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

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To cite this Article Radzyminska-Lenarcik, Elzbieta(2008) 'Influence of the Steric Hindrance, Ligand Hydrophobicity, and DN of solvents on Structure and Extraction of Cu(II) Complexes of 1-Alkyl-2-Ethylimidazoles', Separation Science and Technology, 43: 4, 794 — 814

To link to this Article: DOI: 10.1080/01496390701870655

URL: http://dx.doi.org/10.1080/01496390701870655

Separation Science and Technology, 43: 794–814, 2008

ISSN 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390701870655

Influence of the Steric Hindrance, Ligand Hydrophobicity, and DN of solvents on Structure and Extraction of Cu(II) Complexes of 1-Alkyl-2-Ethylimidazoles

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Abstract: Formation of Cu(II) complexes of 1-alkyl-2-ethylimidazoles (where alkyl = propyl, butyl, pentyl, hexyl, and octyl) has been studied by using the liquid-liquid partition method, at 25°C and a fixed ionic strength of the aqueous phase ($I = 0.5$; $(HL)NO_3$, KNO_3). The complexes were extracted with 2-pentanone, 2-butanol, isoamyl alcohol, 2-ethyl-1-hexanol, dichloromethane, trichloromethane, and toluene. The length of the 1-alkyl group and the nature of solvent have been shown to influence the extraction process. Extraction curves ($\log D_M$ vs. pH) are displaced towards lower pH's with increasing chain length of the 1-alkyl substituent and donor number of the solvents. Stability constants of the complexes in aqueous solution were determined as well as their partition ratios between the aqueous and organic phase. The stability of the Cu(II) complexes increased with increasing 1-alkyl chain length. The stability constants are comparable with β_n ones for the Cu(II) complexes of 1-alkyl-2-methylimidazoles, but smaller than those of the Cu(II)–1-alkylimidazole counterparts. The P_c-partition ratios of the 1-alkyl-2-ethylimidazole complexes with Cu(II) are high, and increased with increasing 1-alkyl chain length and the donor number of the solvents. Both the strong steric effect of the ethyl substituent at position 2 and the bulkiness of the 1-alkyl-2-ethylimidazole molecules as well as the strong electron-donating properties of the solvent molecules have an effect on the change of the coordination number of Cu(II) from 6 to 4. The 4-coordinate Cu(II) complexes (distorted tetrahedron) are more readily extractable by organic solvent

Received 5 June 2007, Accepted 4 November 2007

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than are the 6-coordinate ones and for this reason their partition constants, P_c, are high. This finding offers the possibility of extraction of the Cu(II) ions from a mixture cations.

Keywords: Solvent extraction, Cu(II) complexes, 1-alkyl-2-ethylimidazole, stability constants, partition ratios, steric effect

INTRODUCTION

Substitution of the methyl group at position 2 of the imidazole ring increases by an order of magnitude the basicity of the pyridinic nitrogen atom of a 1,3-diazole. At the same time the substituent hampers the formation of the 2-methylimidazole complexes with metal ions due to the steric hindrance (1). Lowering of the stability of metal complexes due to steric hindrance depends on the nature of the central ion, as well. The largest decrease in the stability has been noticed for 2-methylimidazole complexes of Ni(II), a lightly smaller for octahedral species of Co(II) and Zn(II), and the smallest one for Cu(II) (1, 2). Substitution of bulky alkyl groups at position 1 of a 1,3-diazole molecule results in enhanced hydrophobicity of the imidazoles, thus providing opportunity for extraction of metal complexes of these base with organic solvents (3, 4). Owing to the combined hydrophobic and steric effects, 1-alkyl-2-methylimidazoles provide conditions for separation of the Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) ions (5). Du Preez at all determined the extraction process of Cu(II) complexes with 1-decyl-2-methylimidazole and 1-decyl-4(5)-methylimidazole from perchlorate, chloride, and thiocyjanate solutions at lower pH (4).

The steric effect disappears when the group substituted in the position 2 of the imidazole ring have a donor atom forming the coordination bond, for example oxygen atom.

The complexes of 1-alkyl-2-hydroxymethylimidazoles are more stable than those of 1-alkyl-2-methylimidazoles. This fact may be explained by the possibility of the formation of a chelate ring in the 1-alkyl-2-hydroxymethylimidazole complexes (6, 7). J.G.H. du Preez with coworkers synthesized a new extractant 2-(1-ethylthiomethyl)-1-decylimidazole (8). This ligand formed sparingly extractable six- coordinate Co(II), Ni(II), and Cu(II) chelate complexes from perchlorate, chloride, and thiocyjanate ions, and it did not show the steric hindrance. Recently, one has studied the influence of the steric hindrance and alkyl chain length on the extraction efficiency of Zn(II) and Cu(II) complexes with 1-alkyl-2-methylimidazoles with several organic solvents (9, 10).

Increasing the 2-alkyl chain length from the methyl to the ethyl group has been found to strengthen the steric effect in reactions of 2-ethylimidazole with the Co(II), Ni(II), and Zn(II) ions only, whereas the Cu(II) complexes of 2-methylimidazole and 2-ethylimidazole had comparable stabilities (11).

The purpose of this study was to investigate the influence of the alkyl chain length in position 1 of the imidazole ring, steric effect of ethyl group in the position 2, and the donor number (DN) of solvents on the extraction efficiency of the Cu(II) complexes with five 1-alkyl-2-ethylimidazoles, namely 1-propyl-, 1-butyl-, 1-pentyl-, 1-hexyl-, and 1-octyl-2-ethylimidazole (Fig. 1).

2-Butanol, isoamyl alcohol (hereafter: iso-AmOH), 2-ethylhexanol, dichloromethane, trichloromethane, and toluene were used as water-immiscible solvents. These solvents show large differences in donor proprieties.

EXPERIMENTAL

Reagents

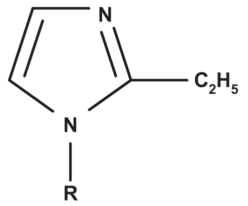
The 1-alkyl-2-ethylimidazoles used in this work were synthesized by A. Skrzypczak, Technical University, Poznan, Poland, according to the literature method (12).

The preparation of stock solutions of copper(II) nitrate and nitric acid (Analytical reagent grade, POCh, Poland) is described in the preceding papers (10, 13). Dichloromethane (POCh, Poland), trichloromethane (POCh, Poland), toluene (POCh, Poland), isoamyl alcohol (POCh, Poland), 2-butanol (Merck), 2-ethyl-1-hexanol (Aldrich), 2-pentanone (Merck), all analytical reagent grade, are used without purification.

