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The Influence of Alkyl Chain Length and Steric Effect on Stability Constants and Extractability of Zn(II) Complexes with 1-Alkyl-4(5)-Methylimidazoles

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ABSTRACT

The present study investigated the extraction of Zn(II) complexes with eight 1-alkyl-4(5)-methylimidazoles (R from C_4H_9 to $C_{11}H_{23}$) from aqueous solution ($I = 0.5$ (KNO_3) at 25°C) with toluene, p-xylene, 2-ethyl-1-hexanol, and dichloromethane. It was found that the extraction curves moved toward lower pH values with an increasing alkyl chain length. Stability constants of the complexes in the aqueous phase were determined as well as partition constants of the extractable species. It was demonstrated that both the stability constants (β_c) and the partition constants (P_c) of the complexes increased with increasing alkyl chain length. Furthermore, owing to the steric effect, pseudo-tetrahedral

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complexes were found to dominate at the second and third complexation steps, thus increasing the stability constants and facilitating extraction of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles.

Key Words: Zn(II) complexes; Solvent extraction; Azole ligand.

INTRODUCTION

Zinc(II) ions have been found to form tetrahedral and octahedral complexes in aqueous solutions with a variety of ligands[1–3] and even with ammonia.[4,5] Among these ligands are imidazole,[6–8] all the, studied so far, water-soluble 1-alkylimidazoles[9–12] and other derivatives.[13–18] Reactions of Zn(II) ions with these bases result in configuration equilibria between the structural forms at several complexation steps:

$$[\mathrm{Zn(H_2O)_{6-n}L_n}]^{2+} \rightleftharpoons [\mathrm{Zn(H_2O)_{4-n}L_n}]^{2+} + 2\mathrm{H_2O} \qquad (1)$$

In our previous works we showed that imidazole derivatives containing the alkyl substituent (Me, Et, Pr, Bu) in positions 2, 4, or 5 showed in the complexation process the steric effect with Co(II), Zn(II), Ni(II), Cu(II), and Cd(II) ions.[19–23] This effect makes clearly difficult the formation of complexes of the coordination number 6 (octahedral and pseudo-octahedral). However the effect did not determine hindrance for the formation of tetrahedral or pseudo-tetrahedral compounds. We found that tetrahedral complexes form most easily with Zn(II), and with more difficulty—with Co(II) and Cd(II).[19,20] The formation of tetrahedral complexes increased total values of stability constants for these complexation steps where in the aqueous solution formed both structural forms (octahedral and tetrahedral). Furthermore, tetrahedral complexes more easily passed from the aqueous phase to the organic solvent.[24–29] However all these statements refer to the systems containing no more than five carbon atoms in the alkyl substituent.

Recently a possibility of researching this problem for a greater number of the same kind of bases was appeared. There was determined the basicity of several homologous series of alkylimidazoles for bases containing from one to a dozen or so of carbon atoms in the alkyl chain. Consequently we were able to carry out wider studies of the influence of the alkyl chain length on the complexation and extraction proprieties of each type of the alkylimidazoles. So far it was shown that the stability constants of Zn(II), Co(II), and Ni(II) complexes with 1-alkylimidazoles grow up with an increase in the alkyl chain length.[12,30,31] Also, the partition constants of these metals compounds passing to the organic phase increase. On higher complexation stages ($1 < n \leq 4$), Zn(II) and Co(II) form the tetracoordination compounds of much higher partition constants. However, the stability of Cu(II) complexes with 1-alkylimidazoles does not depend on the hydrocarbon group length.[32] Generally, the first complex of this metal (CuL) passes to the organic phase, and its partition constants go up with an increase in the alkyl chain length.

This work begins the new series of publications in the metals complexes with imidazole derivatives containing the steric hindrance. The present work investigated the stability constants of Zn(II) complexes with the series of 1-alkyl-4(5)-methylimidazoles containing 8 derivatives (from 1-butyl- up to 1-undecyl-4(5)-methylimidazole). All these bases are difficult to solve in water. In the investigation we used four organic solvents, namely toluene, p-xylene, 2-ethyl-1-hexanol and dichloromethan. We wanted to determine whether the steric effect in general will appear for difficult-water-soluble imidazole bases, and, at the same time, whether it will create conditions for the selective extraction of Zn(II) complexes. The purpose of this work was not only the calculation of the stability constants, but also the determination of their change with an increase in alkyl chain length, and, at the same time, in the basicity of imidazoles.

The basicity of 1-alkyl-4(5)-methylimidazoles in water at 25°C have been found[33] to be linearly related to the number of carbon atoms in the alkyl chain, n:

$$pK_a = 0.0351n + 7.765 \tag{2}$$

From the available investigations it was found that 1,4(5)-dimethylimidazole, the first representative of this homologous series, forms tetrahedral complexes, $[Zn(H_2O)_2L_2]^{2+}$ and $[ZnL_4]^{2+}$, which predominate in the solution. They have been found to be much more readily extractable with benzyl alcohol and cyclohexanone than complexes of other divalent metals.[34] Moreover, from the practical point of view, only hardly water soluble alkylimidazole derivatives are useful for the extraction of metals. Because of low dissolubility in water of the ligands investigated, the choice of research methods is limited, therefore we chose the liquid-liquid partition method.

So far a similar problem for Zn(II) complexes with any type of bases has not been studied. The systems chosen by us can be used as a model, from which conclusions can be useful to the qualification the influence of alkyl substituents in other types of ligands, eg., of alkyl derivatives of pyridine.

Sigel et al.[35] investigated a similar problem. They determined the interrelation between the complex stability and the ligand basicity for imidazole and its simple, sterically unhindered derivatives. Their investigation shows that stability constants of complexes grow linearly with an increase in the ligands basicity.

EXPERIMENT

Reagents

1-Alkyl-4(5)-methylimidazoles were synthesized by Dr. Andrzej Skrzypczak, the Poznan Technical University.[36] The details concerning structural studies and the purity of the compounds are given in the previous paper.[33]

Prior to the preparation of solutions, the potassium and zinc(II) nitrates (both of analytical reagent grade, POCh Gliwice) were recrystallized from double distilled water. The concentration of zinc(II) nitrate in the solution was determined by complexometric titration with EDTA (ethylenediaminetetraacetic acid, disodium salt) and by AAS (atomic absorption spectrophotometry), and that of potassium nitrate by the gravimetric method as potassium sulfate. The remaining reagents were also of analytical grade. Nitric acid (POCh, Gliwice) was standardized against sodium carbonate. 2-Ethyl-1-hexanol (Aldrich), p-xylene (Fluka-Chemika), toluene and dichloromethane (both from POCh, Gliwice) were used as received.

