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

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Abstract: Extraction of Co(II) complexes has been studied with nine derivatives of 1-alkyl-4(5)-methylimidazoles (with $R = C_2H_3$ to $C_{10}H_{21}$) from aqueous solution [$I = 0.5(KNO_3)$ at 25°C] with toluene, trichloromethane, and 2-ethyl-1-hexanol. Stability constants of the complexes formed in the aqueous phase (β_c) as well as partition constants (P_c) of the extracted species were determined. It was demonstrated that both the stability constants and partition constants of the complexes increase with an increasing of the 1-alkyl chain length. The tetrahedral together with octahedral complexes were formed beginning from the second step of complexation. Furthermore, the influence of the bulkiness of the 1-alkyl group on separation process of Co(II) from Zn(II) for extractions with toluene and 2-ethyl-1-hexanol were determined.

Keywords: Co(II) complexes, 1-alkyl-4[5]-methylimidazoles, tetrahedral complexes, stability constants, partition constants

INTRODUCTION

Solvent extraction is one of the most significant methods used for the removal, retrieval, and separation of metals from aqueous solutions (1). For extraction of Co(II) ions the derivatives of phosphoric acid, α-hydroxy oximes,

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β-diketones, amines, substituted pyridines have been used (2–6). The sparingly water-soluble alkylimidazoles and their hydroxyderivatives have also been patented for this purpose (7). In the other patent (8) high-molecular-weight derivatives of alkylimidazoles (e.g. 2-(1-butyl-amino-methyl)-1-decylimidazole) and benzimidazoles have been proposed for extraction of metal ions from an aqueous acidic sulfate solution.

The complexes of Co(II), Zn(II), and Cd(II) with these bases in the aqueous solution reveal the tendency to the changing of the coordination structure from octahedral to tetrahedral compounds (9–12). The configuration equilibrium between these two structural forms can be described by the equation:

$$[M(H_2O)_{6-c}L_c]^{2+} \rightleftharpoons [M(H_2O)_{4-c}L_c]^{2+} + 2H_2O \tag{1}$$

where: M is the central ion, c is the number of the ligand molecules bounded in the complex (complexation step).

The receptivity to the formation of tetrahedral complexes determines the separation of different metal ions. The increased concentration of tetrahedral complexes in the aqueous phase enlarges the probability of passing of these metals into the organic phase, because the tetrahedral compounds are more liophilic than the octahedral one (13, 14). In the complexation process of metal ions with derivatives containing the alkyl group in positions “2”, “4”, or “5” of the 1,3-diazole ring was observed steric effect (15–21). This phenomenon complicates the formation of the octahedral species and simultaneously favors the tetrahedral complexes.

In our previous paper (22) the basicity of four different homologous series of alkylimidazoles for bases containing from one to a twelve atoms in the hydrocarbon group was determined. It made possible the investigation of the influence of the alkyl chain length on the complexation and extraction properties of the particular types of the alkylimidazoles. So far it was determined, that the stability constants of the complexes Co(II), Zn(II), Ni(II) with 1-alkylimidazoles (23–25) as well as the complexes Zn(II) with 1-alkyl-4(5)-methylimidazoles (26) increase with an increasing length of the 1-alkyl substituent. Generally, beginning from the second complexation step, the tetrahedral complexes were formed with Co(II) and Zn(II). In the case of the Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles the steric effect due to the presence of 4(5)-methyl group reduces the values of the stability constants and simultaneously enlarges the values of partition constants as compared to those with derivatives carrying 1-alkyl group only (24, 26).

The purpose of this work was to investigate by the partition method the influence of the alkyl chain length on the stability, structure of the coordination sphere, and the extraction capacity of the Co(II) complexes with the 1-alkyl-4(5)-methylimidazoles (where: alkyl = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, and $C_{10}H_{21}$). Toluene, trichloromethane, and

2-ethyl-1-hexanol were used as organic solvents. Their dipole moments are 0.31, 1.15, 1.74 D, respectively (27).

