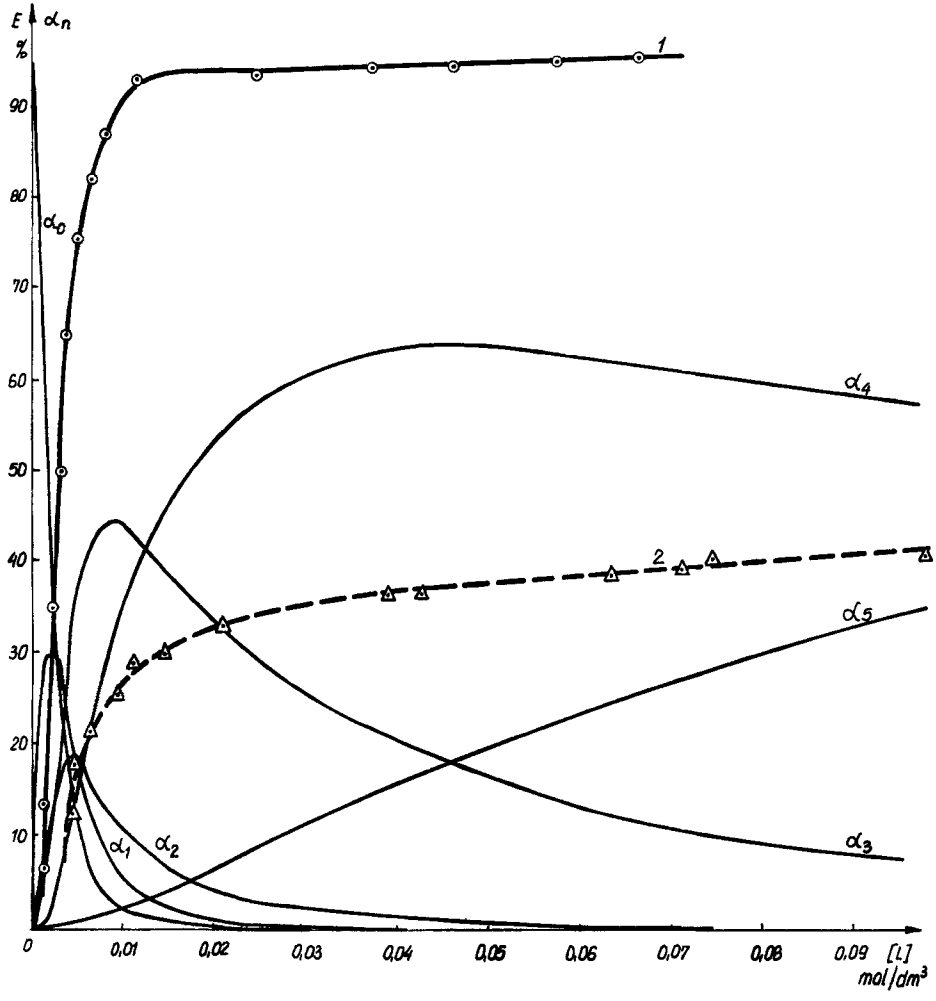

FIG. 3. Extraction percent of Zn(II)–1-ethylimidazole complexes with benzyl alcohol (Curve 1) and with 2-methylpropan-1-ol (Curve 2) compared with the degrees of formation of particular complexes.