The pH meter was calibrated against commercial buffer solutions of pH 4.01 ± 0.01 and 7.00 ± 0.01 (Radiometer, Copenhagen). The readings were additionally checked against dilute hydrochloric acid as recommended by IUPAC.[37]

Equipment

Potentiometric measurements were run on the PHM-250 pH meter (Radiometer, Copenhagen) equipped with the C2401-8 combination electrode (Radiometer, Copenhagen). The concentration of zinc(II) was determined by atomic absorption spectrophotometry using the AAS BUCK Scientific 210 VG-P instrument.

Extraction Procedure

All the measurements were run at 25°C at a fixed ionic strength of the aqueous phase ($I = 0.5$) maintained by KNO_3. The initial concentrations of nitric acid and zinc(II) nitrate in the aqueous phase were fixed at 0.02 and 0.01 mol/L, respectively, while the ligand concentration in the organic phase varied from 0.02 to 0.2 mol/L. Six mL of the aqueous phase was placed in a graduated test tube and the same volume of the 1-alkyl-4(5)-methylimidazole solution in the organic solvent was added. The test tube was then being shaken for 20 min. After attaining equilibrium, the phases were separated, the pH and the concentration of Zn(II) in the aqueous phase were determined by titration with a standardized EDTA solution and by the AAS.

RESULTS AND DISCUSSION

Distribution ratio (D_M) of Zn(II) was used for quantitative description of the extraction process. This variable was calculated from analytical measurements, defined as follows:

$$D_M = \frac{C_M^0 - C_M}{C_M} \tag{3}$$

where C_M^0 is the Zn(II) concentration in the aqueous phase before extraction and C_M is the concentration after reaching partition equilibrium.

The results of the extraction experiments for all the systems studied are presented as plots of logarithms of the distribution ratio between the aqueous and organic phase vs. pH (log $D_M = f(pH)$) for extractions with toluene, p-xylene, 2-ethyl-1-hexanol, and dichloromethane, respectively (Figs. 1–4).

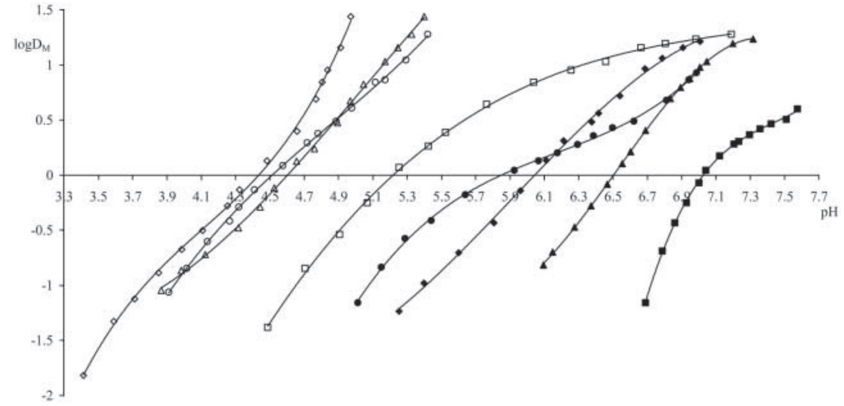


Figure 1. Influence of the alkyl chain length on the extraction of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles into toluene. ■—1-butyl-4(5)-methylimidazole; ▲—1-pentyl-4(5)-methylimidazole; ◆—1-hexyl-4(5)-methylimidazole; ●—1-heptyl-4(5)-methylimidazole; □—1-octyl-4(5)-methylimidazole; △—1-nonyl-4(5)-methylimidazole; ◇—1-decyl-4(5)-methylimidazole; ○—1-undecyl-4(5)-methylimidazole.

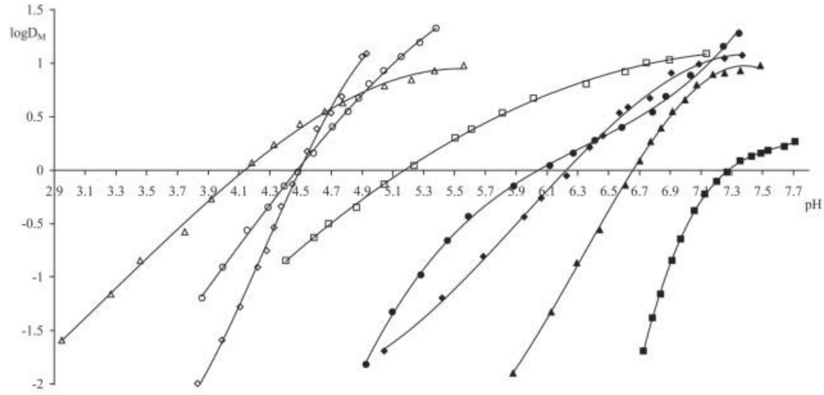


Figure 2. Influence of the alkyl chain length on the extraction of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles into p-xylene. ■—1-butyl-4(5)-methylimidazole; ▲—1-pentyl-4(5)-methylimidazole; ◆—1-hexyl-4(5)-methylimidazole; ●—1-heptyl-4(5)-methylimidazole; □—1-octyl-4(5)-methylimidazole; △—1-nonyl-4(5)-methylimidazole; ◇—1-decyl-4(5)-methylimidazole; ○—1-undecyl-4(5)-methylimidazole.

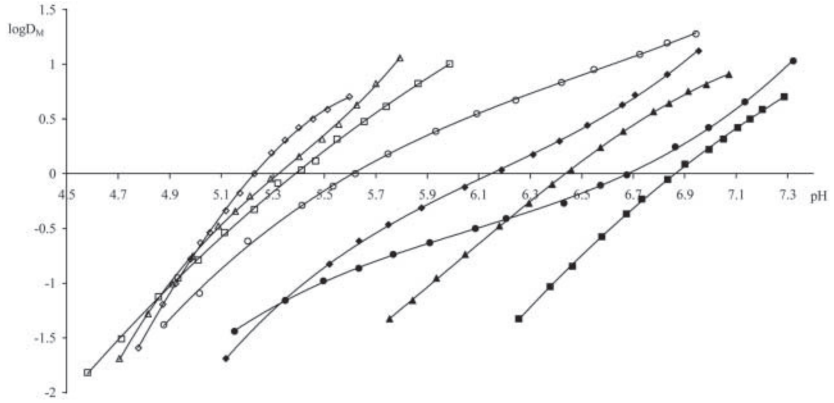


Figure 3. Influence of the alkyl chain length on the extraction of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles into 2-ethyl-1-hexanol. ■—1-butyl-4(5)-methylimidazole; ▲—1-pentyl-4(5)-methylimidazole; ◆—1-hexyl-4(5)-methylimidazole; ●—1-heptyl-4(5)-methylimidazole; □—1-octyl-4(5)-methylimidazole; △—1-nonyl-4(5)-methylimidazole; ◇—1-decyl-4(5)-methylimidazole; ○—1-undecyl-4(5)-methylimidazole.

