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Elzbieta Radzyminska-Lenarcik[a]
[a] Department of Inorganic Chemistry, University of Technology and Life Sciences, Bydgoszcz, Poland

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The Influence of Alkyl Chain Length in 1,2-Dialkylimidazoles on the Extraction Capacity and Structure of Their Copper(II) Complexes

Elzbieta Radzyminska-Lenarcik
Department of Inorganic Chemistry, University of Technology and Life Sciences, Bydgoszcz, Poland

Abstract: Formation of Cu(II) complexes of 1,2-dialkylmidazoles (where 1-alkyl = ethyl, propyl, butyl, pentyl, and hexyl, and 2-alkyl = propyl, butyl, and pentyl) has been studied using the liquid-liquid partition method, at 25°C and at a fixed ionic strength of the aqueous phase (I = 0.5; $(HL)NO_3$, KNO_3). The complexes were extracted with 2-ethyl-1-hexanol, and chloroform. The length of the 1-alkyl, and 2-alkyl groups, and the solvent nature have been shown to influence the extraction process. Extraction curves (log D_M *vs.* pH) are displaced towards lower pH with increasing chain length of the 1-alkyl and 2-alkyl substituents. Stability constants of the complexes in aqueous solution as well as their partition constants between the aqueous and organic phase were determined. The stability of the Cu(II) complexes increased with increasing 1-alkyl chain length. The stability constants were comparable with β_n values for the Cu(II) complexes of 1-alkyl-2-ethylimidazoles, but smaller than those of the Cu(II) – 1-alkylimidazole counterparts. The length of the 2-alkyl substituent has been found to affect both the $pH_{1/2}$ values and the partition constants of the complexes. The partition constants P_1 are small for all of the 1,2-dialkylimidazole complexes with Cu(II), whereas P_2 and P_3 are high and they increase with elongation of the 1-alkyl chain owing to a decrease in the co-ordination number of Cu(II), probably from 6 to 4 at the second and third complexation step. This change is likely to produce square coplanar species, readily extractable with organic solvent. This finding offers the possibility of extraction of the Cu(II) ions from a mixture cations.

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Address correspondence to Elzbieta Radzyminska-Lenarcik, Department of Inorganic Chemistry, University of Technology and Life Sciences, Str. Seminaryjna 3, Bydgoszcz 85-326, Poland. E-mail: elaradz@utp.edu.pl

Keywords: 1,2-Dialkylimidazole, Cu(II) complexes, partition constants, solvent extraction, stability constants, steric effect

INTRODUCTION

Sparingly soluble 1-alkylimidazoles, owing to their strong complexing capacity, are particularly suitable for solvent extraction of transition metal ions, in particular Cu(II) ones. A literature survey on the subject has been given previously (1).

Both the complexing and extraction properties of imidazole bases can be modifiedthrough substitution in a 1,3-diazole molecule of the alkyl group in an appropriate position of the heterocyclic ring. Thus, replacement of the hydrogen-bound nitrogen at position 1 with an n-alkyl increases stability constants, β_n, of its metal complexes and facilitates its extractability with an organic solvent, as expressed by high partition constants of the complexes, P_n (1). On the other hand, substitution at position 2, even with a small alkyl group, results in a steric effect, hindering the formation of complexes with transition metal ions.

By the end of the twentieth century, the influence of the steric effect on the stability of soluble 2-alkylimidazole complexes with the methyl, ethyl, n-propyl, isopropyl, and n-butyl substituents was studied using the potentiometric method. A literature survey encompassing these studies of the Cu(II) complexes with 1-n-alkyl-2-methylimidazoles has been published (2). In the survey, it is demonstrated that the imidazoles could successfully be used for extraction of Cu(II) from aqueous solutions with methylene chloride, chloroform, toluene, and 2-ethylhexanol (2). The extraction of the Cu(II) complexes was aided by high water/solvent partition constants while their stability constants, β_n, were much lower than those of the analogous 1-n-alkylimidazole complexes (1,2).

The steric effect, lowering the stability of complexes of other cations with 1-n-alkyl-2-methylimidazoles, favors the separation of Cu(II), especially from forming himself under the conditions octahedral complexes Ni(II).

Lately, the present author has examined the influence of the steric effect, length of the n-alkyl substituent at position 1, and donor number of the solvent on the structure and the extraction process of Cu(II) complexes with 1-n-alkyl-2-ethylimidazoles (3).

It has also been demonstrated that both the steric effect and bulkiness of the alkylimidazole molecules reduce the coordination number of Cu(II) from 6 to 4. Both the reduction and the accompanying structural changes of the Cu(II) complexes turned out to be favorable for extraction efficiency. This provided an opportunity for the selective extraction of Cu(II) from a mixture of cations.