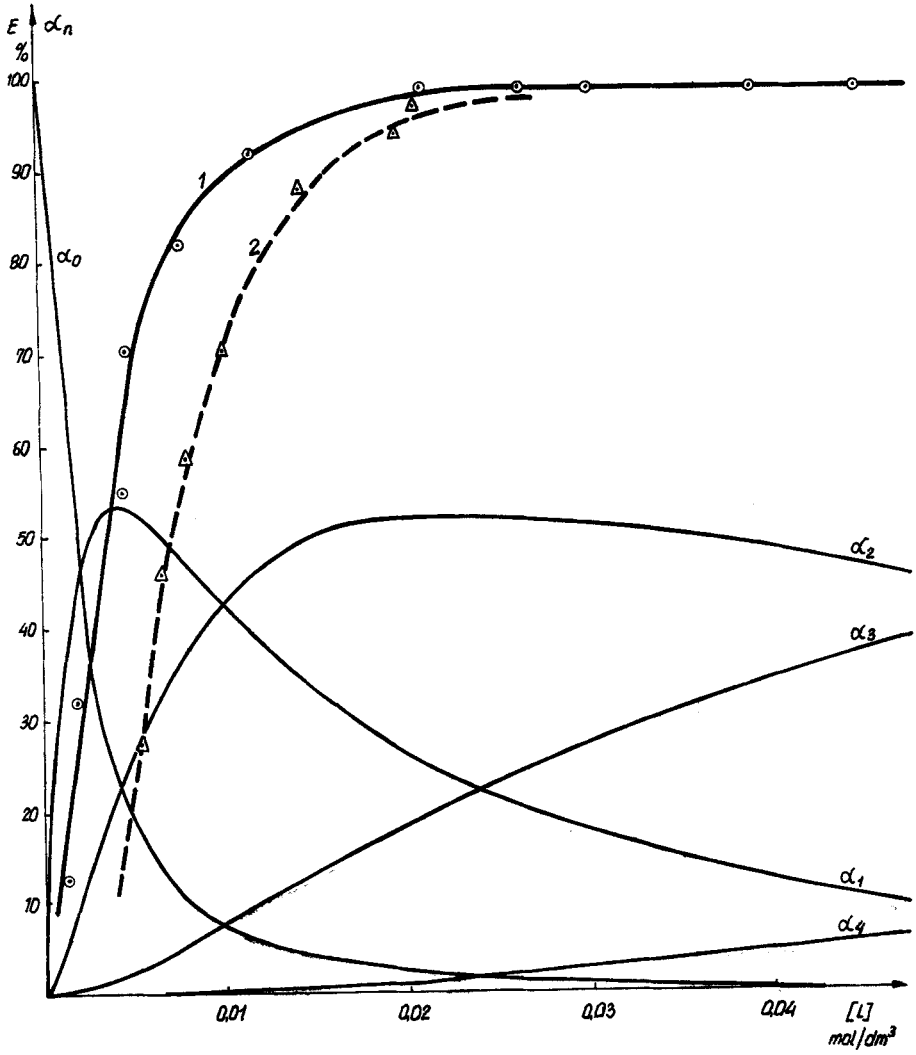

FIG. 4. Extraction percent of Co(II)–1-butylimidazole complexes with 2-methylpropan-1-ol (Curve 1) and with benzyl alcohol (Curve 2) compared with the degrees of formation of particular complexes.