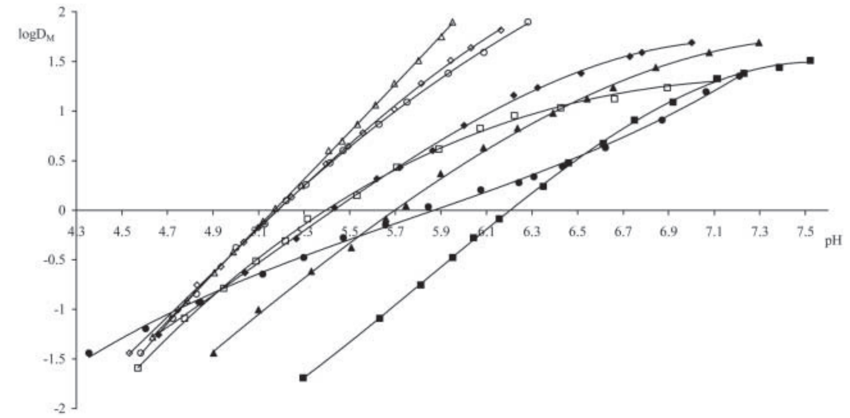


Figure 4. Influence of the alkyl chain length on the extraction of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles into dichloromethane. ■—1-butyl-4(5)-methylimidazole; ▲—1-pentyl-4(5)-methylimidazole; ◆—1-hexyl-4(5)-methylimidazole; ●—1-heptyl-4(5)-methylimidazole; □—1-octyl-4(5)-methylimidazole; △—1-nonyl-4(5)-methylimidazole; ◇—1-decyl-4(5)-methylimidazole; ○—1-undecyl-4(5)-methylimidazole.

As seen, there is a separate curve for each system. With each of the solvents used, the curves are shifted towards lower pH values with an increasing 1-alkyl chain length. The largest shifts toward higher acidities of solution is seen for toluene and p-xylene. For the most hardly soluble 1-alkyl-4(5)-methylimidazoles (those with the nonyl, decyl, and undecyl substituents), the curves tend to form bundles. Slopes of the curves are different and vary depending on the length of the alkyl group and the solvent used. The shape of the curves presented in Figs. 1–4 indicates that, mostly, more than one complex is being extracted.

The plots in Fig. 1 show that the extraction of Zn(II) complexes with imidazole bases with toluene occurs at different pH. The difference in $pH_{1/2}$ (at the $\log D_M = 0$ level) for the extreme curves (i.e., for 1-butyl- and 1-decyl-4(5)-methylimidazoles) is as large as 2.5 pH units. The bundle of curves for three most hardly soluble azoles is located within the pH range of 4.4 to 4.6. The shapes of the majority of the extraction curves ($\log D_M = f(pH)$) presented in Fig. 1 are similar. The only exception provides the curve of 1-heptyl-4(5)-methylimidazole. The shapes of the extraction curves of the complexes with p-xylene (Fig. 2) are similar to those presented in Fig. 1, but they differ more distinctly from one another than those for toluene. They are distributed within a large pH range (4.1 through 7.3 at the $\log D_M = 0$ level). The lowest $pH_{1/2}$ value is seen in the curve of 1-nonyl-4(5)-methylimidazole.

The extraction curves for 2-ethyl-1-hexanol (Fig. 3) intersect the abscissa within the pH range 5.2–6.9. They are similar in shape, with the exception of the 1-heptyl-4(5)-methylimidazole curve. Generally, they are similar to those described for toluene and p-xylene, being, however, less steep.

The extraction curves for dichloromethane (Fig. 4) differ from those described previously. They are closer to one another and intersect the abscissa within the pH range 5.2–6.2. For the three most hydrophobic compounds, the results create almost a single curve. It means that the extraction differences among particular compounds become smaller, which could be due to entering of CH_2Cl_2 molecules in the coordination sphere of Zn(II) ions.

Displacement of the extraction curves toward lower pH values with an increasing 1-alkyl chain length in the 1,3-diazole ring can be explained in terms of either increase in the stability constants of the Zn(II) complexes in the aqueous phase or in the partition constants of the complexes passing to the organic phase. A simultaneous increase in both cannot be ruled out, either.

For the quantitative interpretation of the systems studied, the knowledge of the equilibrium concentration of the free ligand, [L], in the aqueous phase is necessary. This variable was estimated from the pH measurements of the aqueous solution and from the dissociation constant of the protonated azole base, K_a. The pK_a values required are summarized in Table 1. Approximate stability constants for each system were determined by the numerical method using Rydberg's equation [Eq. (4)].[38]

$$\frac{[L]^c}{D_M} = \frac{\beta_1}{P_c \cdot \beta_c}[L] + \frac{1}{P_c \cdot \beta_c} \tag{4}$$

where β_c are stability constants of the complexes formed in the aqueous phase and P_c are partition constants of the complexes between the aqueous solution and organic solvent:

$$P_c = \frac{[ML_c]_{(o)}}{[ML_c]_{(w)}} \tag{5}$$

where $[ML_c]_{(o)}$ and $[ML_c]_{(w)}$ are molar concentrations of complex ML_c in the organic phase and aqueous solution, respectively.

By varying the exponent of [L], a straight line as described by equation $y = ax + b$ was looked for. By dividing coefficients **a** and **b**, the stability constant of the first complex formed in the aqueous phase, β_1, was obtained. Then, using Eq. (6) and the method of curve fitting, accurate β_c and P_c values

Table 1. The pK_a values of alkylimidazoles and the stability constants log β_c of Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in aqueous solution ($I = 0.5$ KNO_3) at 25°C.