The pH-meter was calibrated using commercial buffer solutions (Radiometer) of pH 4.01 ± 0.01 and 7.00 ± 0.01. The pH was also checked against hydrochloric acid according to IUPAC recommendations (14).

Equipment

Potentiometric measurements were carried out on a computer-aided multifunctional pH-meter (PHM 250, Radiometer) equipped with a glass-calomel combination electrode C 2401-8 (Radiometer). The atomic absorption spectrophotometer-BUCK Scientific 210 VGP instrument with a hollow cathode lamp



R = C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_8H_{17}

Figure 1. Chemical structure of 1-alkyl-2-ethylimidazole.

Cu 324.7 was used for the determination of Cu(II) concentration. A Hewlett Packard Agilent 8453 spectrophotometer was used for recording absorption spectra of the Cu(II) complexes over the visible range in the organic phases.

Extraction Procedure

The measurements were run at 25°C and at fixed ionic strength (0.5 mol/L) maintained in the aqueous phase with $KNO_3 + HNO_3$. Before extraction the concentrations of Cu(II) ions and nitric acid in the aqueous phase were constant (0.01 and 0.15 mol/L respectively) and the ligand concentrations in the organic phase were varied from 0.01 to 0.25 mol/L. Six cm^3 of the aqueous phase were placed in a graduated test tube and an equal volume of an 1-alkyl-2-ethylimidazole solution in the organic solvent was added. The test tubes were then shaken for 30 min. The equilibrium was established after a few minutes, however, but no longer than 30 min. After reading the difference in the phase volume, the phases were separated, and the pH of the aqueous phase was measured. The Cu(II) concentration was determined by titration with a standardized EDTA solution and by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

The extraction process in the systems studied was characterized, as previously (9, 10, 13, 15–18) by analyzing the relationship between partition coefficients of Cu(II), expressed as log D_M, and equilibrium pH of the aqueous phase.

The partition coefficients were defined as a distribution ratio of Cu(II) concentration in the aqueous phase before and after attaining equilibrium, and calculated from the following equation:

$$D_M = \frac{C_{Cu(II)(org)}}{C_{Cu(II)(aq)}} = \frac{C_M^0 - C_M}{C_M} \tag{1}$$

where: C_M^0 and C_M denote analytical Cu(II) concentrations in the aqueous phase before and after attaining partition equilibrium, respectively.

The magnitude of D_M depends on the alkylimidazole concentration in both phases, and consequently on the pH.

The partition of the Cu(II) complexes with 1-propyl-2-ethylimidazole was investigated between the aqueous and organic phases using 2-pentanone, 2-butanol, iso-AmOH, and trichloromethane. The results presented as a plot of the copper(II) distribution ratio (log D_M vs. pH) of the aqueous phase are shown in Fig. 2. Extraction of the complexes was most effective with 2-pentanone for which $pH_{1/2} = 6.3$. The extraction curve for iso-AmOH at a level of $D_M = 1$ is displaced in relation to

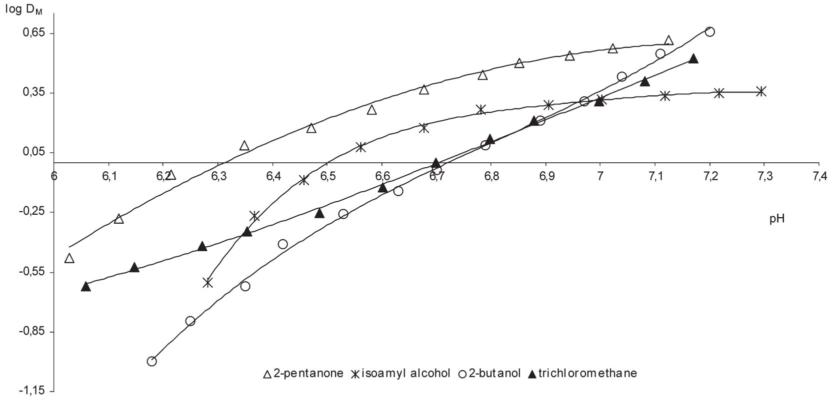


Figure 2. Influence of the solvents on the extraction of Cu(II) complexes with 1-propyl-2-ethylimidazole.

the 2-pentanone curve by 0.2 pH unit towards higher basicity. On the other hand, the $pH_{1/2}$ values for 2-butanol and trichloromethane are comparable, both amounting to around 6.75. At pH's exceeding 6.5 both curves overlap.

Extraction of the Cu(II) complexes with more hydrophobic 1-alkyl-2-ethylimidazoles was investigated using six solvents: 2-ethylhexanol, 2-butanol, iso-AmOH, dichloromethane, trichloromethane, and toluene.

Extraction curves of the Cu(II) complexes with 1-butyl-2-ethylimidazole are presented in Fig. 3. As seen, they form a convergent bundle of curves

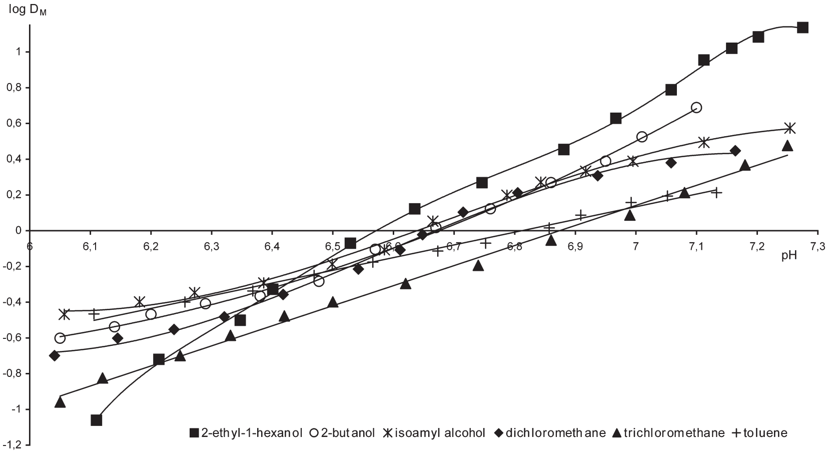


Figure 3. Influence of the solvents on the extraction of Cu(II) complexes with 1-butyl-2-ethylimidazole.

differing in slope relative to the pH axis. The $pH_{1/2}$ values for 2-butanol, iso-AmOH, and dichloromethane are comparable and oscillate around 6.67. The largest difference between the $pH_{1/2}$ values occurs between the 2-ethylhexanol and trichloromethane curves and amounts to 0.27 pH unit. The complexes are most effectively extracted with 2-ethylhexanol. In this case, the $pH_{1/2}$ attains a minimum of 6.58.