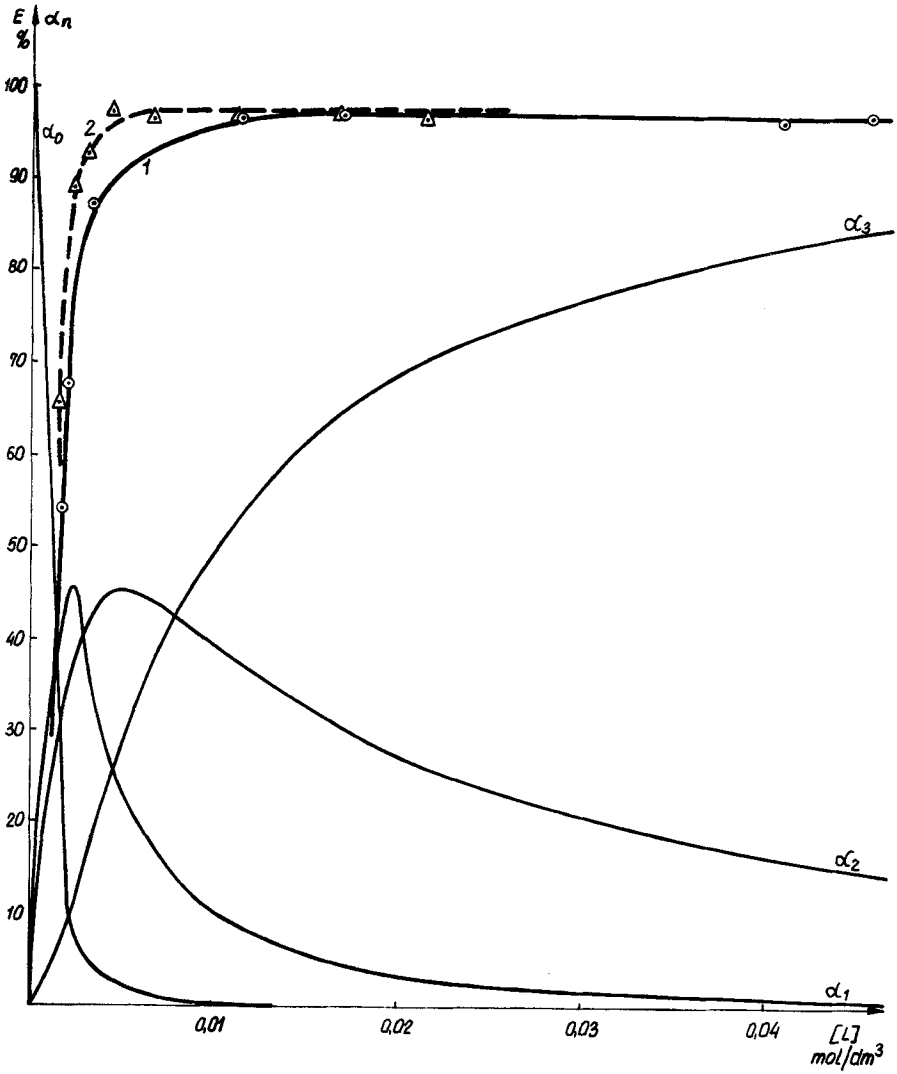

FIG. 5. Extraction percent of Ni(II)–1-butylimidazole complexes with 2-methylpropan-1-ol (Curve 1) and with benzyl alcohol (Curve 2) compared with the degrees of formation of particular complexes.

centration of the metal ion in the aqueous phase after partition equilibrium is reached is

$$C_M = \sum_{n=0}^{n=N} [ML_n] \tag{4}$$

Hence the distribution coefficient, D, is given by

$$D = \frac{C_{M,org}}{C_M} = \frac{\sum_{n=0}^{n=N} [ML_n]_{org}}{\sum_{n=0}^{n=N} [ML_n]} \tag{5}$$

Assuming that the extraction process is dependent on the distribution constants P_n of successive complexes, Eq. (5) can be rewritten in the form

$$D = P_n\alpha_n + P_{n+1}\alpha_{n+1} + \cdots + P_N\alpha_N \tag{6}$$

Data in Figs. 1 to 6 show that the extraction process of a series of complexes starts with a particular complex (that of lowest hydrophobicity) which, in turn, depends on the number of organic ligands attached to the central ion. Accordingly, we made an attempt to solve Eq. (6) graphically in order to determine the individual distribution constants P_n for extractable complexes. An illustration of this solution is provided by Fig. 7. A straight line described by the function $D = f(\alpha_n)$ passes through the origin of the coordinates for only one α_n value. Figure 7 shows that during extraction of the 1-EI complexes with 2-methylpropan-1-ol, a species containing three ligands passes first to the organic phase, except for the Zn(II) complexes where the fourth complex passes first.

In a similar manner, the compositions of the least hydrophobic complexes have been determined for the remaining systems specified in Table 1.

