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# Effect of Alkyl Chain Length on the Extraction of Copper(II) Complexes with 1-Alkyl-2-Methylimidazoles

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# Effect of Alkyl Chain Length on the Extraction of Copper(II) Complexes with 1-Alkyl-2-Methylimidazoles

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**Abstract:** By using the liquid-liquid partition method, the formation of Cu(II) complexes with 1-alkyl-2-methylimidazoles (where alkyl = isobutyl, pentyl, isopentyl, hexyl, octyl, decyl, and dodecyl) has been studied at 25°C and at fixed ionic strength of the aqueous phase ($I = 0.5$; $(HL)NO_3$, $KNO_3$). The complexes were extracted with 2-ethyl-1-hexanol, dichloromethane, trichloromethane and, in one system only, toluene. Stability constants of the complexes in aqueous solution as well as partition constants of the extractable species were determined. It has been shown that the stability constants are invariable and do not depend on the 1-alkyl chain length. The constants were smaller than those of the previously studied Cu(II) – 1-alkylimidazole complexes owing to the steric effect of the methyl group at position 2. The partition constants of the complexes incereased with increasing alkyl chain length. Branched 1-alkyl substituents (isobutyl, isopentyl) suppressed both stability constants and the partition constants of the complexes.

**Keywords:** Solvent extraction, Cu(II) complexes, 1-alkyl-2-methylimidazole, stability constants, partition constants

## INTRODUCTION

Imidazole has been known to form complexes with transition metal ions of a stability matching that of ammonia complexes, although it is a much weaker

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base than ammonia (1). Alkyl substituents at position $\alpha$ to the pyridinic nitrogen atom enhance the basicity of imidazole, but hinder the formation of the alkylimidazole complexes with metal ions. The steric effect has been reported for the methyl (2–4), ethyl (5), n-propyl and isopropyl (6), and n-butyl and isobutyl (7) substituents. This effect has been found to depress the stability constants, mostly of octahedral species, e.g. those of Ni(II). It is also likely to perturb the structure of a coordination polyhedron. With Co(II), Zn(II), and Cd(II) ions, the steric hindrance due to the 2-alkyl substituents is favorable for the formation of tetrahedral species that are far less sensitive to their effects (2–7). This phenomenon is of practical importance because the tetrahedral complexes, being less hydrated, are more readily extractable from aqueous solutions than are the octahedral ones (8–13). This is utilized, the for instance, for the separation of Co(II) and Ni(II).

Our experience has shown that the Cu(II) ion is less sensitive to steric hindrance in reactions with 2-alkylimidazoles than are the Ni(II), Cd(II), and Zn(II) ions (7). The magnitude of the steric effect can be controlled through substitution at position 2 of either small ($CH_3$) or bulky alkyl groups. Elongation of the 1-alkyl substituent increases the hydrophobicity mainly of a metal complex, thus enhancing its extractability with an organic solvent (11–15). Previously we have studied (11) the influence of the steric effect and the alkyl chain length on the extraction efficiency of the Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) complexes with first four members of the homologous series of 1-alkyl-2-methylimidazoles using benzyl alcohol as the organic solvent. It was found that owing to the steric effect of the 2-methyl group, the Cu(II) complexes were extracted at a lowest pH (5.02–5.33) as compared to those of the complexes of the remaining four ions.

Recently the influence of alkyl chain length and steric effect on the extraction of Zn(II) complexes with 1-alkyl-2-methylimidazole was studied (16).

The purpose of this contribution was to identify the phenomena and parameters affecting the extraction of the Cu(II) complexes with sparingly soluble 1-alkyl-2-methylimidazoles. A total number of seven compounds belonging to this family was investigated. Their molecules contain an increasing length of 1-alkyl group ranging from butyl to dodecyl. 2-Ethyl-1-hexanol, dichloromethane, trichloromethane, and toluene (the last-named for the extraction of 1-dodecyl-2-methylimidazole complexes only) were used as solvents.

## EXPERIMENTAL

### Reagents

The 1-alkyl-2-methylimidazoles used in this work were synthesized by A. Skrzypczak, Technical University, Poznan, Poland, according to the literature method (17). The remaining particulars relating to structure elucidation

and checking the purity the of the compounds are given in the preceding article (18).