Extraction curves of the Cu(II) complexes with 1-pentyl-2-ethylimidazole (Fig. 4) are more separated apart on the pH axis than are those for the extraction of the 1-butyl-2-ethylimidazole complexes. The extraction is most effective with 2-ethylhexanol at pH's below 5.7, whereas above this value iso-AmOH becomes the most effective solvent. The curves of dichloromethane and trichloromethane almost overlap over the whole pH range. For 2-butanol, $pH_{1/2}$ is 5.76 and log D_M vs. pH of the aqueous phase function is one of the most rapidly growing with increasing pH of the aqueous phase. The least effective solvent here is toluene ($pH_{1/2} = 5.9$).

Still larger differences in location of the extraction curves corresponding to particular solvents were noticed with the 1-hexyl-2-ethylimidazole complexes of Cu(II) (Fig. 5). The extraction efficiency of those complexes decreased in the following rank order of solvents: 2-ethylhexanol > 2-butanol > iso-AmOH > dichloromethane > trichloromethane > toluene. The curves for the alcohols are situated over a low pH range. The difference in $pH_{1/2}$ between 2-ethylhexanol and toluene is quite large, amounting to 2.5 pH units.

A similar picture is seen with extraction curves of the Cu(II) complexes with 1-octyl-2-ethylimidazole (Fig. 6). The differences in location of the curves on the pH axis are also large. Extraction curves for 2-ethylhexanol and 2-butanol are situated at the lowest pH's. The difference between the

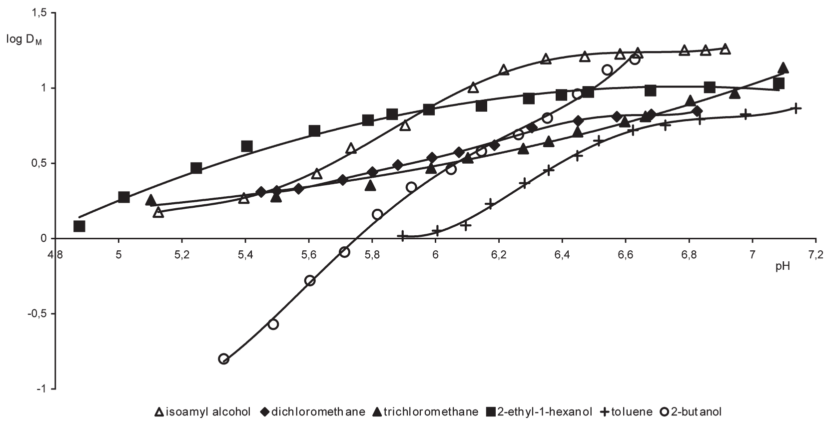


Figure 4. Influence of the solvents on the extraction of Cu(II) complexes with 1-pentyl-2-ethylimidazole.

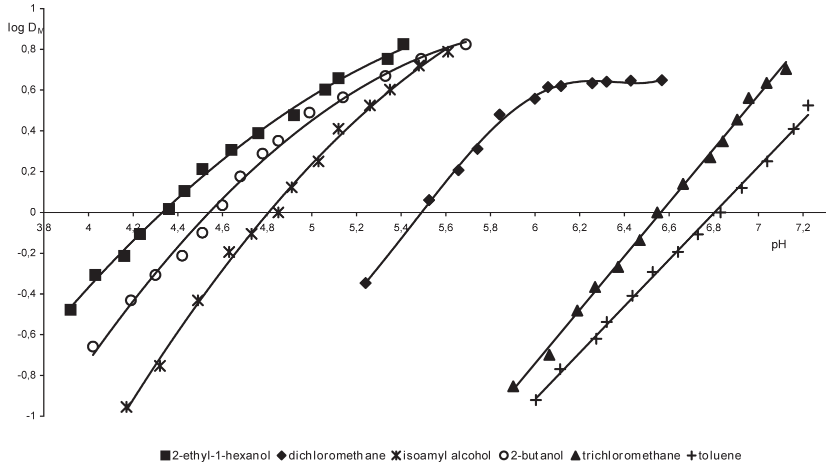


Figure 5. Influence of the solvents on the extraction of Cu(II) complexes with 1-hexyl-2-ethylimidazole.

most effective solvent, 2-ethylhexanol, and the least effective one, toluene, exceeds 2 pH units.

A simultaneous influence of the alkyl chain length of the 1-alkyl-2-ethylimidazoles and the nature of solvent on extraction efficiency of the Cu(II) complexes can also be presented in another way, namely that used in most of our preceding papers (9, 10, 13, 15–18). Accordingly, in five Figures

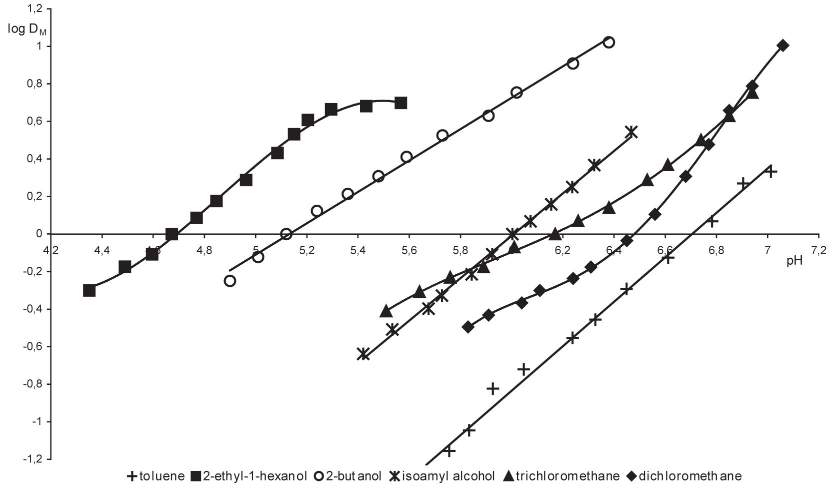


Figure 6. Influence of the solvents on the extraction of Cu(II) complexes with 1-octyl-2-ethylimidazole.