Ligand	pK_a	log β_1	log β_2	log β_3	log β_4	Solvent
4(5)-methylimidazole	7.80[20]	2.48	5.06	7.74	10.52	
1,4(5)−dimethylimidazole	7.75[31]	1.70	4.48	5.40	8.90	
1-butyl−4(5)-methylimidazole	7.93[30]	2.2 ± 0.2	5.0 ± 0.5	5.7 ± 0.6	6.8 ± 0.7	toluene
		2.1 ± 0.2	4.7 ± 0.5	5.6 ± 0.6		p-xylene
		2.2 ± 0.2	4.6 ± 0.5	5.9 ± 0.6		2-ethyl-1-hexanol
		2.1 ± 0.2	4.9 ± 0.5	6.1 ± 0.6		dichloromethane
1-pentyl-4(5)-methylimidazole	7.97[30]	2.5 ± 0.3	5.3 ± 0.5	5.9 ± 0.6		toluene
		2.6 ± 0.3	5.0 ± 0.5	6.0 ± 0.6		p-xylene
		2.5 ± 0.3	4.8 ± 0.5	6.1 ± 0.6		2-ethyl-1-hexanol
		2.3 ± 0.2	5.3 ± 0.5	6.4 ± 0.6		dichloromethane
1-hexyl-4(5)-methylimidazole	8.01[30]	2.9 ± 0.3	5.6 ± 0.6	6.3 ± 0.6		toluene
		2.9 ± 0.3	5.4 ± 0.5	6.5 ± 0.7		p-xylene
		2.9 ± 0.3	5.0 ± 0.5	6.3 ± 0.6		2-ethyl-1-hexanol
		2.7 ± 0.3	5.6 ± 0.6	6.7 ± 0.7		dichloromethane
1-heptyl-4(5)-methylimidazole	8.05[30]	3.2 ± 0.3	5.9 ± 0.6	6.6 ± 0.7		toluene
		3.3 ± 0.3	5.6 ± 0.6	6.9 ± 0.7		p-xylene
		3.2 ± 0.3	5.4 ± 0.5	6.6 ± 0.7		2-ethyl-1-hexanol
		3.1 ± 0.3	5.7 ± 0.6	6.8 ± 0.7		dichloromethane

(*continued*)

Table 1. Continued.

Ligand	pK$_a$	log β_1	log β_2	log β_3	log β_4	Solvent
1-octyl-4(5)-methylimidazole	8.1[30]	3.5 ± 0.4	6.2 ± 0.6	6.9 ± 0.7		toluene
		3.6 ± 0.4	5.8 ± 0.6	7.3 ± 0.7		p-xylene
		3.8 ± 0.4	5.5 ± 0.5	6.9 ± 0.7		2-ethyl-1-hexanol
		3.3 ± 0.3	5.9 ± 0.6	7.0 ± 0.7		dichloromethane
1-nonyl-4(5)-methylimidazole	8.11[30]	3.9 ± 0.4	6.5 ± 0.7	7.3 ± 0.7	11.9 ± 1	toluene
		3.9 ± 0.4	6.2 ± 0.6			p-xylene
		4.1 ± 0.4	5.7 ± 0.6	7.0 ± 0.7		2-ethyl-1-hexanol
		3.5 ± 0.4	6.2 ± 0.6	7.1 ± 0.7		dichloromethane
1-decyl-4(5)-methylimidazole	8.15[30]	4.3 ± 0.4	6.9 ± 0.7	7.7 ± 0.8	12.5 ± 1	toluene
		4.4 ± 0.5	6.6 ± 0.7	8.0 ± 0.8		p-xylene
		4.3 ± 0.4	5.9 ± 0.6	7.1 ± 0.7		2-ethyl-1-hexanol
		3.7 ± 0.4	6.4 ± 0.7	7.2 ± 0.7		dichloromethane
1-undecyl-4(5)-methylimidazole	8.19[30]	4.7 ± 0.5	7.5 ± 0.8	8.2 ± 0.8		toluene
		5.0 ± 0.5	7.2 ± 0.7	8.4 ± 0.9		p-xylene
		4.5 ± 0.5	6.1 ± 0.6			2-ethyl-1-hexanol
		3.8 ± 0.4	6.7 ± 0.7	7.3 ± 0.7		dichloromethane

were found. The results, verified in this way, are collected in Table 1 (stability constants) and Table 2 (partition constants).

$$D_M = \frac{P_c \cdot \beta_c \cdot [L]^c + P_{c+1} \cdot \beta_{c+1} \cdot [L]^{c+1} + P_{c+2} \cdot \beta_{c+2} \cdot [L]^{c+2} + \cdots + P_N \cdot \beta_N \cdot [L]^N}{1 + \beta_1 \cdot [L] + \beta_2 \cdot [L]^2 + \cdots + \beta_N \cdot [L]^N} \tag{6}$$

With the data in Table 1, the influence of the number of carbon atoms at position 1 in imidazole ring on the stability constants at particular complexation steps of Zn(II) can be presented. Respective plots were prepared separately for each solvent used in the investigation of the partition of Zn(II) between the two phases, namely for toluene, p-xylene, 2-ethyl-1-hexanol and dichloromethane (Figs. 5–8, respectively). It is worth noting that the stability constants obtained from extraction experiments were compatible with those obtained from potentiometric measurements carried out earlier for 1,4(5)-dimethylimidazole[34] and 4(5)-methylimidazole[20] as presented in Table 1 and the figures.

At all the complexation steps, the β_c constants distinctly increased with an increasing 1-alkyl chain length. However, this increase is not equal for all the stability constants. The β_2 and β_3 constants are considerably higher, as seen in all figures. β_2 constants were exceptionally high, as compared with those for the first complex formed in the aqueous phase (the β_2 plot is situated considerably higher than the β_1 plot). Consequently, the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles are not formed according to the statistic effect. A new phenomenon emerges here, probably associated with displacement of the configurational equilibrium toward tetrahedral species (Eq. (1), resulting in an enhancement of the β_2 and β_3 values being the sum of the stability constants of both structural forms (tetrahedral and octahedral) ($\beta_2 = \beta_2^t + \beta_2^o$ as well as $\beta_3 = \beta_3^t + \beta_3^o$).

Figures 9–11 represent the influence of solvent on respective stability constants, $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$. At the first complexation step, the smallest and fairly divergent values were obtained in dichloromethane. For the next two steps, the results for toluene and p-xylene are comparable and higher than those for dichloromethane and 2-ethyl-1-hexanol. At the third complexation step, beginning from 1-heptyl-4(5)-methylimidazole onwards, the stability constants increase only slightly for the last mentioned solvents. The results showed in Figures 9–11 prove that dichloromethane and 2-ethyl-1-hexanol molecules are bonding in coordination sphere of Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles. Therefore, the extraction properties of zinc(II) complexes depend on both those ligands.