It was the purpose of this study to investigate the influence of larger 2-alkyl substituents, bonded with the imidazole ring on the efficiency of solvent extraction of Cu(II) with 1,2-dialkylimidazoles. To do this, 3 to 5 heterocyclic bases belonging to three homologous series of the 1,2-dialkylimidazoles were selected, namely the following: 1-ethyl-2-propylimidazole, 1,2-dipropylimidazole, 1-butyl-2-propylimidazole, 1-pentyl-2-propylimidazole, 1-hexyl-2-propylimidazole, 1-ethyl-2-butylimidazole, 1,2-dibutylimidazole, 1-hexyl-2-butylimidazole, 1-ethyl-2-pentylimidazole, 1-butyl-2-pentylimidazole, and 1-hexyl-2-pentylimidazole. Each of these groups of bases carry the same 1-alkyl substituent and gradually elongated 2-alkyls. All of the compounds are strong bases (4). It is worth emphasizing that the complexing capacity and extraction efficiency of the 2-n-pentylimidazoles have not been studied so far. As extractants, chloroform and 2-ethylhexanol have been used as those of which the extraction capacities differ considerably (3).

EXPERIMENTAL

Reagents

1-Alkyl-2-propylimidazoles, 1-alkyl-2-butylimidazoles, and 1-alkyl-2-pentylimidazoles used in this work were synthesized by A. Skrzypczak, Poznan University of Technology, Poznan, Poland, according to a method reported in literature (5). Particulars relating to structure elucidation and checking the purity of the compounds are given in the previous article (4).

The 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 was determined gravimetrically as sulfate. Nitric acid (analytical reagent, POCh, Poland) was standardized against anhydrous sodium carbonate and sodium tetraborate decahydrate.

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

The pH-meter was calibrated using commercial buffer solutions (Radiometer) with pH 4.01 ± 0.01 and 7.00 ± 0.01. The pH was also checked against hydrochloric acid according to IUPAC recommendations (6).

Equipment

Potentiometric measurements were carried out using a multifunctional computer-aided 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 determination of Cu(II) concentration after the extraction process. A Hewlett Packard 8542A Diode Array Spectrophotometer was used for recording the 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 a 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 held constant (0.01 M and 0.015 M, respectively) and ligand concentrations in the organic phase were varied from 0.01 to 0.25 M. A volume of six cm^3 of the aqueous phase was placed in a graduated test tube and an equal volume of a ligand (1-alkyl-2-propylimidazole, 1-alkyl-2-butylimidazole, or 1-alkyl-2-pentylimidazole) 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, not longer than 30 min. After that, it has been checked if any changes in the phase volumes have occurred, then the phases were separated, and the pH of the aqueous phase was measured. Any change in the phase volumes was taken into account during calculation of the quantities of copper(II) that had passed into 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

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

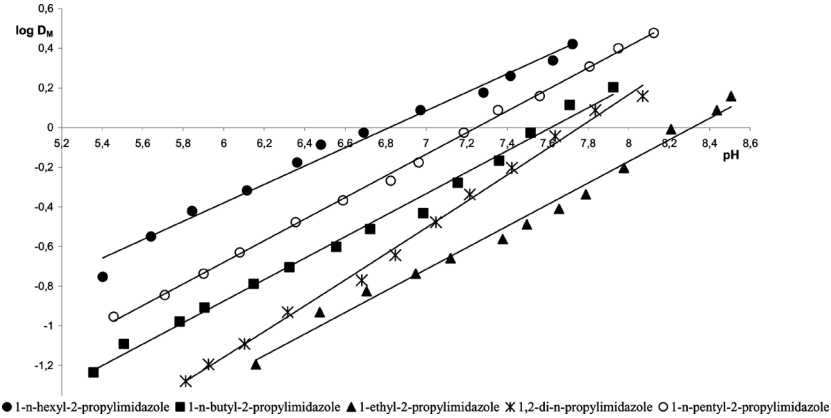

Figure 1. Influence of the alkyl chain length of 1-alkyl-2-propylimidazoles on the extraction of Cu(II) complexes into 2-ethylhexanol.

Then, log $D_M = f(pH)$ plots were made for each series of the heterocyclic bases, separately for 2-ethylhexanol and chloroform. Extraction curves for each of the 1,2-dialkylimidazole groups in alcoholic solutions are shown in Figs. 1–3. Those for the Cu(II) extraction using 2-ethylhexanol with 1-n-alkyl-2-propylimidazoles, 1-n-alkyl-2-butylimidazoles and 1-n-alkyl-2-pentylimidazoles are represented in Figs. 1–3, respectively.

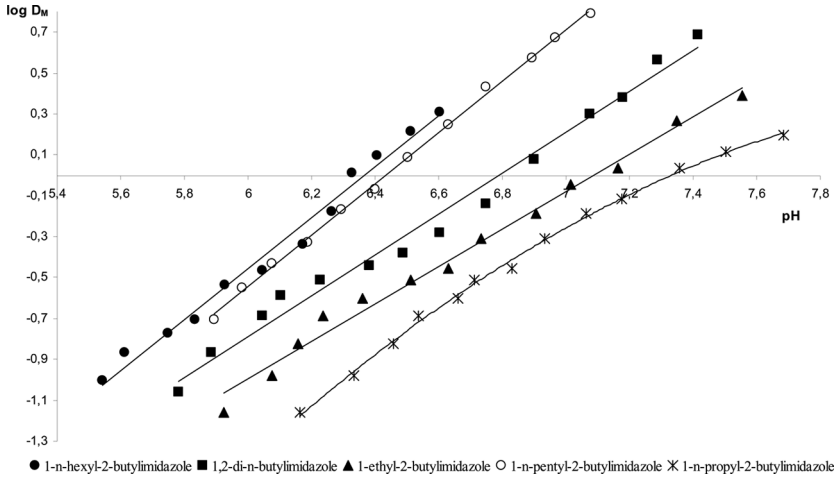

Figure 2. Influence of the alkyl chain length of 1-alkyl-2-butylimidazoles on the extraction of Cu(II) complexes into 2-ethylhexanol.