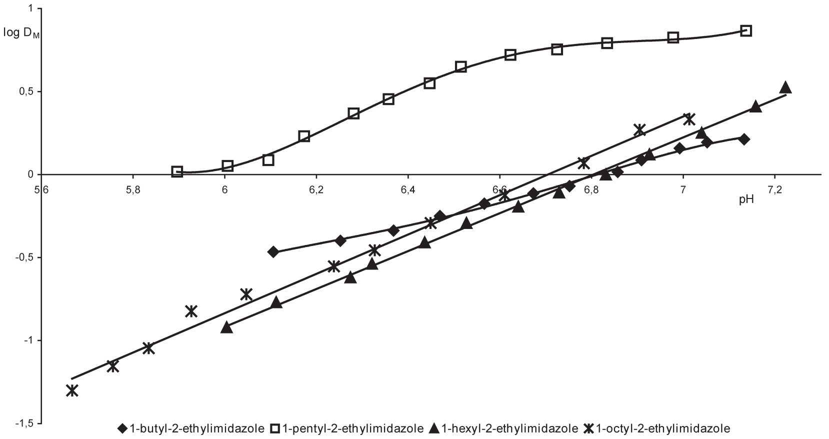


Figure 7. Influence of the alkyl chain length of 1-alkyl-2-ethylimidazoles on the extraction of Cu(II) complexes into toluene.

(Nos. 7 through 11), the influence is shown of the 1-alkyl chain length on extraction of the Cu(II) complexes with five solvents: toluene (Fig. 7), dichloromethane (Fig. 8), trichloromethane (Fig. 9), 2-butanol (Fig. 10), and 2-ethylhexanol (Fig. 11).

Mutual positions of the extraction curves, log $D_M = f(pH)$, for toluene (Fig. 7), dichloromethane (Fig. 8), and trichloromethane (Fig. 9) are quite unexpected and at odds with a picture of extraction of the complexes of Cu(II) and other cations with homologous series of the previously studied alkylimidazoles

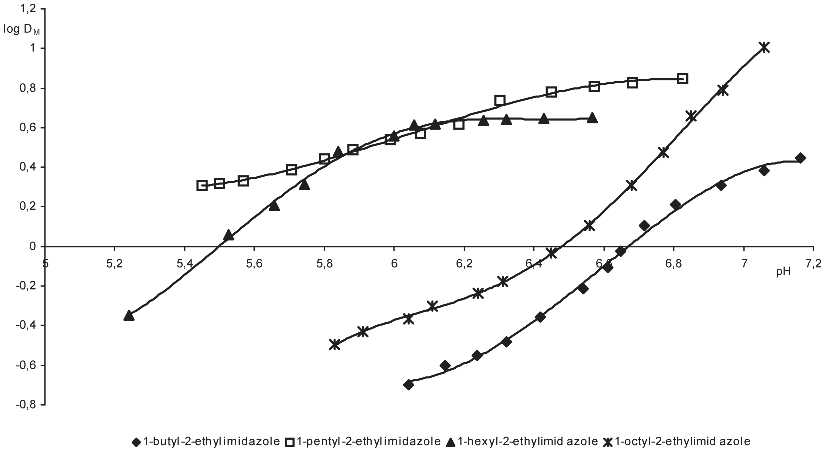


Figure 8. Influence of the alkyl chain length of 1-alkyl-2-ethylimidazoles on the extraction of Cu(II) complexes into dichloromethane.

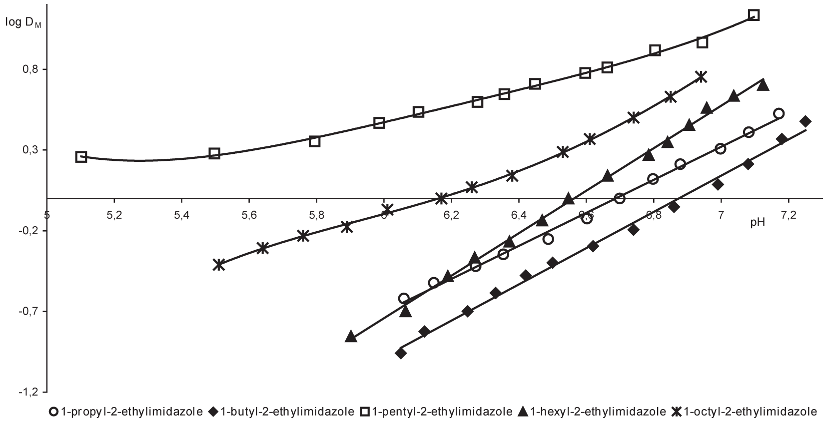


Figure 9. Influence of the alkyl chain length of 1-alkyl-2-ethylimidazoles on the extraction of Cu(II) complexes into trichloromethane.

(9, 10, 13, 15–18). Thus, with increasing 1-alkyl chain length, the extraction curves of particular ligands should locate themselves over gradually decreasing pH ranges. In contrast to this, as seen in Fig. 7, at the lowest pH's the Cu(II) complexes with 1-pentyl-2-ethylimidazole ($pH_{1/2} = 5.9$) are extracted with toluene, whereas the curves of more hydrophobic alkylimidazole complexes are shifted by ca 0.7 pH unit towards higher pH's. This is quite an unexpected phenomenon. Equally unexpected is the mutual location of the extraction curves for dichloromethane (Fig. 8) where two curves of the Cu(II) complexes of 1-pentyl-2-ethylimidazole and 1-octyl-2-ethylimidazole are located close to each other over the range of low pH, whereas those of the 1-butyl-2-

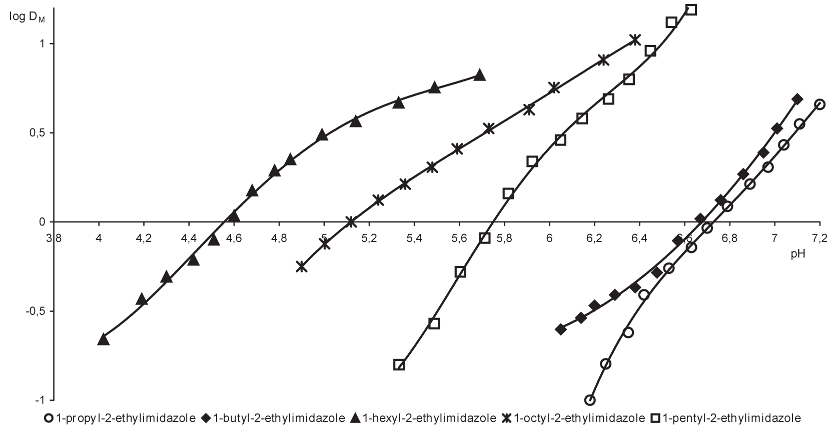


Figure 10. Influence of the alkyl chain length of 1-alkyl-2-ethylimidazoles on the extraction of Cu(II) complexes into 2-butanol.