Potassium and copper(II) nitrates, both of analytical reagent grade (POCh, Poland) were crystallized twice from double-distilled water. Concentration of the Cu(II) salt was determined by titration with EDTA and that of potassium nitrate gravimetrically as sulfate. Nitric acid (analytical reagent, POCh) was standardized against anhydrous sodium carbonate and sodium tetraborate decahydrate.

Trichloromethane (POCh, Poland), dichloromethane (POCh, Poland), toluene (POCh, Poland) and 2-ethyl-1-hexanol (Aldrich), all the analytical reagents, were used as received.

The pH-meter was calibrated using commercial buffer solutions (Radiometer) of pH $4.01 \pm 0.01$ and $7.00 \pm 0.01$. The pH was also checked against hydrochloric acid according to IUPAC recommendations (19).



## 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 Cu 324,7 was used for the determination of Cu(II) concentration. A Hewlett Packard 8542A Diode Array Spectrophotometer was used for recording absorption spectra of the Cu(II) complexes in the organic phase over the visible region.

## Extraction Procedure

The measurements were run at 25°C and at fixed ionic strength (0.5) maintained in the aqueous phase with $KNO_3 + HNO_3$. Before extraction, concentrations of the metal ions and nitric acid in the aqueous phase were constant (0.01 M and 0.15 M, respectively) and the ligand concentrations in the organic phase were varied from 0.01 to 0.25 M. Six $cm^3$ of the aqueous phase were placed in a graduated test tube and an equal volume of an 1-alkyl-2-methylimidazole solution was added in the organic solvent. The test tubes were then shaken for 30 min. The equilibrium was established after a few minutes; however, no longer than 30 min. After that the difference in the phase volume was read out, the phases were separated, and the pH of the aqueous phase was measured. Any change in the phase volumes has been taken into account regarding the calculation of the quantities of copper(II) that had passed to the organic phase. The Cu(II) concentration was determined by titration with a standardized EDTA solution and by atomic absorption

spectrophotometry. Visible absorption spectra of the organic layer were subsequently recorded.

## RESULTS AND DISCUSSION

The distribution ratio ($D_M$) of copper(II) in the systems studied was calculated on the basis of the Cu(II) concentrations in the aqueous phase before and after attaining equilibrium from the following equation:

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

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

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

The distribution ratio of the Cu(II) complexes of 1-alkyl-2-methylimidazoles in water/organic solvent systems for three solvents (2-ethyl-1-hexanol,

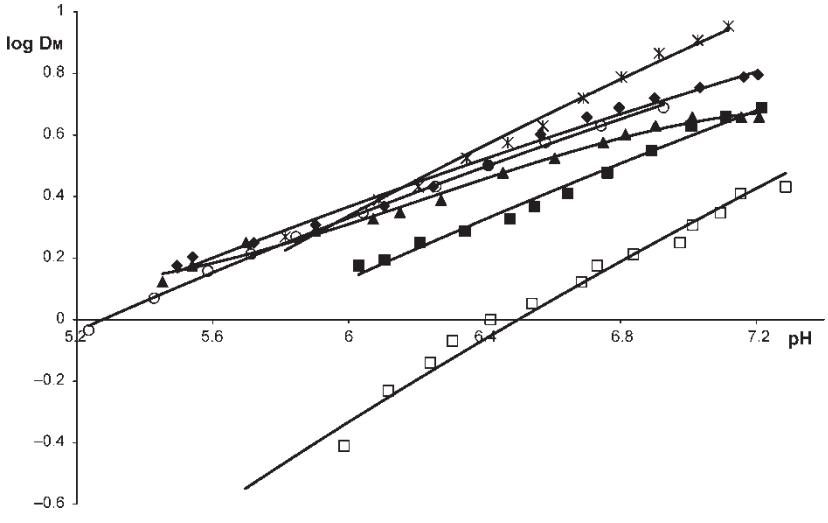


***Figure 1.*** Influence of the alkyl chain length on the extraction of Cu(II) complexes with 1-alkyl-2-methylimidazoles into 2-ethyl-1-hexanol at 25°C and constant ionic strength of aqueous solution I = 0.5 K($HNO_3$). Analytical concentration of 1-alkyl-2-methylimidazoles in the organic phase varied from 0.01 mol/L to 0.25 mol/L (corresponding to the lowest and the highest pH, respectively). ■ – 1-pentyl –2-methylimidazole; □ – 1-*iso*pentyl-2-methylimidazole; ▲ – 1-hexyl-2-methylimidazole; ○ – 1- octyl-2-methylimidazole; ◆ – 1- decyl-2-methylimidazole; ∗ – 1-dodecyl-2-methylimidazole.