EXPERIMENTAL

Reagents

Dr. Andrzej Skrzypczak, (Technical University, Poznan, Poland) (28) synthesized 1-alkyl-4(5)-methylimidazoles. The structural details and the purity of these compounds were described in the previous work (22). The potassium and Co(II) nitrates, both of analytical reagent grade (POCh Gliwice), were recrystallized from double-distilled water. The concentration of Co(II) nitrate in aqueous solution was determined by complexometric titration with EDTA (disodium salt of ethylenediaminetetraacetic acid) and by using atomic absorption spectroscopy method (AAS). The concentration of potassium nitrate was determined gravimetrically as potassium sulphate (29). Nitric acid (analytical reagent grade, POCh Gliwice) was standardized against anhydrous sodium carbonate. 2-ethyl-1-hexanol (Aldrich), toluene, and trichloromethane (both from POCh, Gliwice), all of analytical reagent grade, were used as received. The pH meter was calibrated by using commercial buffer solutions of pH 4.01 ± 0.01 and 7.00 ± 0.01 (Radiometer, Copenhagen). The values of pH were also checked against dilute hydrochloric acid as recommended by IUPAC (30).

Equipment

Potentiometric measurements were run on the PHM-250 pH meter (Radiometer, Copenhagen) equipped with the C2401-8 combination electrode (Radiometer, Copenhagen). The low concentrations of Co(II) in aqueous solution were determined with atomic absorption spectrophotometry by using the AAS BUCK Scientific 210 VG-P instrument. The absorption specters of the organic phase after extraction of the Co(II) complexes were recorded on UV-VIS 8452A spectrophotometer (Hewlett Packard, USA).

Extraction Procedure

The measurements were run at 25°C at a fixed ionic strength of the aqueous phase ($I = 0.5$) maintained by KNO_3. Before extraction the concentrations of the Co(II) nitrate and nitric acid in the aqueous phase were constant 0.01 and 0.02 mol/L respectively, and the ligand concentrations in the organic phase were varied from 0.02 to 0.2 mol/L. Six milliliters of the aqueous phase were 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 tubes were then shaken for 30 minutes at 25°C. After attaining equilibrium, the both phases were separated. The values of pH of the aqueous phase were measured, as well as the Co(II) concentrations by titration with a standardized EDTA solution and by using atomic absorption spectroscopy method were determined. The absorption spectra over the visible range were taken in organic phase.

RESULTS AND DISCUSSION

To describe the process of extraction quantitatively distribution ratio (D_M) of Co(II) was used between the aqueous and organic phases, and defined as follows:

$$D_M = \frac{C_M^o - C_M}{C_M} \tag{2}$$

where: C_M^o is the Co(II) concentration in the aqueous phase before extraction and C_M is the concentration after reaching distribution equilibrium.

The results of the extraction experiments for all the systems studied are presented as plots of logarithm of the distribution ratio of Co(II) between the aqueous and organic phase as a function of pH of the aqueous phase, separately for extractions with toluene, trichloromethane, and 2-ethyl-1-hexanol, respectively (Figs. 1–3).

Data in Fig. 1 show that extraction of Co(II) complexes with particular imidazole derivatives in toluene runs at different pH ranges. The difference in $pH_{1/2}$ (pH at the $\log D_M = 0$) for the extreme curves (for 1-heptyl- and 1-decyl-4(5)-methylimidazole) amounts to ca 3.0 pH units. The most distinct differences of the location of the curves in the co-ordinate system are seen between 1-nonyl-, 1-decyl-4(5)-methylimidazole and other more readily water-soluble bases. Extraction curves for these two last-named 1-alkyl-4(5)-methylimidazoles is located within the pH range of 4.9 to 5.4. The extraction process does not occur for readily soluble water bases: 1-ethyl-, 1-propyl-, and 1-butyl-4(5)-methylimidazole.