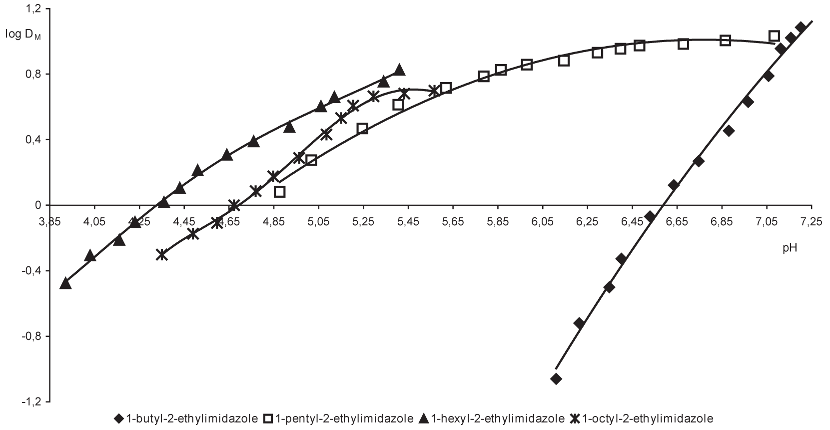


Figure 11. Influence of the alkyl chain length of 1-alkyl-2-ethylimidazoles on the extraction of Cu(II) complexes into 2-ethylhexanol.

ethylimidazole and 1-octyl-2-ethylimidazole complexes appear at higher pH values. Only in the case of extraction of the complexes with trichloromethane (Fig. 9) the mutual location of the extraction curves resembles that expected one, although even in this case there are some irregularities. Namely, the 1-pentyl-2-ethylimidazole curve is displaced to the left = hand side towards lower pH's, whereas that of 1-butyl-2-ethylmidazole is located utmost to the right. Figures 10 and 11 for 2-butanol and 2-ethylhexanol, respectively, represent a typical situation where the extraction curves are gradually displaced towards lower pH values with increasing hydrophobicity on account of elongation of the 1-alkyl chain. Some deviation from this rule is seen in the extraction of the Cu(II) complexes with 1-hexyl-2-ethylimidazole.

These anomalies in the mutual location of the extraction curves on the pH axis show that molecules of a majority of the solvents used compete for the space in the coordination sphere of the central ion with molecules of the heterocyclic ligands. Figures 7 through 11 also show that the influence of particular solvents on the process of extraction of the Cu(II) complexes with 1-alkyl-2-ethylimidazoles is variable and distinctly dependent on the bulkiness of molecules of the imidazole derivatives.

To demonstrate the influence of the solvents on the extraction process of Cu(II) a dependence between $pH_{1/2}$ and the Gutmann's donor number (19, 20), DN, of the solvents used was investigated (see Fig. 12). As seen, the $pH_{1/2}$ value for each extraction system decreases with increasing donor number of solvent. At the same time, there is a sort of hydrophobic–solvation synergism whereby the influence of the donor strength of solvents escalates with increasing 1-alkyl chain length. To find the reason for this behavior, it is necessary to get parameters determining the extraction process in the systems studied.

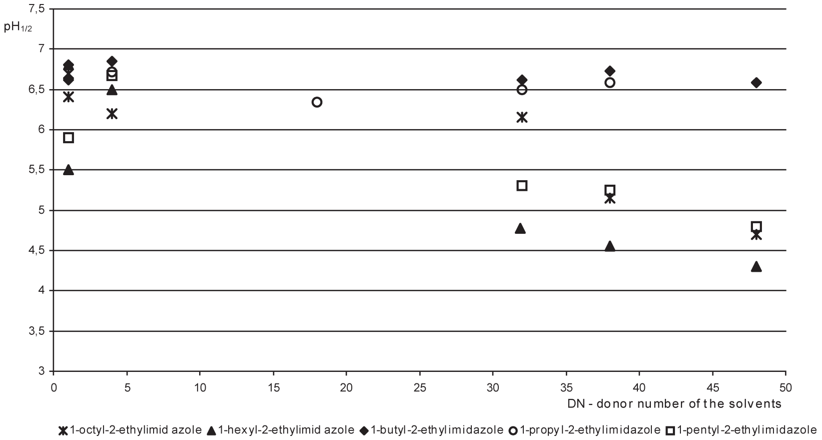


Figure 12. Influence of the Gutmann's donor number (DN) of the solvents and the alkyl chain length on $pH_{1/2}$ values of extraction of Cu(II) complexes with 1-alkyl-2-ethylimidazoles.

The extraction process of the complexes is described by Equation (2):

$$D_M = \frac{P_c\beta_c[L]^c + P_{c+1}\beta_{c+1}[L]^{c+1} + \ldots\ldots + P_N\beta_N[L]^N}{\sum_{n=0}^{n=N}\beta_n[L]^n} \tag{2}$$

where: β_n and β_c are cumulative stability constants of the Cu(II) complexes with 1-alkyl-2-ethylimidazole in the aqueous phase, P_c are organic solvent/water partition ratio of the this complexes, ($P_c = [ML_c]_{(org)}/[ML_c]_{(aq)}$), [L] is the free ligand concentration (mol/L) in the aqueous phase, and c is the number of ligands molecules in the first Cu(II) complex that is so hydrophobic that it freely passes into the organic phase (20–22).

To learn which of the parameters, P_n or β_n, affects the partitioning of Cu(II) between the two phases, both stability constants of the complexes and their partition ratios had to be determined. The required free azole base concentrations in the aqueous phase at equilibrium, [L], were found from the following equation:

$$[L] = \frac{K_a[HL^+]}{[H_3O^+]} \tag{3}$$

where K_a is the dissociation constant of the protonated ligand HL^+, $[HL^+]$ is the concentration of the conjugate acid of the ligand equal to analytical concentration of nitric acid (mol/L) in the aqueous phase. The pK_a values of the homologous series of 1-alkyl-2-ethylimidazole needed for the calculations were taken from reference (23).

The pooled D_M values and the corresponding sets of independent variable [L] were used for the determination of stability constants β_n of the Cu(II) complexes by using the equation proposed by Rydberg (20, 21):

$$\frac{[\mathrm{L}]^{c}}{\mathrm{D_M}} = \frac{\sum_{\mathrm{n=0}}^{\mathrm{n=N}} \beta_{\mathrm{n}}[\mathrm{L}]^{\mathrm{n}}}{\mathrm{P}_c\beta_c} \tag{4}$$

Equation (4) can be used for the determination of composition of the first complex being extracted from the aqueous phase, and stability constant, β_1, of the first complex formed in the aqueous phase. To do this, the shape of function $[\mathrm{L}]^c/\mathrm{D_M} = \mathrm{f}[\mathrm{L}]$ is monitored when varying exponent c between 1 and 6. In this way a bundle of curves was obtained of which only one was a straight line with positive slope and b values. It is assumed that the c value is equal to the number of ligand molecules attached to the central ion in the first complex being extracted. This procedure has successfully been used in the preceding studies (9, 10, 13, 15–18).