The P_n value of a particular complex was found from the slope of plot of the function $D = f(\alpha_n)$. To determine the P_n values of successive complexes passing to the organic phase, a function D_1 has been plotted for each system:

$$D_1 = D - P_n\alpha_n = P_{n+1}\alpha_{n+1} \tag{7}$$

If necessary, the following function has also been employed:

$$D_2 = D_1 - P_{n+1}\alpha_{n+1} \tag{8}$$

Thus, for each of the systems studied, the number of complexes passing

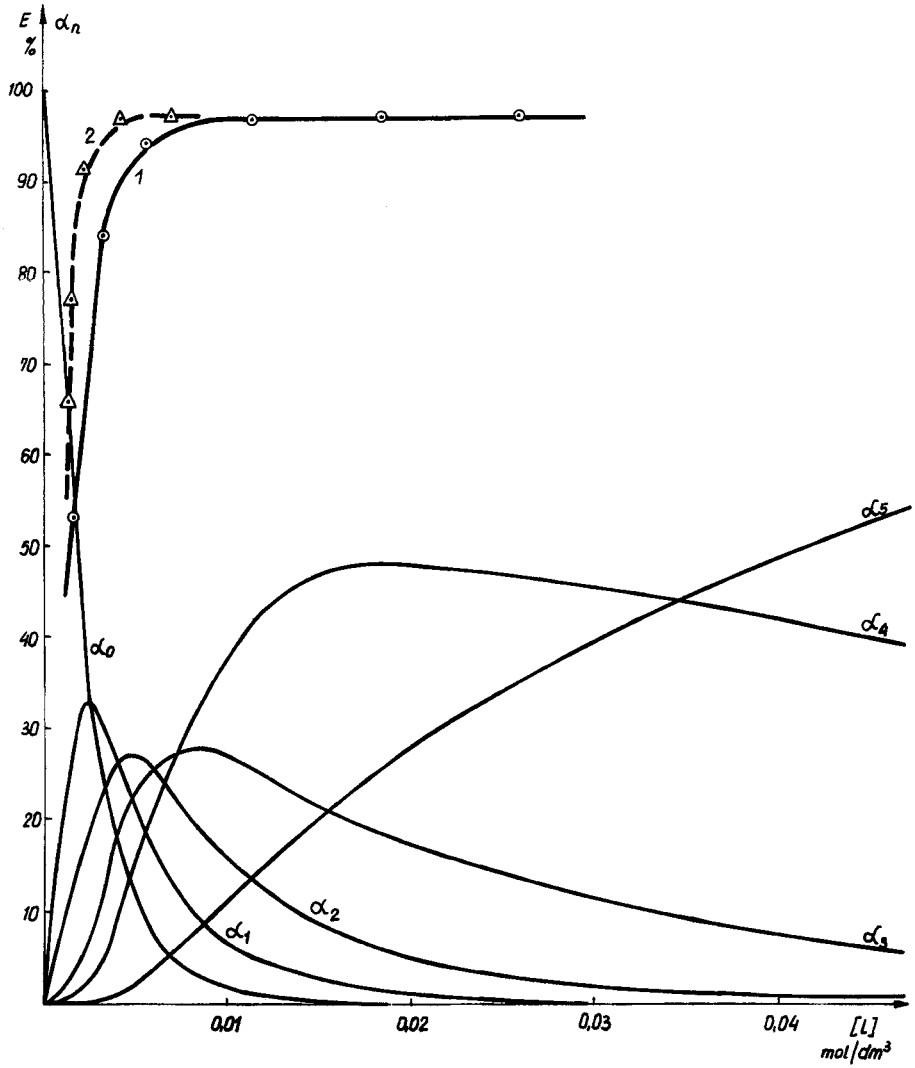

FIG. 6. Extraction percent of Zn(II)–1-butylimidazole complexes with 2-methylpropan-1-ol (Curve 1) and with benzyl alcohol (Curve 2) compared with the degrees of formation of particular complexes.