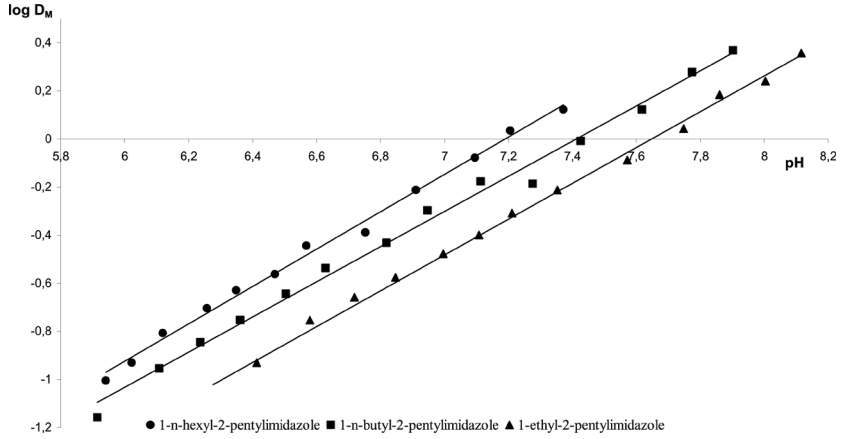

Figure 3. Influence of the alkyl chain length of 1-alkyl-2-pentylimidazoles on the extraction of Cu(II) complexes into 2-ethylhexanol.

In all the figures, there is visible a distinct, previously reported (1–3), regularity in the displacement of the curves towards lower pH values of the aqueous phase upon elongation of the 1-alkyl substituent. This finding is of practical importance, since the extraction of Cu(II) with a more hydrophobic alkylimidazole can be performed at a lower concentration of the heterocyclic base in the solvent.

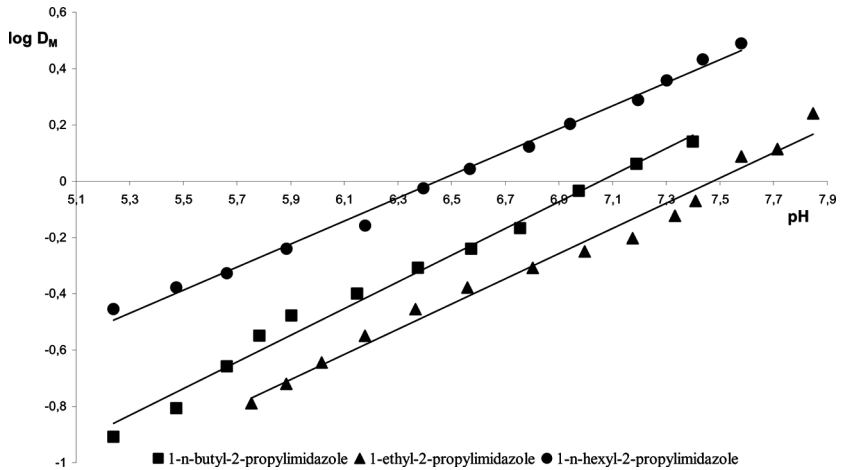

Figure 4. Influence of the alkyl chain length of 1-alkyl-2-propylimidazoles on the extraction of Cu(II) complexes into chloroform.

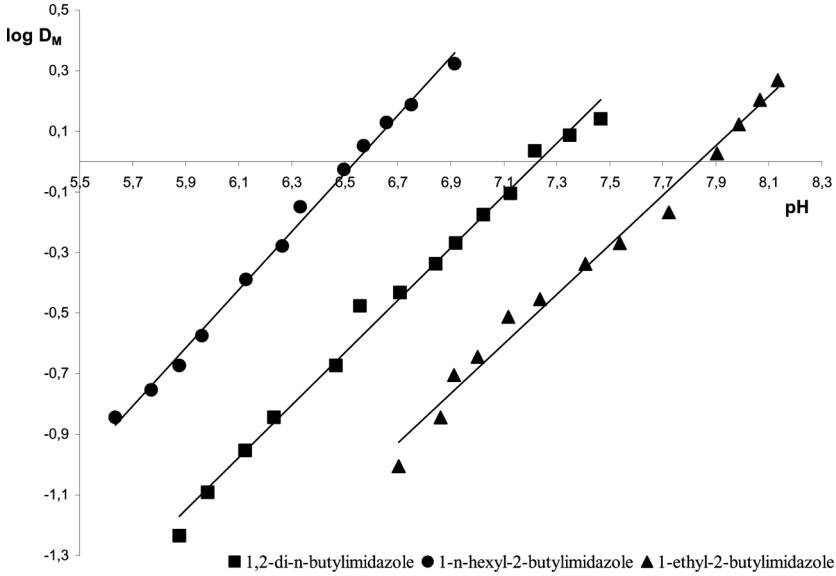

Figure 5. Influence of the alkyl chain length of 1-alkyl-2-butylimidazoles on the extraction of Cu(II) complexes into chloroform.