The stability constants, β_{n}, obtained in this way are collected in Table 1 for each organic solvent and ligand. The β_{n} constants are comparable with those previously determined by potentiometric method for the Cu(II) complexes of 2-ethylimidazole (11). They increase only slightly with increasing 1-alkyl chain length, similar to the case with the 1-alkyl-2-methylimidazole complexes (10). The β_{n} values for both homologous series are comparable.

To determine the number, composition and extractability of the Cu(II) complexes passing into the organic phase, respective partition ratio, P_c, as defined by Eq. (2), were determined from the following relationship between extraction coefficient, $\mathrm{D_M}$, and mole fractions of successive complexes, α_{n}:

$$\mathrm{D_M} = \mathrm{P}_c\alpha_c + \mathrm{P}_{c+1}\alpha_{c+1} + \mathrm{P}_{c+2}\alpha_{c+2} + .. + \mathrm{P_N}\alpha_{\mathrm{N}} \tag{5}$$

P_c and α_c characterize the first in the series of consecutive complexes containing c ligand molecules, which is capable of passing into the organic phase (20–22). The calculations were accomplished numerically. I looked for the first straight line, which passed through the origin of the coordinates. In this way, partition ratio, P_c, of the first extractable complex was determined. Partition ratios, $\mathrm{P_n}$, obtained in this way are collected in Table 1.

The influence of nature solvent and the hydrophobic properties of the ligand on the partition of the Cu(II) complexes with 1-alkyl-2-ethylimidazoles is best visualized by plots of partition ratios, P_c, against 1-alkyl chain length ($\mathrm{C_x}$) (Figs. 13–15).

In Fig. 13 there is a distinct linear increase of $\mathrm{P_1}$ values for toluene and almost linear for dichloromethane and trichloromethane. However, with a strongly electron-donating solvents (2-butanol, isoamyl alcohol, and 2-ethylhexanol), beginning from 1-butyl-2-ethylimidazole, the slope of the $\mathrm{P_1} = \mathrm{f(C_x)}$ straight line dramatically increases with increasing 1-alkyl chain length. A similar deviation exhibit all alcohols in the $\mathrm{P_2} = \mathrm{f(C_x)}$ function presented in Fig. 14. These findings can be explained in terms of a structural

Table 1. Stability constants log β_c and partition constants P_c of the Cu(II) complexes with 1-alkyl-2-ethylimidazoles in aqueous solution (I = 0.5 (HL)NO_3, KNO_3) at 25°C

Ligand	pK_a	log β_1	log β_2	log β_3	Solvent	P_1	P_2	P_3
1-Propyl-2-ethylimidazole	8.03	3.40	6.28	7.52	2-Butanol	20	68	1,015
		3.97	7.33	8.05	2-Pentanol	30	87	550
		3.72	6.87	7.76	2-Pentanone	15	42	60
		3.93	7.25	7.98	Trichloromethane	40	65	450
1-Butyl-2-ethylimidazole	8.27	3.52	6.50	8.04	2-Butanol	65	105	1,260
		4.08	7.54	8.85	2-Pentanol	46	125	870
		3.87	7.15	8.27	2-Ethyl-1-hexanol	18	375	1,670
		4.65	8.58	9.76	Dichloromethane	25	140	1,100
		3.82	7.06	8.34	Trichloromethane	70	160	1,320
		3.71	6.85	8.15	Toluene	12	43	400
1-Pentyl-2-ethylimidazole	8.31	3.56	6.58	8.11	2-Butanol	120	325	1,580
		4.10	7.57	8.79	2-Pentanol	92	350	1,100
		3.95	7.30	8.76	2-Ethyl-1-hexanol	38	631	2,100
		4.46	8.24	9.83	Dichloromethane	98	202	1,450
		4.05	7.48	8.80	Trichloromethane	70	160	1,320
		3.70	6.83	8.22	Toluene	19	72	

1-Hexyl-2-ethylimidazole	8.36	3.61	6.67	8.17	2-Butanol	190	780	2,100
		4.12	7.61	8.84	2-Pentanol	120	470	1,400
		4.00	7.39	8.82	2-Ethyl-1-hexanol	45	950	2,700
		4.55	8.40	9.87	Dichloromethane	105	187	1,900
		4.22	7.80	9.02	Trichloromethane	82	190	1,700
		3.71	6.91	8.26	Toluene	15	100	
1-Octyl-2-ethylimidazole	8.44	3.80	7.02	8.47	2-Butanol	320	860	3,500
		4.00	7.40	8.65	2-Pentanol	86	600	1,800
		4.30	7.94	9.35	2-Ethyl-1-hexanol	72	1,300	3,600
		4.53	8.37	9.68	Dichloromethane	140	260	2,500
		4.25	7.85	8.76	Trichloromethane	96	240	2,800
		3.78	6.98	8.05	Toluene	17	120	

The given values of the constants β_n and P_n carry 10% tolerance.

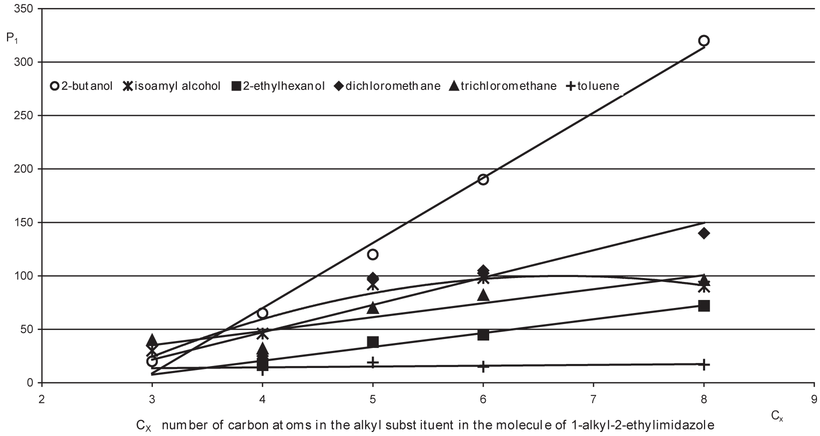


Figure 13. Influence of the alkyl chain length on the partition ratios (P_1) of Cu(II) complexes with 1-alkyl-2-ethylimidazoles.