Table 2. The partition constants P_c of Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles between aqueous phase and organic solvent at 25°C and constant ionic strength $I = 0.5$ (KNO_3).

Ligand	P_1	P_2	P_3	P_4	Solvent
1-butyl−4(5)-methylimidazole	0.20 ± 0.02	3.5 ± 0.3	30 ± 3	8500 ± 100	toluene
	1.0 ± 0.1	2.3 ± 0.2	60 ± 5		p-xylene
	0.30 ± 0.03	10 ± 1	65 ± 5		2-ethyl-1-hexanol
	3.5 ± 0.3	65 ± 6	400 ± 50		dichloromethane
1-pentyl-4(5)-methylimidazole	0.30 ± 0.03	11 ± 1	1800 ± 200		toluene
	3.0 ± 0.3	22 ± 2	2000 ± 200		p-xylene
	0.60 ± 0.05	50 ± 5	200 ± 20		2-ethyl-1-hexanol
	8 ± 0.8	330 ± 30	2000 ± 200		dichloromethane
1-hexyl-4(5)-methylimidazole	0.40 ± 0.05	50 ± 5	6000 ± 500		toluene
	5.0 ± 0.5	60 ± 5	$4 \times 10^4 \pm 4000$		p-xylene
	1.0 ± 0.1	95 ± 10	300 ± 30		2-ethyl-1-hexanol
	15 ± 1.5	600 ± 50	5000 ± 500		dichloromethane
1-heptyl-4(5)-methylimidazole	0.50 ± 0.05	100 ± 10	$2 \times 10^4 \pm 2000$		toluene
	7.0 ± 0.7	110 ± 10	$3 \times 10^5 \pm 3 \times 10^4$		p-xylene
	1.2 ± 0.1	210 ± 20	450 ± 50		2-ethyl-1-hexanol
	20 ± 2	750 ± 80	8000 ± 100		dichloromethane

1-octyl-4(5)-methylimidazole	0.70 ± 0.07	300 ± 30	$4 \times 10^4 \pm 4000$		toluene
	14 ± 1.4	200 ± 20	$3 \times 10^6 \pm 3 \times 10^5$		p-xylene
	1.7 ± 0.2	350 ± 30	1000 ± 100		2-ethyl-1-hexanol
	26 ± 2.6	900 ± 100	$2 \times 10^4 \pm 2000$		dichloromethane
1-nonyl-4(5)-methylimidazole	0.9 ± 0.1	800 ± 90	$10^5 \pm 10^4$	$3 \times 10^7 \pm 3 \times 10^6$	toluene
	50 ± 5	300 ± 30			p-xylene
	3.0 ± 0.3	800 ± 80	3000 ± 300		2-ethyl-1-hexanol
	32 ± 3	1200 ± 120	$5.5 \times 10^4 \pm 5500$		dichloromethane
1-decyl-4(5)-methylimidazole	1.2 ± 0.1	1200 ± 120	$2 \times 10^5 \pm 2 \times 10^4$	$4 \times 10^8 \pm 4 \times 10^7$	toluene
	80 ± 8	600 ± 60	$10^7 \pm 10^6$		p-xylene
	4.0 ± 0.4	1500 ± 150	6000 ± 600		2-ethyl-1-hexanol
	36 ± 4	1300 ± 130	$9 \times 10^4 \pm 10^4$		dichloromethane
1-undecyl-4(5)-methylimidazole	1.7 ± 0.2	1500 ± 150	$3 \times 10^5 \pm 3 \times 10^4$		toluene
	150 ± 15	1000 ± 100	$10^8 \pm 10^7$		p-xylene
	5.5 ± 0.5	2000 ± 200			2-ethyl-1-hexanol
	40 ± 4	1200 ± 120	$1.1 \times 10^5 \pm 10^4$		dichloromethane

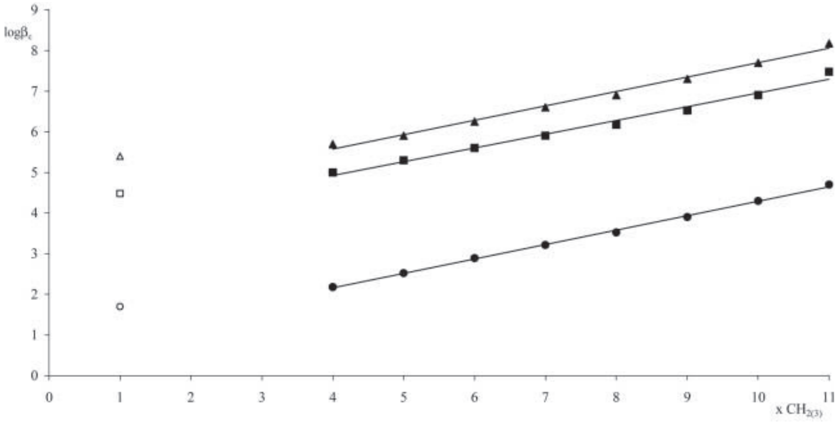


Figure 5. Influence of the alkyl chain length in the position "1" on the stability constants (log β_c) of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in toluene. ●—log β_1; ■—log β_2; ▲—log β_3; ○, □, △—potentiometric results.

Figure 12 shows stability constants of the Zn(II) complexes with 1-alkylimidazoles (Fig. 13a)[12] and 1-alkyl-4(5)-methylimidazoles (Fig. 13b) averaged for all the solvents used. The results for 4(5)-methyl derivatives are lower at all complexation steps, in particular, for the second and third complexes. This is due to the steric hindrance, which hampers penetration of

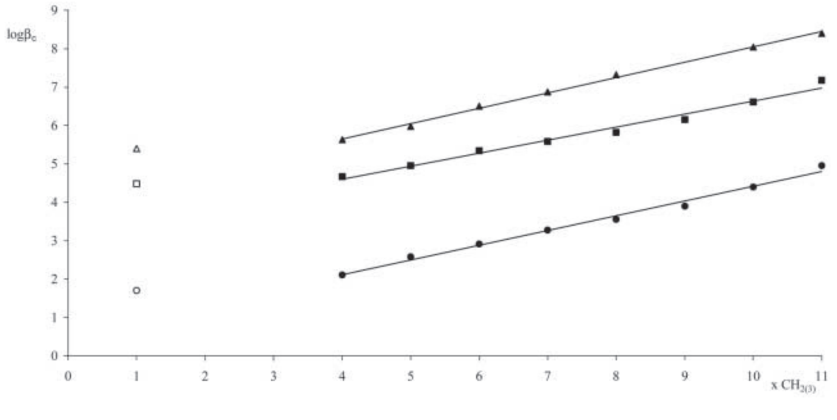


Figure 6. Influence of the alkyl chain length in the position "1" on the stability constants (log β_c) of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in p-xylene. ●—log β_1; ■—log β_2; ▲—log β_3; ○, □, △—potentiometric results.