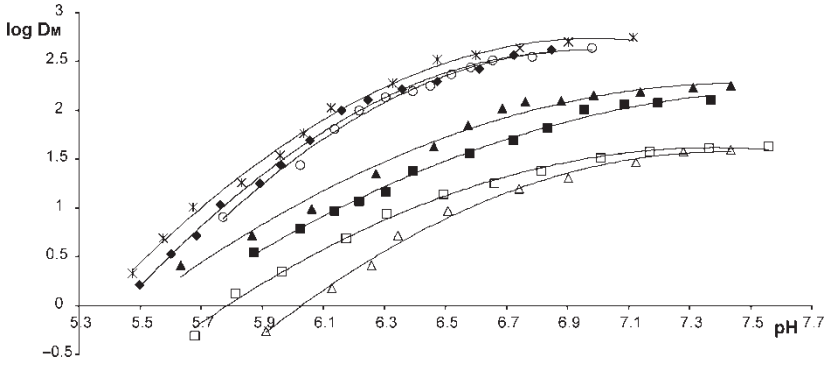


***Figure 2.*** Influence of the alkyl chain length on the extraction of Cu(II) complexes with 1-alkyl-2-methylimidazoles into dichloromethane at 25°C and constant ionic strength of aqueous solution I = 0.5 K($HNO_3$). Analytical concentration of 1-alkyl-2-methylimidazoles, the same as given in Fig. 1. △ – 1-*iso*butyl –2-methylimidazole; ■ – 1-pentyl –2-methylimidazole; □ – 1-*iso*pentyl-2-methylimidazole; ▲ – 1-hexyl-2-methylimidazole; ○ – 1- octyl-2-methylimidazole; ◆ – 1- decyl-2-methylimidazole; ∗ – 1-dodecyl-2-methylimidazole.



dichloromethane, and trichloromethane), as a function of log $D_M$ *vs.* pH of the aqueous phase, are summarized in Figs. 1–3. The curves were drawn using the least-squares fits. The magnitude of log $D_M$ is relatively small for the first solvent (a −0.4 to 1.0 range), larger for trichloromethane (−0.2 to 1.4), and the largest for dichloromethane (−0.3 to 2.7).

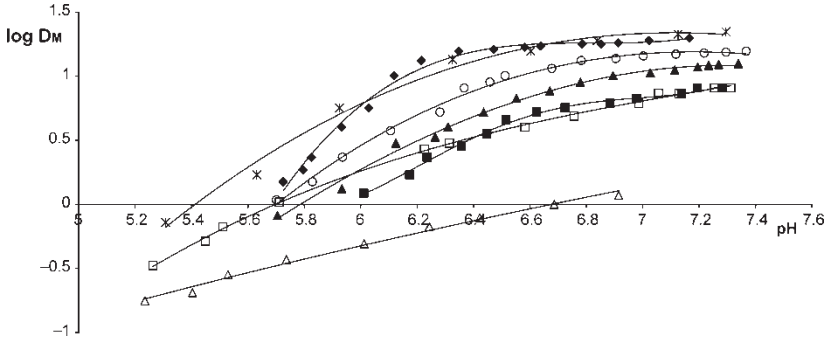


***Figure 3.*** Influence of the alkyl chain length on the extraction of Cu(II) complexes with 1-alkyl-2-methylimidazoles into trichloromethane at 25°C and constant ionic strength of aqueous solution I = 0.5 K($HNO_3$). Analytical concentration of 1-alkyl-2-methylimidazoles, the same as given in Fig. 1. △ – 1-*iso*butyl –2-methylimidazole; ■ – 1-pentyl –2-methylimidazole; □ – 1-*iso*pentyl-2-methylimidazole; ▲ – 1-hexyl-2-methylimidazole; ○ – 1- octyl-2-methylimidazole; ◆ – 1- decyl-2-methylimidazole; ∗ – 1-dodecyl-2-methylimidazole.