Next, in Figs. 4–6, the partition of Cu(II) between chloroform and water phases is shown. Also, in this case, all the log $D_M = f(pH)$ curves are similar in shape and slope as those obtained for the 2-ethylhexanol solvent. There is also observable a similar influence of the increase in

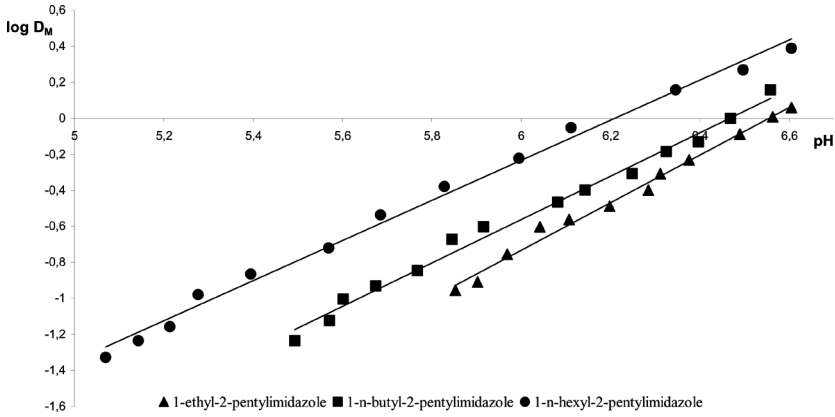

Figure 6. Influence of the alkyl chain length of 1-alkyl-2-pentylimidazoles on the extraction of Cu(II) complexes into chloroform.

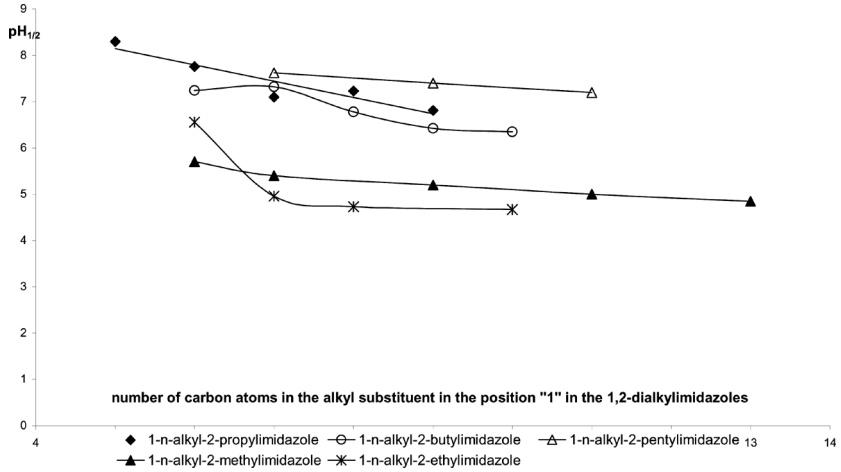

Figure 7. Influence of the alkyl chain length on $pH_{1/2}$ values of extraction of Cu(II) complexes with 1,2-dialkylimidazoles into 2-ethylhexanol.

the ligand (extractant) hydrophobicity on the pH of extraction of the Cu(II) complexes.

To visualize the influence of the differences in the alkyl chain length on the efficiency of Cu(II) extraction with both extractants, a relationship has been established between $pH_{1/2}$ (pH for $D_M = 0$) and the number of carbon atoms in both alkyl substituents at positions 1 and 2, for 2-ethylhexanol (Fig. 7) and chloroform (Fig. 8). Previously reported results for 1-n-alkyl-2-methylimidazoles (2) and 1-n-alkyl-2-ethylimidazoles (3) are

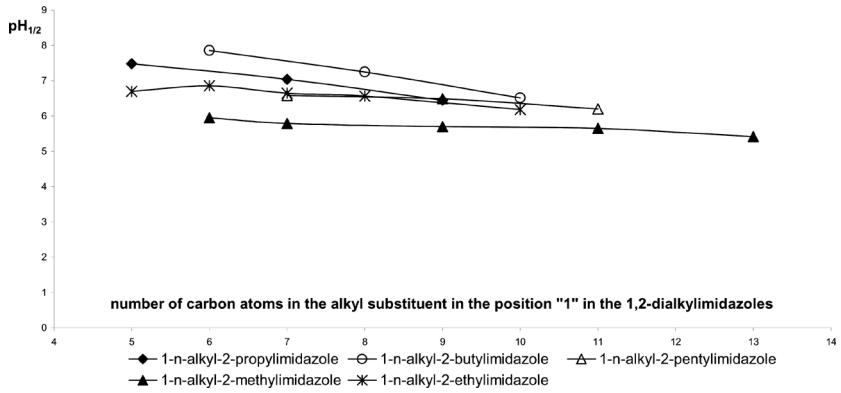

Figure 8. Influence of the alkyl chain length on $pH_{1/2}$ values of extraction of Cu(II) complexes with 1,2-dialkylimidazoles into chloroform.