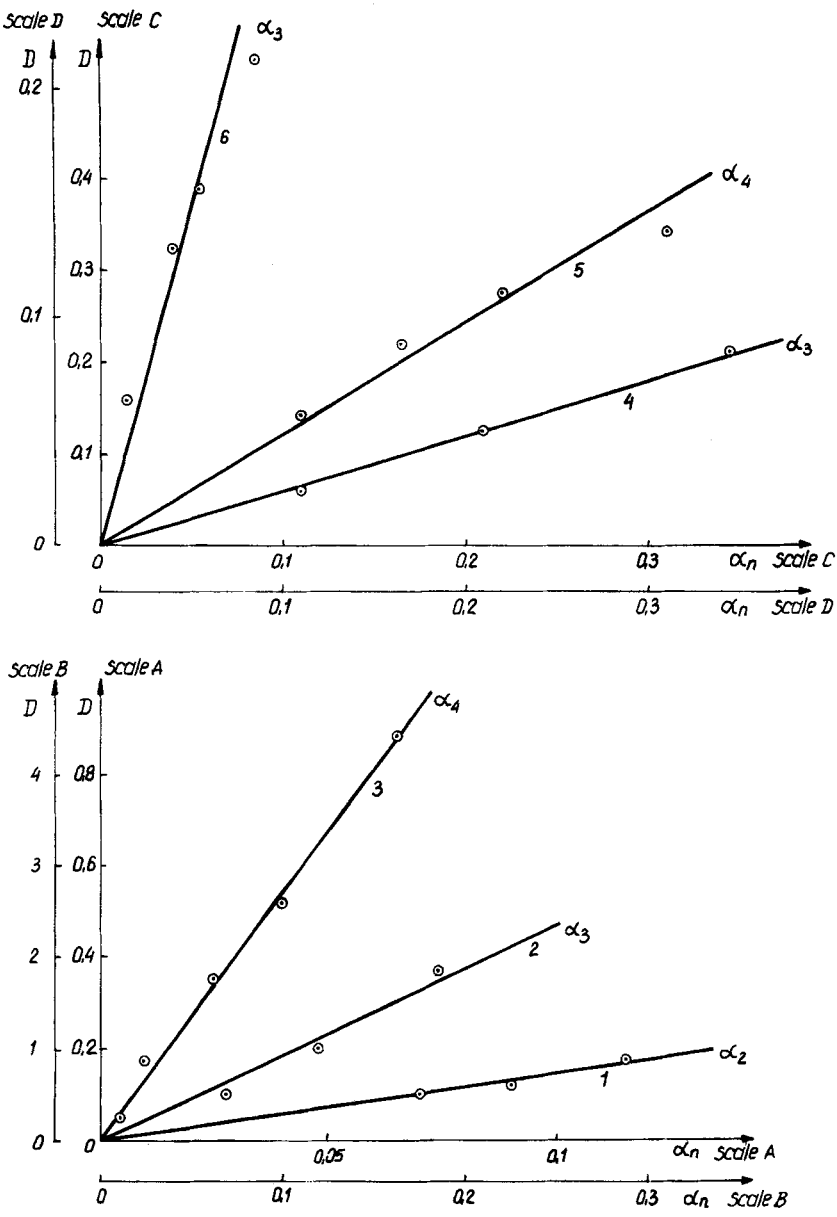

FIG. 7. Total distribution coefficient vs degree of formation of a particular 1-ethylimidazole complex in the aqueous phase. Benzyl alcohol extractant: (1) Co, Scale A; (2) Zn, Scale B; (3) Ni, Scale A. 2-Methylpropan-1-ol extractant: (4) Ni, Scale C; (5) Zn, Scale C; (6) Co, Scale D.

TABLE 1

Distribution Coefficients of Particular Complexes

Ligand	Extractant	Metal ion	First extractable complex	Distribution coefficients of individual complexes				
				P_2	P_3	P_4	P_5	P_6
1-Ethylimidazole	2-Methyl-	Co	α_3		3.0	3.8		
	propan-1-ol	Ni	α_3		0.6	0.8	2.3	
		Zn	α_4			1.2		
	Benzyl	Co	α_2	1.5	5.1	13.3	137.5	
	alcohol	Ni	α_4			13.5	29.8	
		Zn	α_3		9.5	15.7	46.2	
1-Butylimidazole	2-Methyl-	Co	α_2	5.0	104.4			
	propan-1-ol	Ni	α_3		38.5			
		Zn	α_4			91.0		
	Benzyl	Co	α_3		29.3	1440.0		
	alcohol	Ni	α_3		113.3			
		Zn	α_4			420.0		

to the organic layer was determined and the appropriate P_n values were calculated.