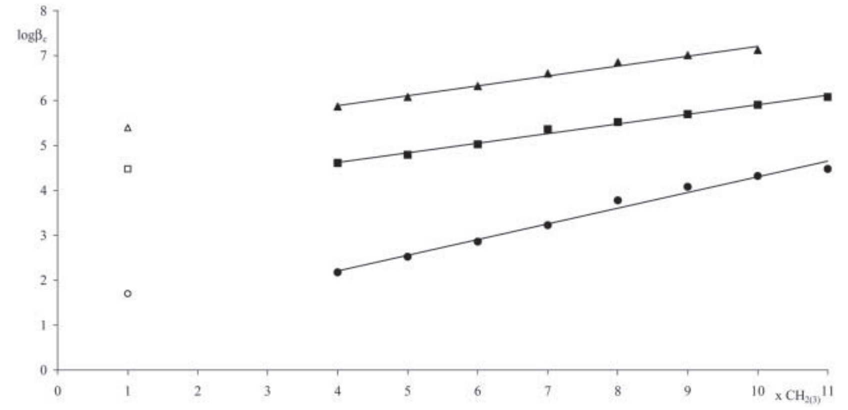


Figure 7. Influence of the alkyl chain length in the position "1" on the stability constants (log β_c) of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in 2-ethyl-1-hexanol. ●—log β_1; ■—log β_2; ▲—log β_3; ○, □, △—potentiometric results.

the heterocyclic ligand into the coordination sphere of the central ion. As a result, the tetrahedral species are less stable as compared to those substituted at position 1 only, but are more readily extractable with the organic solvent owing to smaller number of coordinated water molecules.

Figure 14 shows the influence of the bulkiness of the 1-alkyl group on partition constants of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles

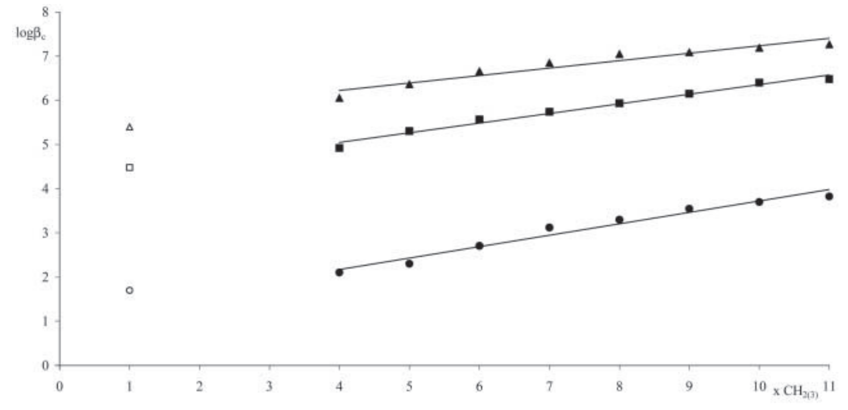


Figure 8. Influence of the alkyl chain length in the position "1" on the stability constants (log β_c) of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in dichloromethane. ●—log β_1; ■—log β_2; ▲—log β_3; ○, □, △—potentiometric results.

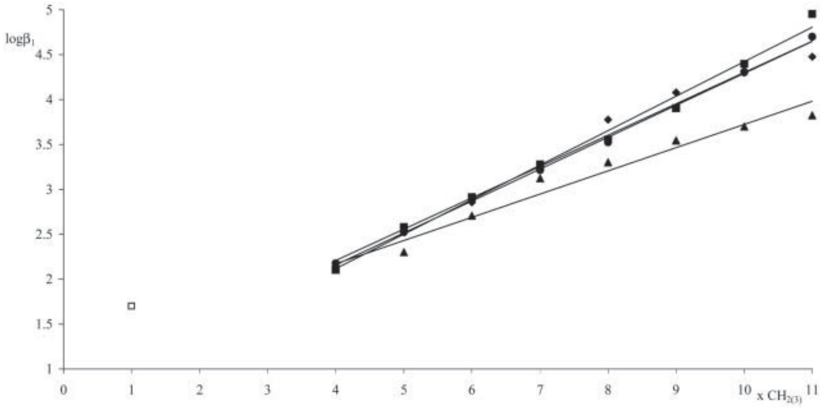


Figure 9. Influence of solvent on the stability constants β_1 of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles. ●—toluene; ■—p-xylene; ▲—dichloromethane; ◆—2-ethyl-1-hexanol; □—potentiometric results.

in systems with non-polar solvents, toluene and p-xylene. The partition constants of the first and second complex, [ML] (P_1) and [ML_2] (P_2) respectively, increase only slightly. In particular, the P_1 constants for toluene are very low. Again, a distinct increase is seen for the third complexes, [ML_3] (P_3), and exceptionally high for p-xylene. Consequently, the extraction of Zn(II) depends mostly on P_2 and P_3 constants. In comparison with the partition

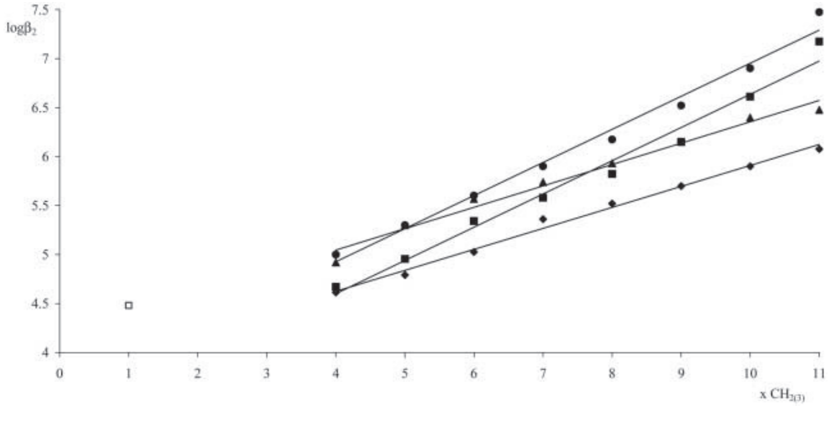


Figure 10. Influence of solvent on the stability constants β_2 of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles. ●—toluene; ■—p-xylene; ▲—dichloromethane; ◆—2-ethyl-1-hexanol; □—potentiometric results.