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

Ligand [references]	pKa [8]	log β_1 (potentiometric method)	log β_1 (extraction method)	log β_2 (extraction method)	log β_3 (extraction method)	solvent	P_1	P_2	P_3
1,2-dimethylimidazole (9)	8.21	3.70							
1-ethyl-2-methylimidazole (10)	8.21	3.52							
1-propyl-2-methylimidazole (10)	8.25	3.67							
1-butyl-2-methylimidazole (10)	8.18	3.74							
1-pentyl-2-methylimidazole (2)	8.27		3.50	6.59	9.18	Chloroform	1.23	29	
						2-ethyl-1-hexanol	2.5	15	
1-hexyl-2-methylimidazole (2)	8.32		3.52	6.63	8.98	Chloroform	2.7	35	
						2-ethyl-1-hexanol	4	26	
1-octyl-2-methylimidazole (2)	8.40		3.53	6.65	9.65	chloroform	2.9	42	
						2-ethyl-1-hexanol	4.8	38	
1-decyl-2-methylimidazole (2)	8.49		3.54	6.68	9.44	Chloroform	3.08	50	
						2-ethyl-1-hexanol	6	52	
1-dodecyl-2-methylimidazole (2)	8.57		3.58	6.75	9.37	Chloroform	3.2	3.2	
						2-ethyl-1-hexanol	9.2	65	
1-propyl-2-ethylimidazole (3)	8.03		3.93	6.93	7.75	Chloroform	40	65	450
1-butyl-2-ethylimidazole (3)	8.27		3.82	7.15	8.40	Chloroform	32	50	900
						2-ethyl-1-hexanol	18	375	1,670
1-pentyl-2-ethylimidazole (3)	8.31		4.46	7.30	8.54	Chloroform	70	160	1,320

					2-ethyl-1-hexanol	38	631	2,100
1-hexyl-2-ethylimidazole (3)	8.36	4.15	7.43	8.62	Chloroform	82	190	1,700
					2-ethyl-1-hexanol	45	950	2,700
1-octyl-2-ethylimidazole (3)	8.44	4.11	7.59	8.23	Chloroform	96	240	2,800
					2-ethyl-1-hexanol	72	1,300	3,600
1-ethyl-2-propylimidazole [this work]	8.27	3.14	5.51	6.19	Chloroform	40	120	380
		3.37	5.91	6.64	2-ethyl-1-hexanol	25	100	950
1-butyl-2-propylimidazole [this work]	8.35	3.25	5.70	6.40	Chloroform	65	200	750
		3.48	6.10	6.85	2-ethyl-1-hexanol	30	400	1,100
1-hexyl-2-propylimidazole [this work]	8.43	3.43	6.02	6.76	Chloroform	90	450	900
		3.60	6.32	7.10	2-ethyl-1-hexanol	50	620	1,300
1-ethyl-2-butylimidazole [this work]	8.31	3.51	6.16	6.92	Chloroform	35	160	420
		3.07	5.39	6.05	2-ethyl-1-hexanol	15	150	900
1,2-dibutylimidazole [this work]	8.39	3.44	6.04	6.79	Chloroform	60	270	800
		3.23	5.67	6.37	2-ethyl-1-hexanol	30	460	1,000
1-hexyl-2-butylimidazole [this work]	8.47	3.78	6.63	7.45	Chloroform	70	500	850
		3.25	5.70	6.40	2-ethyl-1-hexanol	40	700	1,200
1-ethyl-2-pentylimidazole [this work]	8.31	3.34	5.86	6.58	Chloroform	20	200	480
		3.11	5.46	6.13	2-ethyl-1-hexanol	10	180	800
1-butyl-2-pentylimidazole [this work]	8.39	3.34	5.86	6.58	Chloroform	40	250	500
		3.27	5.74	6.45	2-ethyl-1-hexanol	20	500	1,100
1-hexyl-2-pentylimidazole [this work]	8.47	3.20	5.61	6.30	Chloroform	45	450	780
		3.18	5.54	6.22	2-ethyl-1-hexanol	30	720	950

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

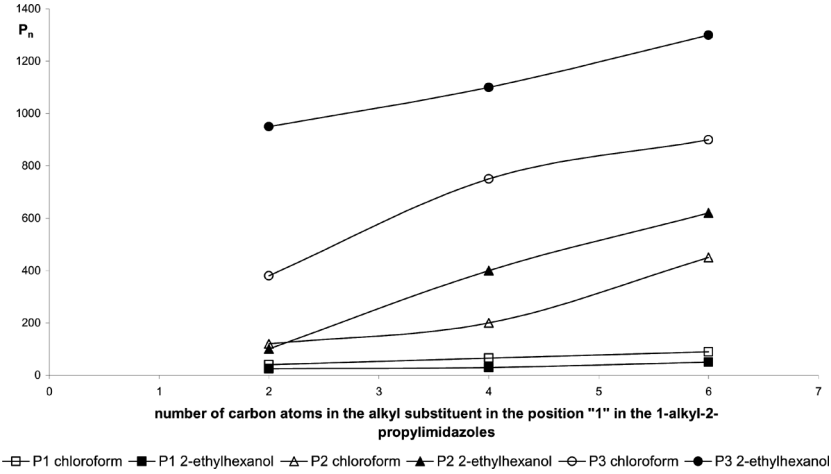

Figure 9. Influence of the alkyl chain length on the partition ratios (P_n) of Cu(II) complexes with 1-alkyl-2-propylimidazoles.