For each solvent, the extraction curves (log $D_M$ *vs*. pH) are distinctly displaced towards lower pH's with increasing 1-alkyl chain length. This is useful from the practical point of view, because by using alkylimidazoles with long alkyls Cu(II) can be extracted at low pH's (and consequently low concentrations of the heterocyclic base in both phases). A similar regularity has previously been reported for the extraction of Co(II), Ni(II), Zn(II), and Cu(II) with 1-alkylimidazoles [12,13,15,20] and 1-alkyl-4(5)-methylimidazoles (14).

An interesting finding has been noticed with 1-pentyl-2-methylimidazole and its 1-isopentyl isomer. Namely, replacing the 1-pentyl compound by 1-isopentyl resulted in depressing the $D_M$ value and displacement of the extraction curve towards higher pH values. A similar behavior was noticed with 1-isobutyl-2-methylimidazole.

The formation of the complexes might occur described by the following equations:

$$[Cu(H_2O)_N]^{2+} + nHL^+ = [Cu(H_2O)_{N-n}Ln]^{2+} + nH_3O^+ \text{or}$$

$$[Cu(H_2O)_N]^{2+} + nL^+ = [Cu(H_2O)_{N-n}Ln]^{2+} + nH_2O.$$

The remaining water particles in coordination sphere of the copper(II) can be replaced by anions $NO_3^-$, and also the solvent molecules (S). If the complex containing eg. c molecules of ligand ($0 < c < N$), the $ML_c$ complex is hydrophobic enough to pass into the organic phase. Of course, the complex c+1 will have considerably greater chances to pass.

The extraction process of the complexes is described by the equations 2–4:

$$D_M = \frac{[ML_c]_{(org)} + [ML_{c+1}]_{(org)} + \cdots + [ML_N]_{(org)}}{[M]_{(aq)} + [ML]_{(aq)} + [ML_2]_{(aq)} + \cdots + [ML_N]_{(aq)}} \quad (2)$$

$$[ML_c]_{(org)} = P_c[ML_c]_{(aq)} = P_c\beta_c[L]^c \quad (3)$$

where: $\beta_n$ and $\beta_c$ are cumulative stability constants of the complexes in the aqueous phase, $P_c$ are organic solvent/water partition constants of the 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 (21–23).

On the basis of Eqs (2) and (3), we obtain the following relationship:

$$D_M = P_c\beta_c[L]^c + P_{c+1}\beta_{c+1}[L]^{c+1} + \cdots + P_N\beta_N[L]^N \quad (4)$$

To learn which of the parameters, $P_n$ or $\beta_n$, affects the partitioning of Cu(II) between the two phases, both stability constants of the complexes and their partition constants had to be determined. The required free azole

base concentrations in the aqueous phase at equilibrium, [L], were found from the following equation:

$$[L] = \frac{K_a[HL^+]}{[H_3O^+]} \tag{5}$$

where $K_a$ is the dissociation constant of the protonated ligand $HL^+$, and $[HL^+]$ 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-methylimidazoles needed for the calculations were taken from reference (18).

The pooled $D_M$ values and the corresponding sets of independent variable [L] were used for the determination of stability constants $\beta_n$ of the Cu(II) complexes by using the equation proposed by Rydberg (21–23):

$$\frac{[L]^c}{D_M} = \frac{\sum_{n=0}^{n=N} \beta_n [L]^n}{P_c \beta_c} \tag{6}$$

Equation (6) can be used for the determination of composition of the first complex being extracted from the aqueous phase, and stability constant, $\beta_1$, of the first complex formed in the aqueous phase. To do this, the shape of function $[L]^c/D_M = f[L]$ is monitored when varying exponent c between 1 and 6. In this way a bundle curve was obtained of which only one was a straight line with a 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 method was used previously (12–16, 20).

Stability constants, $\beta_n$, obtained in this way are collected in Table 1 for each organic solvent together with the previously determined stability constants of the Cu(II) complexes with water-soluble 1-alkyl-2-methylimidazoles (3, 5, 11) determined earlier by the potentiometric method.