The shapes of the extraction curves for trichloromethane as a solvent (Fig. 2) differ more distinctly from one another to those presented in Fig. 1. In this case the most suitable extractants of Co(II) are three of the most hydrophobic 1-alkyl-4(5)-methylimidazoles (those with the octyl-, nonyl-, and decyl- substituents). Extraction curves for these derivatives are largest when shifted towards lower values of pH of the aqueous phase. The difference in $pH_{1/2}$ between extreme curves is smaller than for toluene, amounting to 2.2 pH units.

The extreme curves of distribution of Co(II) by using 2-ethyl-1-hexanol (Fig. 3) are separated from one another by ca 2.0 pH units at $\log D_M = 0$. The majority of plots of $\log D_M$ vs. pH for this solvent are straight lines. In

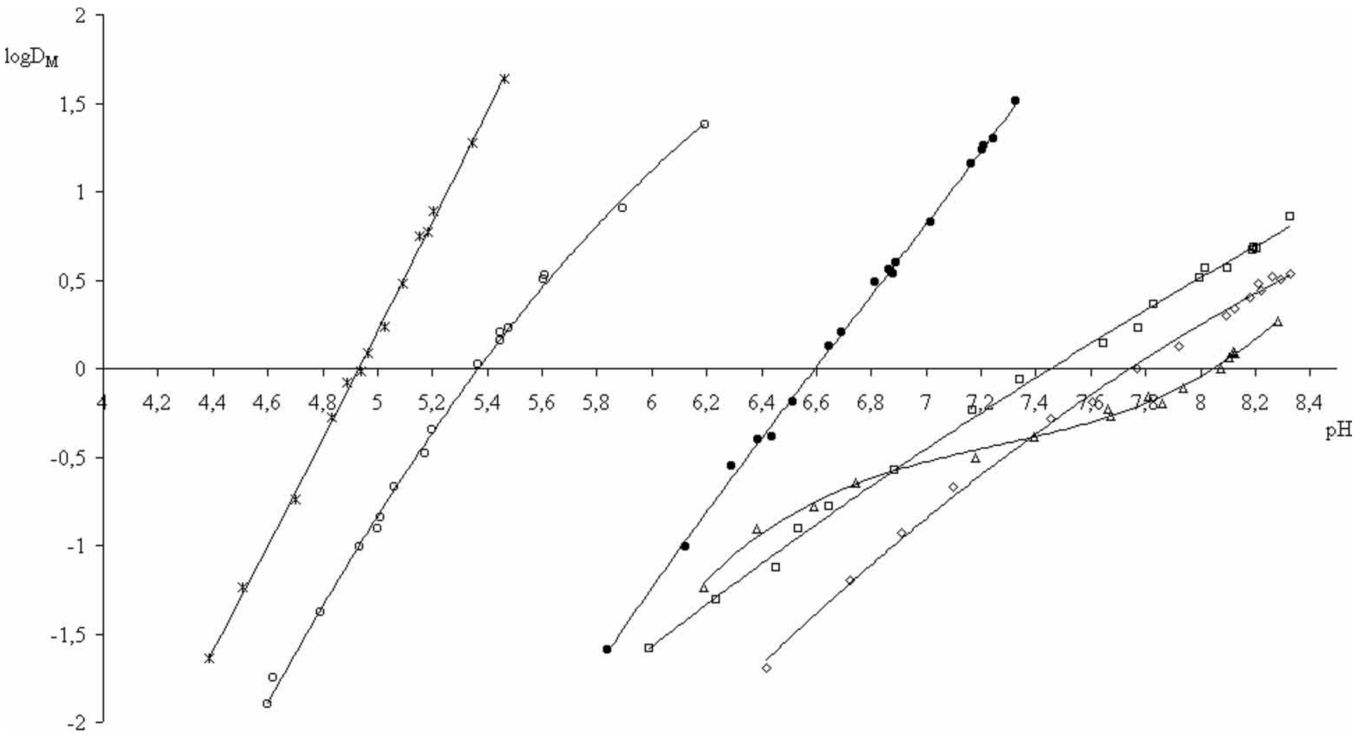