also included for comparison. These plots distinctly demonstrate the influence of steric hindrance due to 2-alkyl substitution on the extraction efficiency of Cu(II). If the influence were identical for all of the 2-alkylimidazoles, then the data points in Figs. 7 and 8 would constitute a single set. In this case, however, separate curves were obtained for each type of alkyl derivatives.

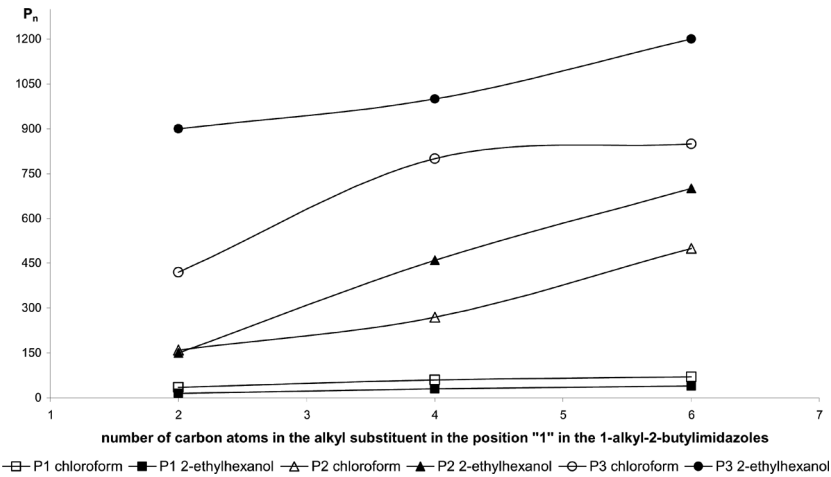

Figure 10. Influence of the alkyl chain length on the partition ratios (P_n) of Cu(II) complexes with 1-alkyl-2-butylimidazoles.

In 2-ethylhexanol, the lowest suppression of the $pH_{1/2}$ values was noticed for 1-alkyl-2-ethylimidazoles, a slightly smaller for 1-alkyl-2-methylimidazoles and still smaller influence for 1-alkyl-2-n-propyl- and 1-alkyl-2-n-butylimidazoles. A comparable influence on the $pH_{1/2}$ is seen for 1-n-alkyl-2-pentylimidazoles, this being, however, slightly weaker than that for 1-alkyl-2-n-propylimidazole and 1-alkyl-2-n-butylimidazole.

In the case of Cu(II) extraction with the same 1,2-dialkylimidazoles in chloroform solutions (Fig. 8), the shapes of the curves resemble those recorded in 2-ethylhexanol, but they are more closer to one another and the Cu(II) complexes with 1-n-alkyl-2-methylimidazoles are extracted at lower pH values.

The general conclusion drawn from the data represented in Figs. 7 and 8 is that the dominant steric effects among the substituents at position 2 of the 1,2-dialkylimidazoles are due to the methyl and ethyl groups.

Both figures (7 and 8) show that the solvents have a considerable effect on the extraction capacity of the Cu(II) complexes with 1,2-dialkylimidazoles. This influence has previously been noticed and discussed in the paper dealing with the extraction of Cu(II) using 1-n-alkyl-2-ethylimidazoles (3).

In order to get a more consistent information about the influence of both the hydrophobic and steric effects on the extraction of Cu(II) complexes with 1,2-di-n-alkylimidazoles, stability constants, β_n, of the complexes in the aqueous phase and the corresponding solvent/water partition constants, P_n, were calculated from the following equation,

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

where: β_n and β_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 ligand molecules in the first Cu(II) complex that is hydrophobic enough to freely pass into the organic phase (7,8). This methodology was used previously (1–3).

Stability constants, β_n, obtained in this way are shown in Table 1 for each organic solvent together with the previously determined stability constants of Cu(II) complexes with 1-n-alkyl-2-methylimidazoles (2) and 1-n-alkyl-2-ethylimidazoles (3).

The stability constants of the Cu(II) complexes with 1-n-alkyl-2-propyl-, 1-n-alkyl-2-butyl and 1-n-alkyl-2-pentylimidazoles are comparable, only slightly lower than those with the 1-n-alkyl-2-methyl- and 1-n-alkyl-2-ethylimidazoles.

Owing to the steric effect of the 2-alkyl substituents the constants are lower by one order of magnitude than those of the 1-n-alkylimidazole Cu(II) complexes (1).