The following points are worth emphasizing here:

i. Stability constants derived from extraction experiments for higher 1-alkyl-2-methylimidaoles match those determined potentiometrically for water-soluble ligands of the homologous series – 1,2-dimethylimidazole (3), 1-ethyl-2-methylimidazole (4), 1-propyl-2-methylimidazole (6) and 1-butyl-2-methylimidazole (11). The stability constants determined by the partition method with the use of the different solvents have the similar values for the given ligand. So, their mean value can be calculated.
ii. The data presented in Table 1 show that the stability constants of all the 1-alkyl-2-methylimidazole complexes with Cu(II) are invariant, regardless of the alkyl chain length and $pK_a$ of the imidazole base. This phenomenon I was previously found for Cu(II) complexes with 1-alkylimidazoles (20). It is quite a surprising finding, because the stability constants of the previously studied complexes of Co(II) (12), Ni(II)

***Table 1.*** Stability constants log $\beta_c$ and partition constants $P_c$ of the Cu(II) complexes with 1-alkyl-2-methylimidazoles in aqueous solution (I = 0.5 $K(H)NO_3$) at 25°C.

| Ligand | $pK_a$ | log $\beta_1$ | log $\beta_1$ medium | log $\beta_2$ | log $\beta_2$ medium | log $\beta_3$ | solvent | $P_1$ | $P_2$ | $P_3$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1,2-dimethylimidazole (3) | 8.21 | 3.70 | | 6.80 | | 9.18 | | | | |
| 1-ethyl-2-methylimidazole (4) | 8.21 | 3.52 | | 6.60 | | 8.98 | | | | |
| 1-propyl-2-methylimidazole (6) | 8.25 | 3.67 | | 7.23 | | 9.65 | | | | |
| 1-butyl-2-methylimidazole (11) | 8.18 | 3.74 | | 6.98 | | 9.44 | | | | |
| 1-isobutyl-2-methylimidazole | 8.03 | 3.48 | | 6.56 | | 8.46 | dichloromethane | 1.4 | 12 | 80 |
| | | 3.56 | | 6.71 | | | trichloromethane | 0.24 | 6.5 | |
| 1-pentyl-2-methylimidazole | 8.27 | 3.52 | | 6.64 | | 9.18 | dichloromethane | 15 | 271 | 458 |
| | | 3.53 | 3.50 | 6.66 | 6.59 | | trichloromethane | 1,23 | 29 | |
| | | 3.44 | | 6.48 | | | 2-ethyl-1-hexanol | 2.5 | 15 | |
| 1-isopentyl-2-methylimidazole | 8.27 | 3.40 | | 6.41 | | | dichloromethane | 2.7 | 60 | |
| | | 3.39 | 3.44 | 6.39 | 6.49 | | trichloromethane | 0.38 | 11 | |
| | | 3.53 | | 6.66 | | | 2-ethyl-1-hexanol | 1.8 | 9.5 | |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1-hexyl-2-methylimidazole | 8.32 | 3.60 | | 6.79 | | 8.98 | dichloromethane | 26 | 307 | 590 |
| | | 3.51 | 3.52 | 6.62 | 6.63 | | trichloromethane | 2.7 | 35 | |
| | | 3.44 | | 6.48 | | | 2-ethyl-1-hexanol | 4 | 26 | |
| 1-octyl-2-methylimidazole | 8.40 | 3.63 | | 6.84 | | 9.65 | dichloromethane | 29 | 346 | 725 |
| | | 3.52 | 3.53 | 6.64 | 6.65 | | trichloromethane | 2.9 | 42 | |
| | | 3.44 | | 6.48 | | | 2-ethyl-1-hexanol | 4.8 | 38 | |
| 1-decyl-2-methylimidazole | 8.49 | 3.65 | | 6.88 | | 9.44 | dichloromethane | 41 | 395 | 840 |
| | | 3.54 | 3.54 | 6.68 | 6.68 | | trichloromethane | 3.08 | 50 | |
| | | 3.44 | | 6.48 | | | 2-ethyl-1-hexanol | 6 | 52 | |
| 1-dodecyl-2-methylimidazole | 8.53 | 3.60 | | 6.79 | | 9.37 | dichloromethane | 48 | 432 | 980 |
| | | 3.60 | 3.58 | 6.79 | 6.75 | | trichloromethane | 3.2 | 58 | |
| | | 3.55 | | 6.69 | | | 2-ethyl-1-hexanol | 90.2 | 65 | |
| | | 3.57 | | 6.72 | | | toluene | 1.6 | 34 | |

The given values of the constants $\beta_n$ and $P_n$ carry 10% tolerance.