change in the coordination polyhedron of the Cu(II) complexes. Both the strong steric effect and the bulkiness of the alkylimidazole molecules as well as the strong electron-donating properties of the solvent molecules contribute to the change of the coordination number of Cu(II) from 6 to 4. As a result, there is a simultaneous release of two water molecules attached to the Cu(II) ion. The resulting 4-coordinate Cu(II) complexes are more readily extractable by the organic solvent than the 6-coordinate ones and for this reason their partition constants, P_c, are high. In the case of $P_3 = f(C_x)$, (Fig. 15), the partition ratios are markedly higher and increase linearly with

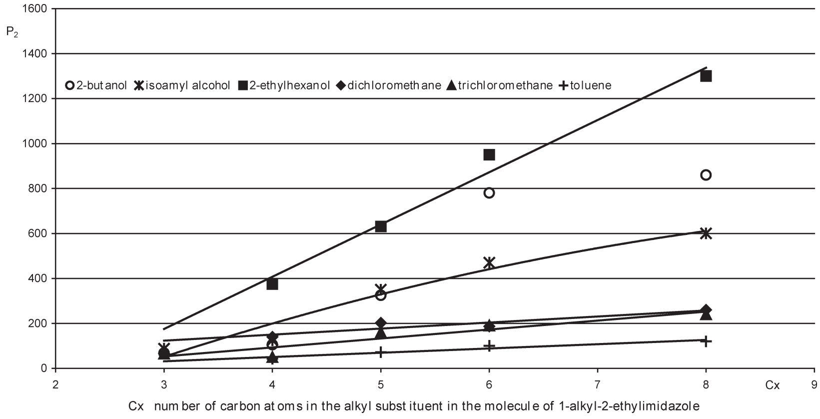


Figure 14. Influence of the alkyl chain length and solvents on the partition ratios (P_2) of Cu(II) complexes with 1-alkyl-2-ethylimidazoles.

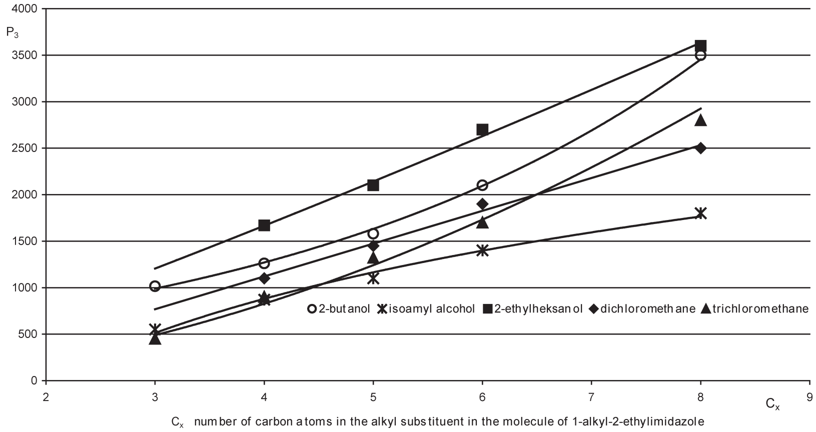


Figure 15. Influence of the alkyl chain length on the partition ratios (P_3) of Cu(II) complexes with 1-alkyl-2-ethylimidazoles.

1-alkyl chain length. It can be assumed that those complexes have a similar structure of the coordination polyhedron and coordination number 4.

This process is likely to facilitate the extraction of the 4-coordinate Cu(II) species being formed as they contain a less number of coordinated water molecules according to the following equations characterizing partition ratios P_1, P_2, and P_3, respectively:

$$[Cu(NO_3)_2(H_2O)_xL] + S \longleftrightarrow [Cu(NO_3)_2LS]NO_3 + x\ H_2O \tag{6}$$

$$[Cu(NO_3)_2(H_2O)_yL_2] + S \longleftrightarrow [Cu(NO_3)L_2S]NO_3 + y\ H_2O \tag{7}$$

$$[Cu(NO_3)_2(H_2O)L_3] + S \longleftrightarrow [CuL_3S](NO_3)_2 + H_2O \tag{8}$$

A similar behavior of the $P_c = f(C_x)$ functions has been reported for the Co(II) and Zn(II) complexes of 1-alkylimidzoles (15, 16), 1-alkyl-2-methylimidazoles (9) and 1-alkyl-4(5)-methylimidazoles (18).

A proof in favor of that interpretation can be afforded by absorption spectra of the Cu(II) complexes in organic phase. In Fig. 16, the spectra of the Cu(II) complexes of 1-hexyl-2-ethylimidazole in toluene are presented at increasing pH of the aqueous phase, whereas Fig. 17 shows analogous spectra of the Cu(II) complexes of 1-octyl-2-ethylimidazole in dichloromethane. In toluene, a peak appearing around 600 nm is displaced slightly towards shorter wavelengths upon raising pH. Again, in dichloromethane (Fig. 17) a maximum around 640 nm is shifted towards longer wavelengths.

In Figs. 18 and 19, two flat and broadened spectra are shown with strong bands over the range 570–680 nm. The former represents the Cu(II)

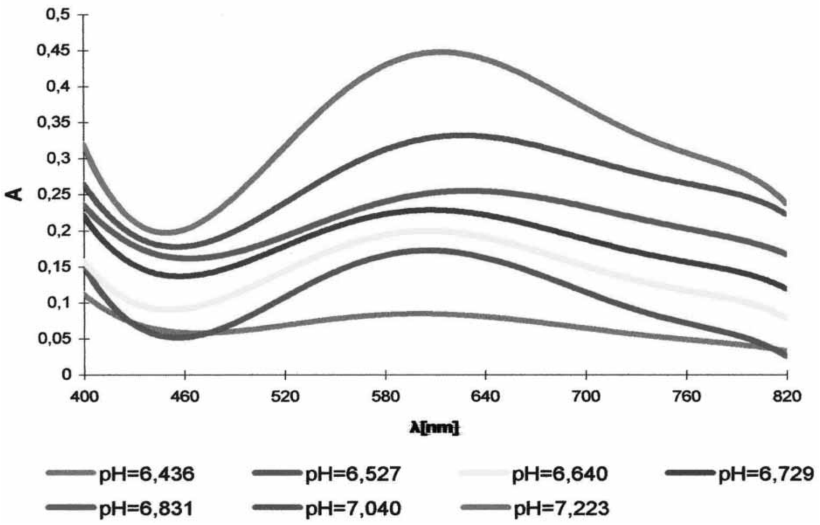


Figure 16. Absorption spectra of organic phase after extraction of the Cu(II) with 1-hexyl-2-ethylimidazole in toluene together with the corresponding pH of the aqueous phase.

complexes of 1-hexyl-2-ethylimidazole in iso-AmOH and the latter the Cu(II) complexes of 1-octyl-2-ethylimidazole in 2-ethylhexanol. In Fig. 19 a distinct maximum emerges around 645 nm and a strong absorbance over the long-wave range.