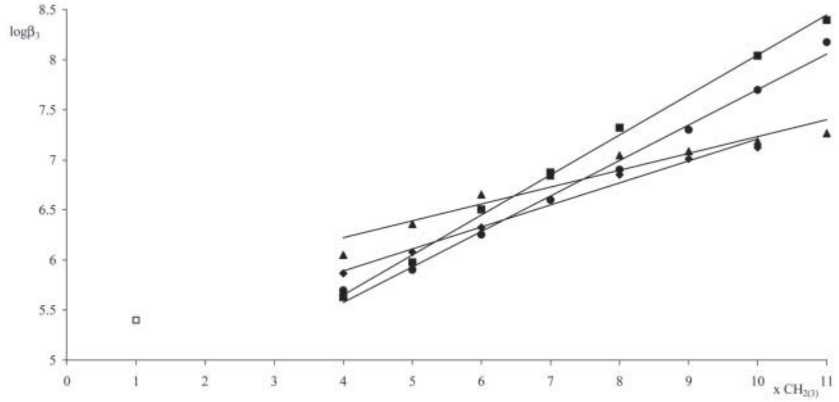


Figure 11. Influence of solvent on the stability constants β_3 of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles. ●—toluene; ■—p-xylene; ▲—dichloromethane; ◆—2-ethyl-1-hexanol; □—potentiometric results.

constants for the first complex, [ML], the results for the second, [ML_2], and third, [ML_3], are by one and two orders of magnitude, respectively, higher. It is likely that beginning from the second step, there are extracted complexes with the coordination number of 4, which are much more readily extractable.

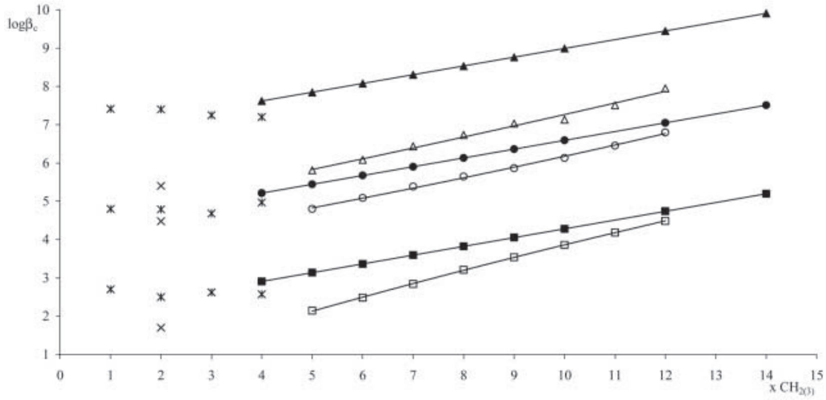
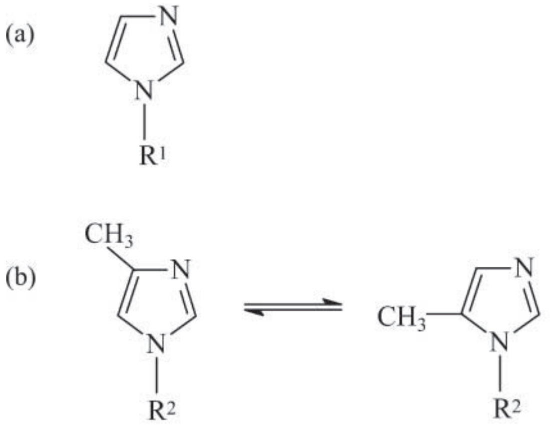


Figure 12. Plots of log β_c vs. the number of carbon atoms in 1-alkyl chain for the Zn(II) complexes with 1-alkylimidazoles. ■—log β_1; ●—log β_2; ▲—log β_3 and 1-alkyl-4(5)-methylimidazoles: □—log β_1; ○—log β_2; △—log β_3; ∗,×—potentiometric data.



$R^1 = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}$

$R^2 = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, C_{10}H_{21}, C_{11}H_{23}$

Figure 13. Chemical structure of 1-alkylimidazoles (a) and 1-alkyl-4(5)-methylimidazoles (b).

In case of partition constants of the complexes extracted with polar solvents, dichloromethane and 2-ethyl-1-hexanol (Fig. 15), the relations between the constants and the number of carbon atoms in the azole molecule are essentially similar as before. At the first and second complexation steps the partition constants increase only slightly. In dichloromethane, P_2 constants, beginning from 1-hexyl-4(5)-methylimidazole onwards, are almost constant. At the third step, the increase in the constants is distinct in 2-ethyl-1-hexanol beginning from 1-octyl-4(5)-methylimidazole onwards and less distinct in dichloromethane.

CONCLUSIONS

The extraction curves ($\log D_M = f(pH)$) were shifted toward lower pH values with an increasing 1-alkyl chain length. In all the solvents studied, extraction curves for the last three compounds of the 1-alkyl-4(5)-methylimidazole series formed a bundle. The lowest $pH_{1/2}$ values were obtained for the 1-nonyl-4(5)-methylimidazole Zn(II) complexes in p-xylene ($pH_{1/2} = 4.1$) and for the 1-decyl-4(5)-methylimidazole ones in toluene and p-xylene ($pH_{1/2} = 4.4$).