Figure 1. Influence of pH on the extraction of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles into toluene (at 25°C and constant ionic strength of the aqueous solution I = 0.5(KNO$_3$)) ● -1-pentyl-4(5)-methylimidazole; □ 1-hexyl-4(5)-methylimidazole; △ 1-heptyl-4(5)-methylimidazole; ◇ 1-octyl-4(5)-methylimidazole; ○-1-nonyl-4(5)-methylimidazole; ∗1-decyl-4(5)-methylimidazole.

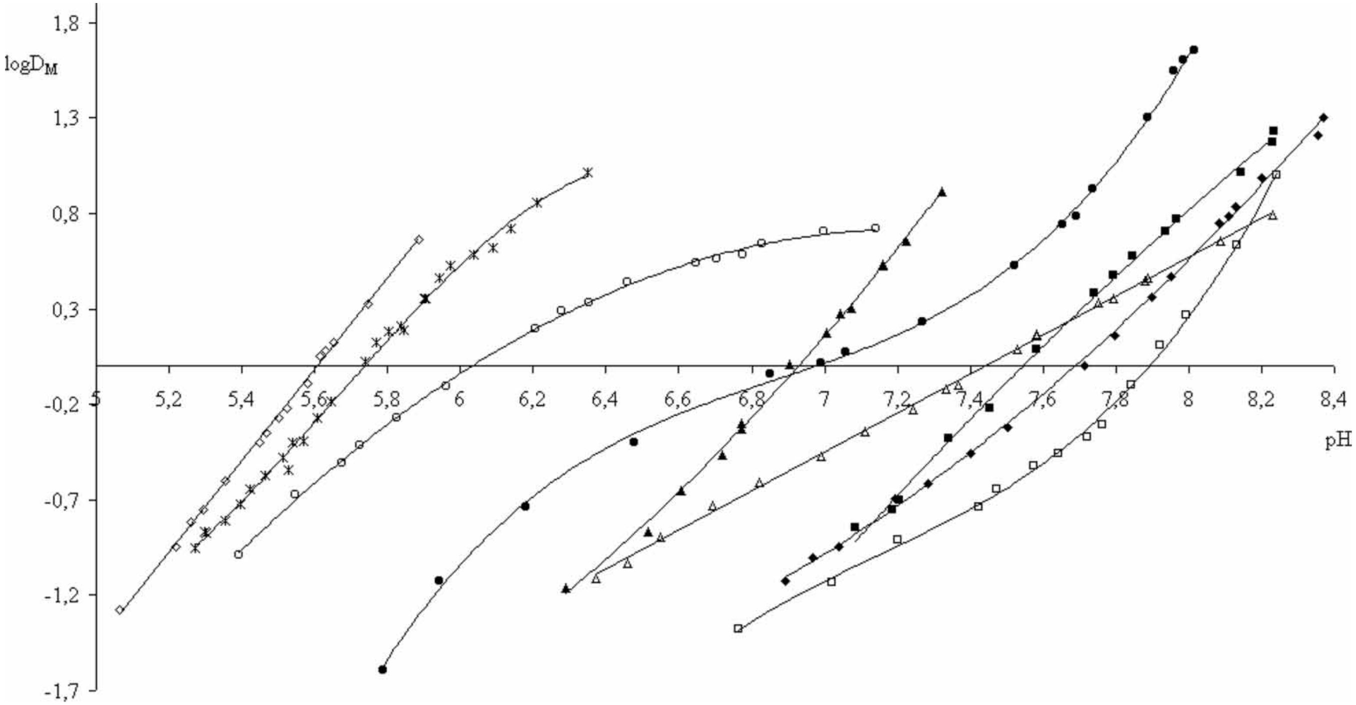

Figure 2. Influence of pH on the extraction of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles into trichlorometane (at 25°C and constant ionic strength of the aqueous solution I = 0.5(KNO$_3$)). ■-1-ethyl-4(5)-methylimidazole; ▲-1-propyl-4(5)-methylimidazole; ◆-1-butyl-4(5)-methylimidazole; ● -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-detyl-4(5)-methylimidazole.