The data in Table 1 bring some interesting information on the extraction of the Cu(II) complexes with 1,2-di-n-alkylimidazoles as far as their solvent/water partition constants, P_n, are concerned. The respective relationships between the partition constants and the number of carbon atoms in 1-alkyl of a particular 1,2-dialkylimidazole molecule are represented in Figs. 9–11 (for the 1-alkyl-2-propyl-, 1-alkyl-2-butyl- and 1-alkyl-2-pentylimidazole complexes, respectively). The P_1 values are low for all of the compounds, and virtually independent of the increasing hydrophobicity of the molecules associated with elongation of the 1-alkyl substituent. Those in chloroform are slightly larger than the constants recorded in 2-ethylhexanol. On the other hand, the relationships for P_2 and P_3 are quite different. First, the constants are large and high, being higher in 2-ethylhexanol than in chloroform. Second, the values distinctly increase upon elongation of the 1-alkyl substituent. This suggests that at the second complexation step, the coordination number of the central ion is probably reduced from 6 to 4. The strongly electron-donating 2-ethylhexanol molecules are likely to be favoring this phenomenon. Accordingly, the reactions can be described by the following equations:

$$[Cu(NO_3)_2(H_2O)_xL_2] + S \longleftrightarrow [Cu(NO_3)L_2S]NO_3 + xH_2O \qquad (3)$$

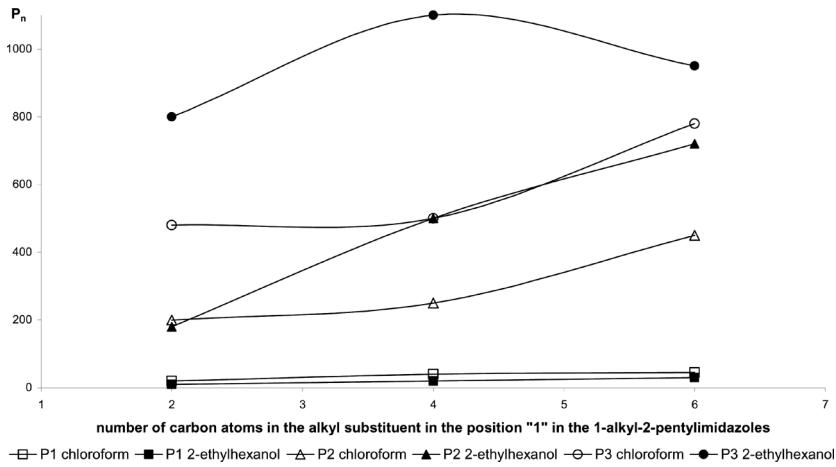

Figure 11. Influence of the alkyl chain length on the partition ratios (P_n) of Cu(II) complexes with 1-alkyl-2-pentylimidazoles.

$$[Cu(NO_3)(H_2O)_xL_3]NO_3 + S \longleftrightarrow [CuL_3S](NO_3)_2 + xH_2O \qquad (4)$$

where: L – molecule of 1,2-dialkylimidazole, and S – molecule of solvent.

Owing to the modification of the coordinational polyhedron, complexes devoid of the water molecule in the coordination sphere of Cu(II) of enhanced extractability are formed.

Evidence in favor of that interpretation can be afforded by absorption spectra of the Cu(II) complexes in organic phase. In Fig. 12, the spectra of the Cu(II) complexes of 1,2-dibutylimidazole in chloroform are presented at increasing pH values of the aqueous phase, whereas Fig. 13 shows analogous spectra of the Cu(II) complexes of 1-hexyl-2-butylimidazole in 2-ethylhexanol. In chloroform (Fig. 12), a peak appearing around 650 nm is displaced slightly towards shorter wavelengths upon raising pH. Again, in 2-ethylhexanol (Fig. 13) a maximum around 600 nm is observed. In Fig. 14, absorption spectra of the 1,2-dibutylimidazole complexes in 2-ethylhexanol are shown with peaks around 620 nm. However, upon raising the ligand concentration in the aqueous and organic phases, other peaks around 540 nm appear which at the highest pH values, surpass those at 620 nm. This is indicative of the formation of Cu(II) complexes of stronger ligand fields at higher ligand concentrations in both phases. It can thus be hypothesized that the complexes are square co-planar, as is the case with binding different ligands of distorted structures (11–13).