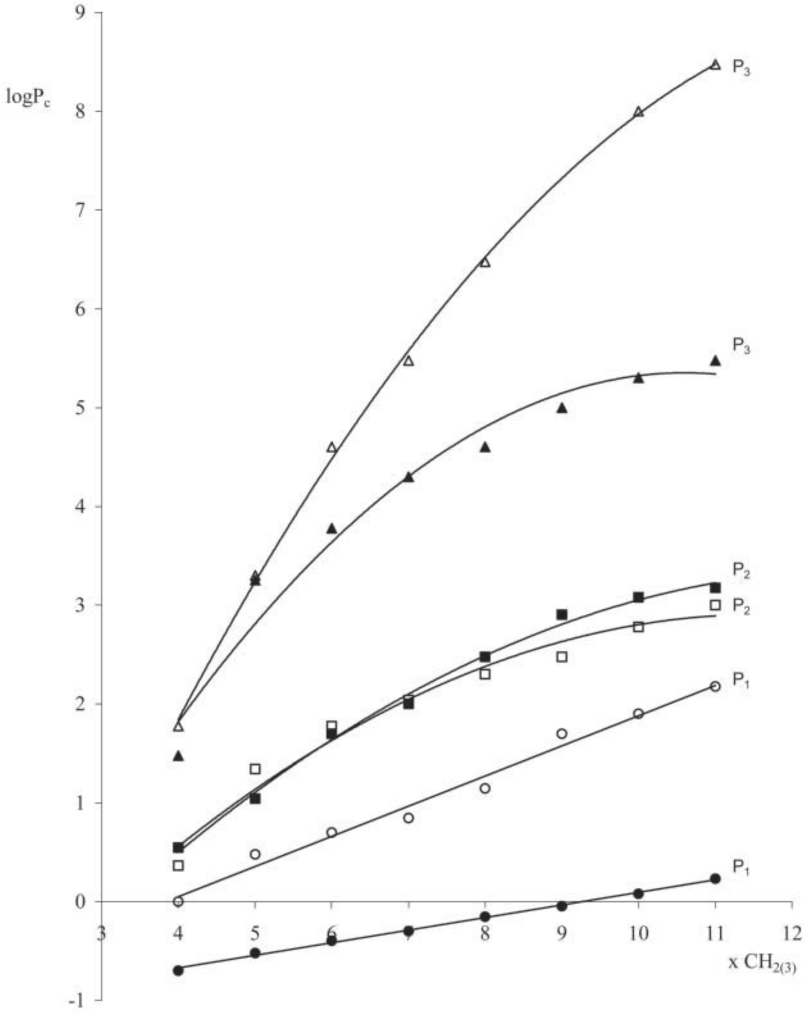


Figure 14. Influence of the alkyl chain length in the position “1” on the partition constants (P$_1$, P$_2$, P$_3$) of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in toluene: ●, ■, ▲ and p-xylene: ○, □, △.

Stability constants of the complexes formed in the aqueous phase increased with an increasing alkyl chain length of the 1,3-diazoles. This referred especially to β_2 and β_3 and was indicative of mounting contribution of tetrahedral species, which enhanced the overall stability constants. The nature of the solvent was also crucial. Higher values were obtained in nonpolar

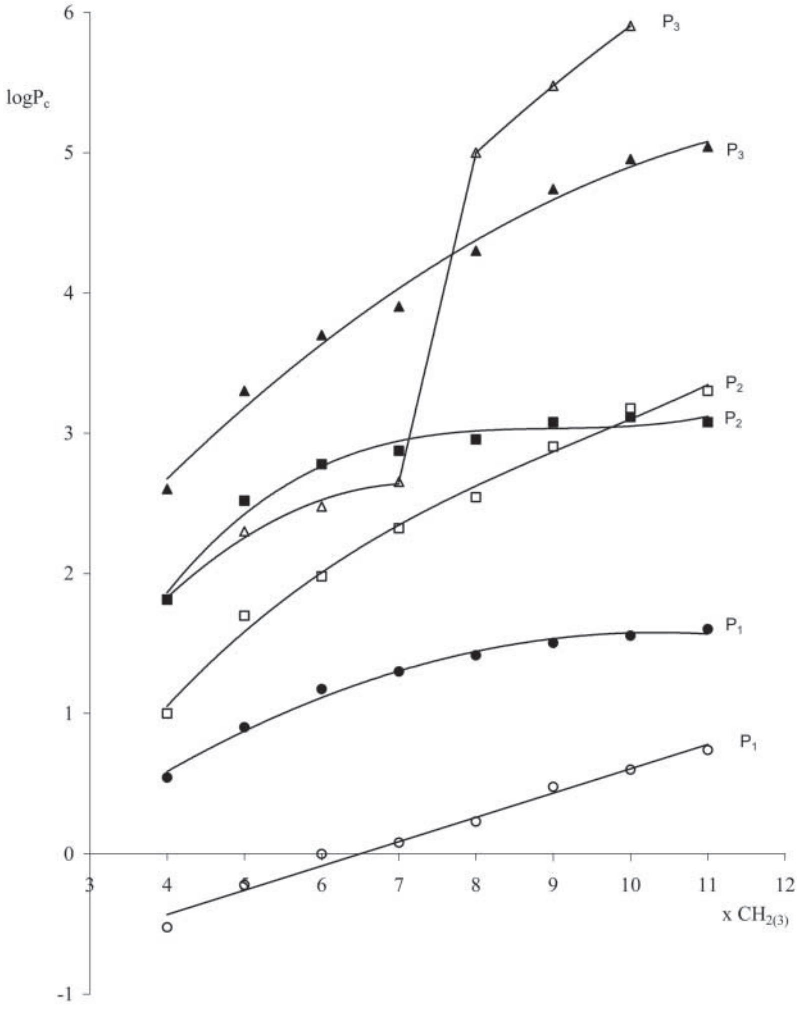


Figure 15. Influence of the alkyl chain length in the position "1" on the partition constants (P_1, P_2, P_3) of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in dichloromethane: ●, ■, ▲ and 2-ethyl-1-hexanol: ○, □, △.

solvents (toluene and p-xylene) as compared to the polar ones (2-ethyl-1-hexanol and dichloromethane).

The steric effect due to the presence of 4(5)-methyl group suppressed the values of stability constants of the Zn(II) complexes as compared to those with derivatives carrying 1-alkyl group only.

An increase in hydrophobicity of ligands resulted in an increase in partition constants of the complexes. In particular, there was a considerable increase in the P_2 and P_3 constants during extraction with p-xylene. In addition, the steric hindrance displaced the configurational equilibrium toward tetrahedral species, this resulting in an increase in the partition constants as compared to those obtained for the 1-alkylimidazole complexes.

For the tetrahedral complexes passing into organic phase one can assume the following composition: $[ZnLS(NO_3)_2]$, $[ZnL_2(NO_3)_2]$, and $[ZnL_3(NO_3)](NO_3)$, where L – 1-alkyl-4(5)-methylimidazole, S – solvent molecule.

Out of the azoles investigated by us, three most hydrophobic derivatives (1-nonylo-, 1-decylo- and 1-undecylo-4(5)-methylimidazole) can be used in practice to the selective extraction of Zn(II) ions from aqueous solutions, as they ensure a high value of the distribution ratio D_M at a very low pH of the aqueous phase (about 4.5 units).

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