In order to verify the validity of the P_n values, they were employed for calculation of the E values for any ligand concentration. To do this, a correlation between E and D is required. From Eqs. (1), (5), and (6) it follows that the functions are correlated by

$$E = \frac{D}{1 + D} = \frac{P_n\alpha_n + P_{n+1}\alpha_{n+1} + \cdots + P_N\alpha_N}{1 + P_n\alpha_n + P_{n+1}\alpha_{n+1} + \cdots + P_N\alpha_N} \qquad (9)$$

For randomly chosen free ligand concentrations at equilibrium, the α_n values were calculated from Eq. (3), and these values were substituted into Eq. (9) to calculate E. The results were considered reliable when the E values calculated from Eq. (9) were in agreement with those taken from a graph of the function $D = f([L])$. Relevant data are shown in Table 1.

As seen in Table 1, the P_n values correspond excellently with the position of the extraction curves in Figs. 1 to 6. For instance, at small P_n values, both the $E = f([L])$ and $\alpha_n = f([L])$ curves have a similar shape and are close to each other [cf. the Co(II)—1-EI and Ni(II)—1-EI systems]. At high P_n values the $E = f([L])$ curves lie markedly higher than the corresponding $\alpha_n = f([L])$ curves.

The correlation between the two functions is less clear in cases where several complexes are simultaneously extracted [cf. extraction of the Co(II)—1-EI and Zn(II)—1-EI complexes with benzyl alcohol]. Absorption spectra of both phases containing the complexes revealed that six coordinate species pass into the organic phase.

Data in Table 1 also show that complexes containing 2 to 5 ligand molecules are being extracted. The remaining $(6 - n)$ coordination sites are probably occupied by the extractant molecules.

Our previous studies (*3*, *4*) showed that Zn(II) forms four- and six-coordinate species with both imidazoles. Hence it is reasonable to infer that the four-coordinate species, being more hydrophobic, will be extracted first. However, with 1-EI, the third, fourth, and fifth complexes are extracted. Consequently, one may assume that these complexes are six-coordinate. The structure of extractable Zn(II)—1-BI species, where a compound containing four ligands is extracted first, is still more difficult to determine. Perhaps a solvated salt, $[ML_4](NO_3)_2$, is extracted in this case. A major part of the complexes studied passes to the organic phase, probably in the form of solvated salts of the composition $[ML_nS_{6-n}](NO_3)_2$ or $[ML_nS_{5-n}NO_3]NO_3$, where S denotes an extractant molecule.

CONCLUSIONS

1. In each of the systems studied there is a close correlation between the extraction percent, E, and α_n functions describing stepwise formation of complexes in solution. The degree of correlation depends on the distribution constant values, P_n, of the particular species passing to the organic phase.

2. In no system studied has the extraction of species containing six coordinated ligands been observed. Hence, during extraction, one or more sites in the coordination sphere of the central ion can be occupied by extractant molecule(s).

3. In 1-ethylimidazole systems the extraction occurs much more readily with benzyl alcohol than with 2-methylpropan-1-ol. This can be explained by assuming that the molecules of benzyl alcohol coordinate to the central ion, making the whole complex more hydrophobic than in the case of 2-methylpropan-1-ol.

4. With 1-butylimidazole, differences in E between the two extractants are small because the butyl group itself imparts a fairly good hydrophobicity to the extractable molecule.

5. In the system considered, solvated salts of composition $[ML_nS_{6-n}](NO_3)_2$ or $[ML_nS_{5-n}NO_3]NO_3$ are extracted.

6. With the 1-EI and 1-BI complexes of Zn(II), no distinct difference could be noted between the values of individual distribution constants for tetrahedral and octahedral species.

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