(15) and Zn(II) (13, 14, 16) increased with increasing chain length of the 1-alkyl substituents. Moreover, the stability constants $\beta_n$ of the Cu(II) complexes are considerably higher than those of Ni (II) (11). It proves that the participation of the $\pi_{M\rightarrow L}$ bonding in the interaction of ions $Cu^{2+}$ with molecules of 1-alkyl-2-methylimidazoles is significant, though certainly smaller than in 1-alkylimidazoles (20).

Having in hand the whole pool of $\beta_n$ values obtained potentiometrically for the Cu(II) complexes with 1-alkyl-2-methylimidazoles, it is easy to find $\beta_2$ and $\beta_3$ from the extraction data. A listing of the $\beta_1$, $\beta_2$, and $\beta_3$ values is shown in Table 1.

In order to determine the number, composition, and extractability of the complexes passing into the organic phase, respective partition constants, $P_c$, as defined by Eq. (3), were determined from the following relationship between distribution ratio, $D_M$, and mole fractions of successive complexes, $\alpha_n$:

$$D_M = P_c\alpha_c + P_{c+1}\alpha_{c+1} + P_{c+2} + \cdots + P_N\alpha_n \qquad (7)$$

$P_c$ and $\alpha_c$ characterize the first in the series of consecutive complexes containing *c* ligand molecules, which is capable of passing into the organic phase (21, 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 constants, $P_c$, of the first extractable complex was determined. Partition constants $P_{c+1}$, $P_{c+2}$ . . . and so on, were determined similarly from the relations $D_M = f(\alpha_{c+1})$, $D_M = f(\alpha_{c+2})$. . . .and so on (23).

Partition constants, $P_c$, obtained in this way are collected in Table 1. Moreover, the constants were determined from Eq. (4) using the least-squares method.

With 2-ethyl-1-hexanol and trichloromethane, only two complexes, ML and $ML_2$, have been extracted. Their partition constants, $P_1$ and $P_2$ (Table 1) are small. Again, with dichloromethane three successive complexes: ML, $ML_2$, and $ML_3$, could be extracted. Their partition constants, $P_c$, are larger than those with the two aforementioned solvents.

Partition constants, $P_c$, of all the extracted complexes increase in the following series: $P_1 < P_2 < P_3$. Moreover, they increase linearly with increasing 1-alkyl chain length (Fig. 4).

Mainly the second complex $ML_2$ and partly the third $ML_3$ decide on the extraction Cu(II) cation by 1-alkyl- 2-methylimidazoles. The extraction Co(II), Ni(II), and Zn(II) was determined by higher complexes, mainly $ML_3$ and $ML_4$. It results that complexes Cu(II) with 1-alkyl- 2-methylimidazoles attain hydrophobicity proprieties more quickly than analogous compounds of cations of other metals. This can be due to the stronger bond in the coordination sphere of nitrate anions and of molecules of the solvent by $Cu^{2+}$. Perhaps, in this case, the deformations structural of the coordination sphere

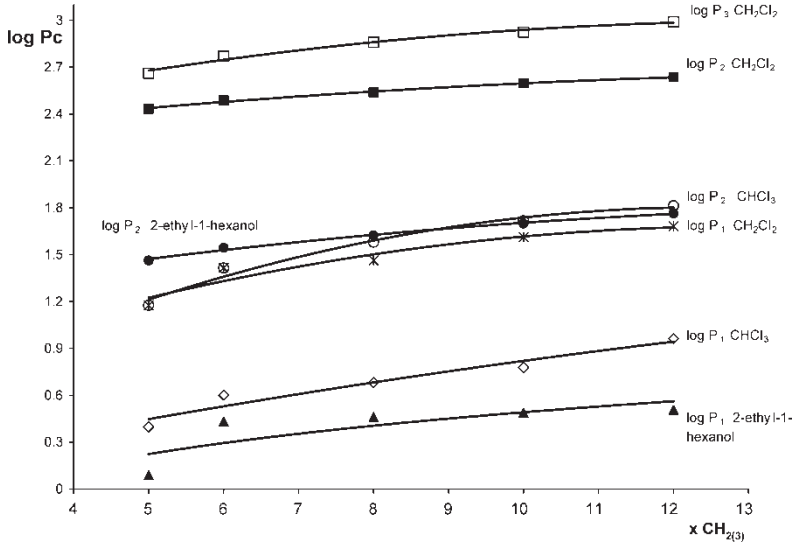


***Figure 4.*** Influence of the alkyl chain length in the position "1" on the partition constants (log $P_1$, log $P_2$, log $P_3$) of the Cu(II) complexes with 1-alkyl-2-methylimidazoles.

of the copper(II) occur that make possible even the chelate bond of anions $NO_3^-$ (24).