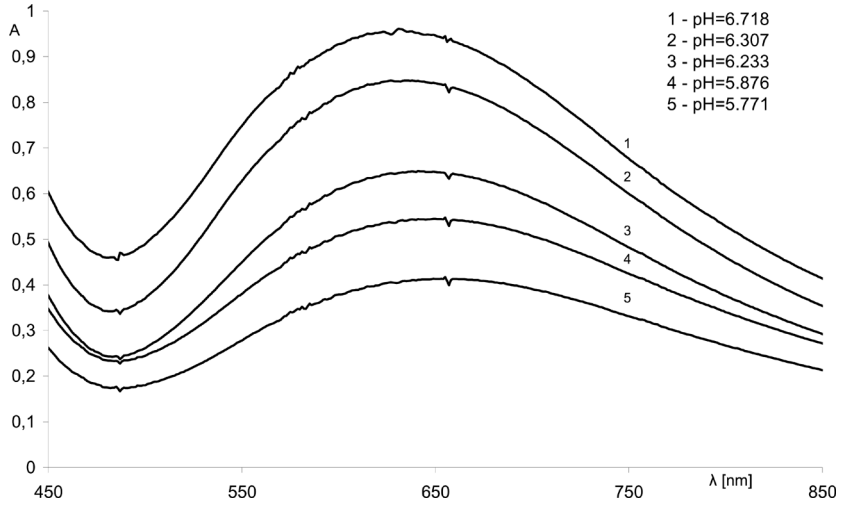

Figure 12. Absorption spectra of organic phase after extraction of the Cu(II) with 1,2-dibutylimidazole in chloroform together with the corresponding pH of the aqueous phase.

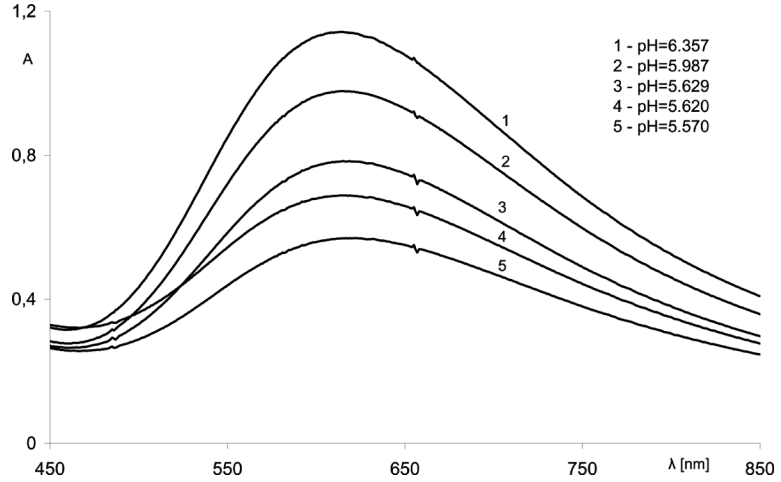

Figure 13. Absorption spectra of organic phase after extraction of the Cu(II) with 1-hexyl-2-butylimidazole in 2-ethylhexanol together with the corresponding pH of the aqueous phase.

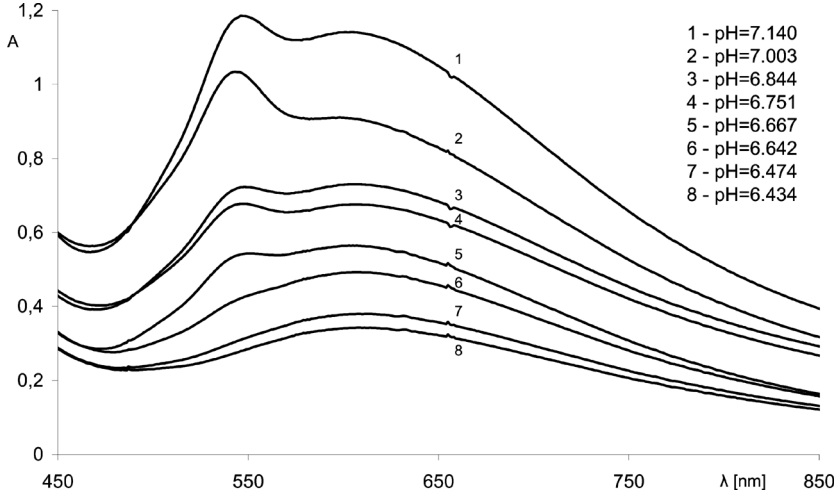

Figure 14. Absorption spectra of organic phase after extraction of the Cu(II) with 1,2-dibutylimidazole in 2-ethylhexanol together with the corresponding pH of the aqueous phase.

CONCLUSIONS

1. All of the 2-alkyl substituted imidazoles are characterized by a steric effect, operating during the formation of their Cu(II) complexes.
2. Replacement of the 2-methyl substituent by a 2-ethyl one considerably strengthens the steric effect, while further elongation of the alkyl chain (n-propyl, n-butyl, n-pentyl) has a minor influence.
3. The steric effect reduces the stability of the complexes. For instance, the stability constants of the 1,2-di-n-alkylimidazole complexes are considerably lower than those of the 1-n-alkylimidazole ones. The constants of the complexes are comparable for the same 1-alkyl substituent in the ligands.
4. Elongation of the 1-alkyl chain displaces the extraction curves towards lower $pH_{1/2}$ values owing to an increase in partition constants, P_n, for the complexes.
5. As a result of the concerted action of steric hindrance due to 2-alkyl substituent, 1-alkyl chain length, and the solvent's electron-donating power, the coordination number of the central ion becomes reduced, this resulting in structural changes in the Cu(II) complexes. This phenomenon facilitates extraction of the complexes owing to enhancement of the partition constants, P_2 and P_3. Furthermore, the phenomenon provides an opportunity for selective extraction of Cu(II) from a mixture containing Zn(II), Co(II), Ni(II), and Cd(II) ions.

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