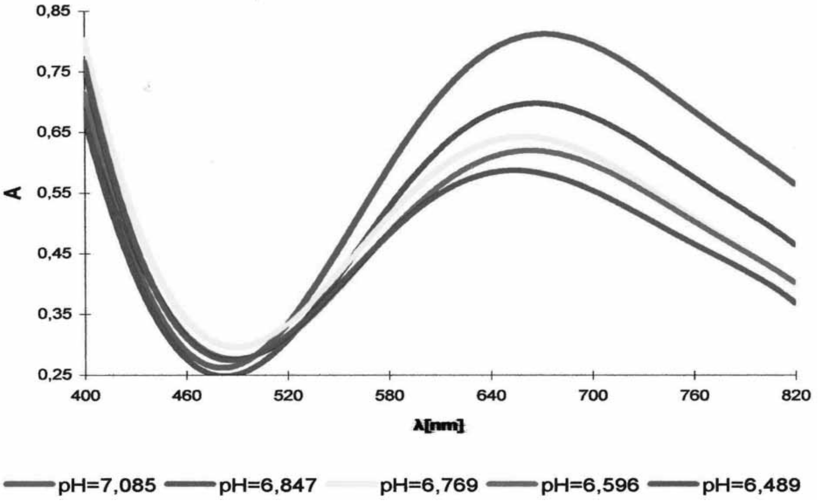


Figure 17. Absorption spectra of organic phase after extraction of the Cu(II) with 1-octyl-2-ethylimidazole in dichloromethane together with the corresponding pH of the aqueous phase.

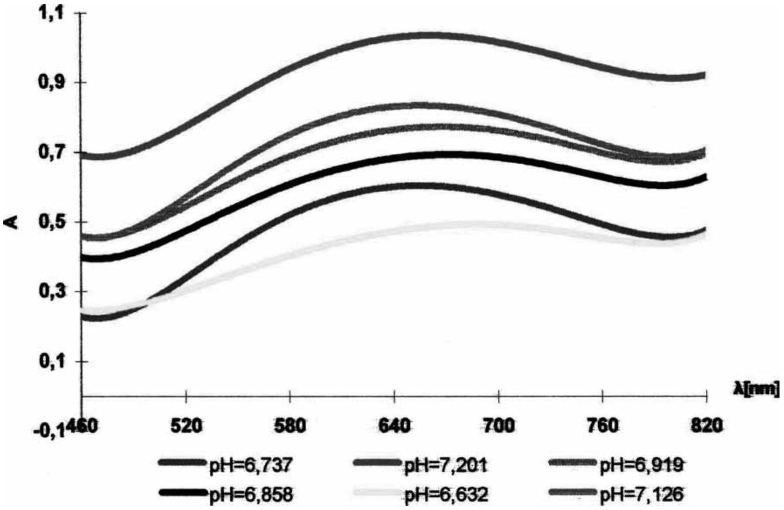


Figure 18. Absorption spectra of organic phase after extraction of the Cu(II) with 1-hexyl-2-ethylimidazole in isoamyl alcohol together with the corresponding pH of the aqueous phase.

The spectra reveal that with increasing heterocyclic ligand concentration in the alcoholic phase complexes of gradually decreasing coordination numbers and a weaker ligand field appear. It can thus be assumed that these are distorted tetrahedron (pseudotetrahedral) Cu(II) complexes.

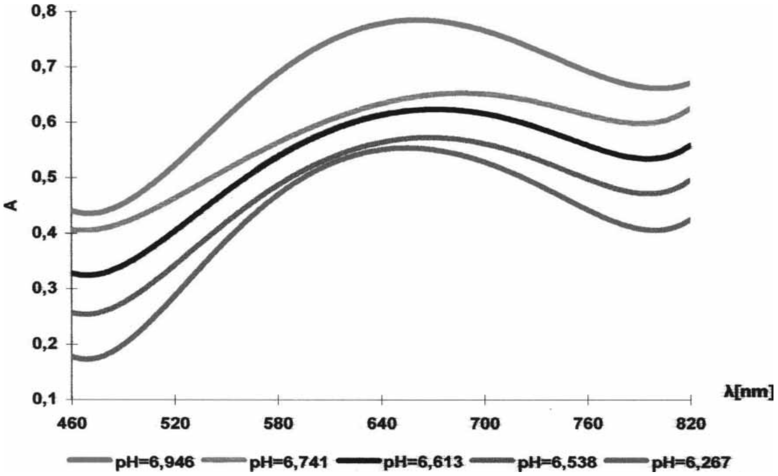


Figure 19. Absorption spectra of organic phase after extraction of the Cu(II) with 1-octyl-2-ethylimidazole in 2-ethylhexanol together with the corresponding pH of the aqueous phase.

CONCLUSIONS

1. In spite of the considerable steric effect due to the presence of the ethyl substituent, the stability of the 1-alkyl-2-ethylimidazole complexes of Cu(II) is comparable with that of the 1-alkyl-2-methylimidazole complexes.
2. The complexes are readily extractable with sparingly water-soluble alcohols of high donor numbers and more weakly at the use of dichloromethane, trichloromethane, and toluene.
3. With increasing 1-alkyl chain length, extraction curves ($\log D_M = f(pH)$) are displaced towards lower pH's, i.e. towards lower ligand concentrations in aqueous solution.
4. The extraction curves are also displaced towards lower pH's with increasing donor strength of the alcohols; the higher the donor number of an alcohol, the lower the $pH_{1/2}$ value becomes.
5. Both the strong steric effect and the bulkiness of the alkylimidazole molecules as well as the strong electron-donating properties of the solvent molecules all contribute to the change of the coordination number of Cu(II) from 6 to 4.
6. The change in the coordination number of the complexes depends on 1-alkyl chain length and donor properties of alcohols. It occurs mostly at the second and third step of coordination, although with some alcohols, e.g. 2-butanol, it occurs at the first step, as well.
7. Cu(II) complexes with three 1-alkyl-2-ethylimidazole molecules in the coordination sphere are most probably pseudotetrahedral.
8. The reduction of the coordination number and the accompanying structural changes of the coordination sphere of the Cu(II) complexes are favorable for the extraction efficiency owing to high partition ratios P_c. This phenomenon is a quite novel scientific finding in the situation of Cu(II) complexes formed with alkylimidazoles in aqueous solutions. This provides an opportunity for the selective extraction of Cu(II) from a mixture containing Zn(II), Co(II), Ni(II), and Cd(II) ions.

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