To verify the $\beta_n$ and $P_c$ constants, $D_M$ values were calculated from experimental concentrations of free 1-hexyl-2-methylimidazoles, [L] for toluene

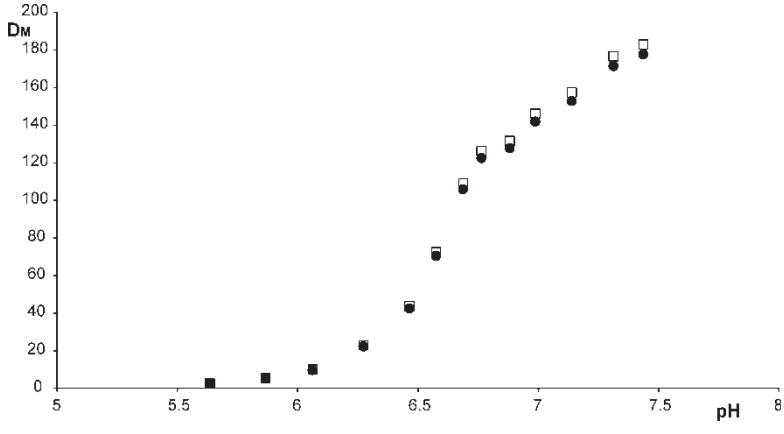


***Figure 5.*** Comparison of the obtained experimental and calculated values $D_M$ vs. pH on the extraction of Cu(II) complexes with 1-hexyl-2methylimidazole for toluene as a solvent. ● – $D_M$ experimental; □ – $D_M$ calculated.

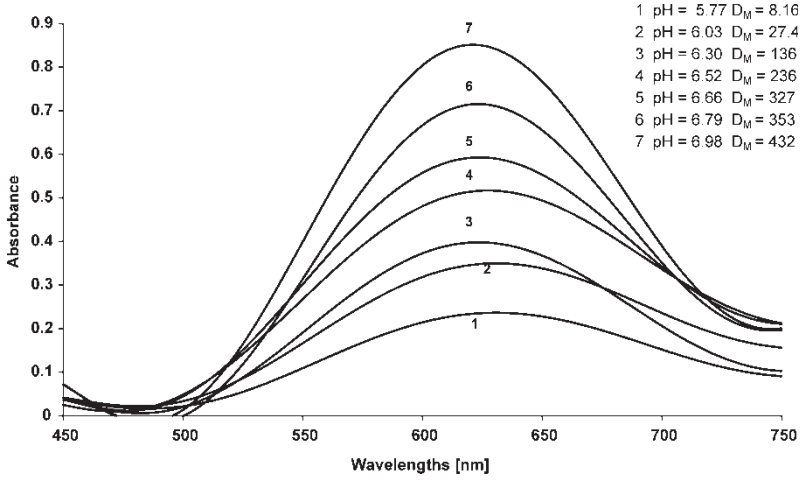


***Figure 6.*** Absorbtion spectra of organic phase after extraction of the Cu(II) complexes with 1-octyl-2-methylimidazole in 2-ethyl-1-hexanol together with the corresponding pH of the aqueous phase and logarithms of distribution constant $D_M$.

systems. The pooled $D_M$ values were then compared with the experimental pool for this ligand. The results are shown in Fig. 5.

The Cu(II) complexes of 1-alkyl-2-methylimidazoles are deep-blue in the organic phase. Their electronic spectra are shown in Figs. 6–8. Upon raising the ligand concentration, the absorption maxima become slightly displaced

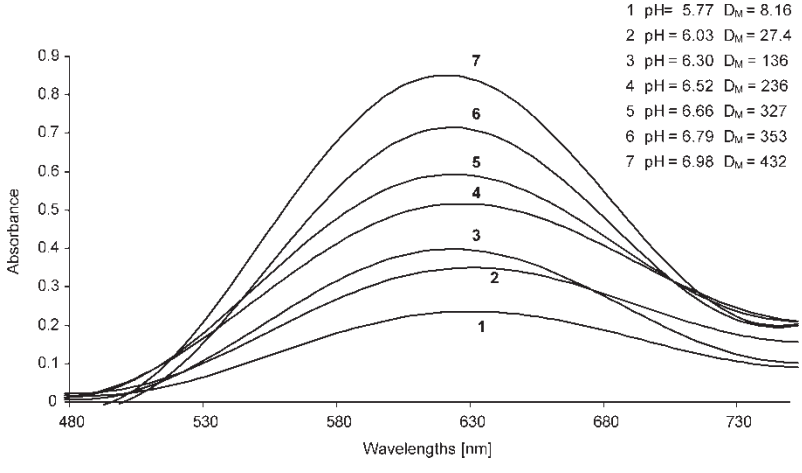


***Figure 7.*** Absorbtion spectra of organic phase after extraction of the Cu(II) complexes with 1-octyl-2-methylimidazole in dichloromethane together with the corresponding pH of the aqueous phase and logarithms of distribution constant $D_M$.

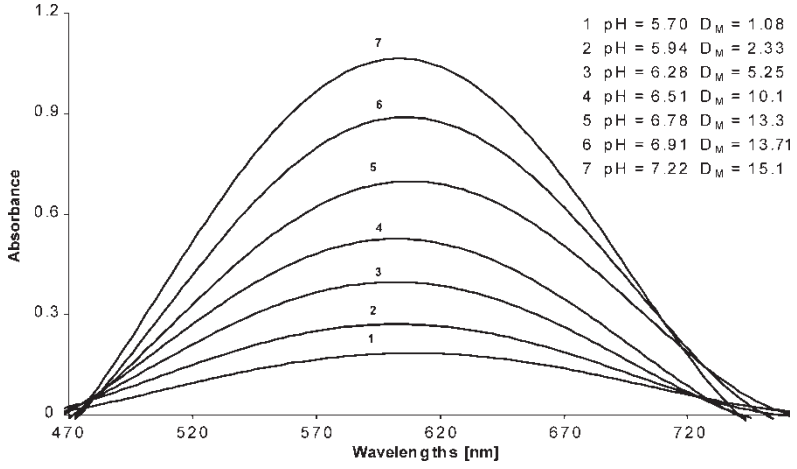


***Figure 8.*** Absorbtion spectra of organic phase after extraction of the Cu(II) complexes with 1-octyl-2-methylimidazole in trichloromethane together with the corresponding pH of the aqueous phase and logarithms of distribution constant $D_M$.



towards shorter wavelengths. The maxima do not change upon increasing the 1-alkyl chain length. It can thus be hypothesized that the complexation of the Cu(II) ion does not significantly change the structure of the coordination polyhedron of the ion. The shapes of the spectra in Figs. 6–8 show that at least two complexes are being extracted. The location of the absorption maximum depends on the solvent used.

Du Preez maintained the formation of Cu(II) complexes with alkylimidazole which had the coordinative number smaller from 6. Du Preez utilized 1-decylimidazole, 1-decyl-2-methylimidazole, and 1-decyl-4(5)-methylimidazole to extract Cu(II) from the perchlorate, the chloride, and the thiocyjanate solutions (25).

## Summary

The steric effect due to the 2-methyl substituent decreases the stability of the Cu(II) complexes with 1-alkyl-2-methylimidazoles. Although these ligands are stronger bases than 1-alkylimidazoles, they form less stable complexes due to decreased contribution of the $\pi_{M\rightarrow L}$ back donation in the complexes of 1-alkyl-2-methylimidazoles. However, the contribution still remains significant because the stability constants, $\beta_n$, of the complexes do not depend on the alkyl chain length and increasing basicities of the ligands, as was the case with 1-alkylimidazoles.

From nitrate-containing solutions of the Cu(II) complexes with 1-alkyl-2-methylimidazoles, either two or three complexes are extracted with 2-ethyl-1-

hexanol, trichloromethane, and dichloromethane. An increasing bulkiness of the imidazole ligands does not significantly affect the structure of the coordination sphere of the Cu(II) complexes. It can thus be suggested that the extractable species have the following composition: $[CuL(NO_3)_2S]$, $[CuL_2(NO_3)_2S]$ and $[CuL_3(NO_3)_2S]$ where S denotes a solvent molecule.

Bearing in mind the possibility of chelation of $Cu^{2+}$ with nitrate ions (24) it can be assumed that the extractable complexes are coordinatively saturated.

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