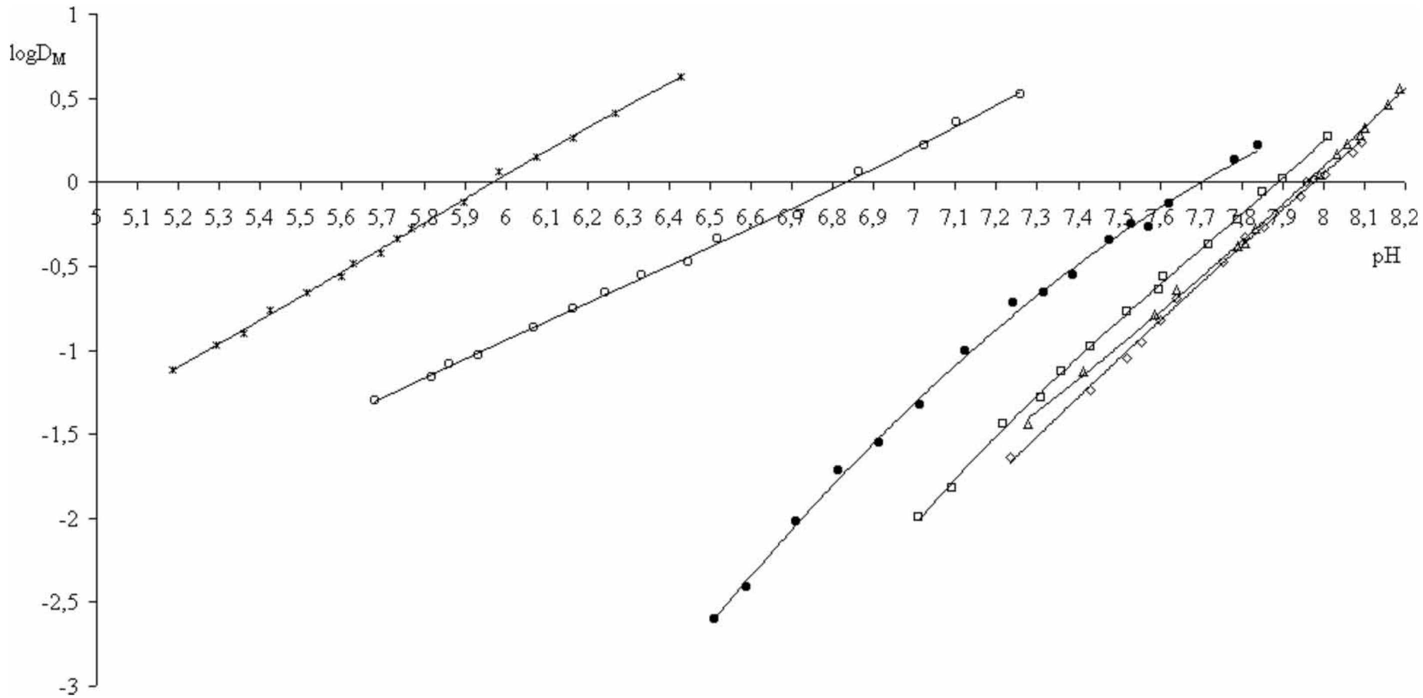

Figure 3. Influence of pH on the extraction of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles into 2-ethyl-1-hexanol (at 25°C and constant ionic strength of the aqueous solution I = 0.5(KNO_3)). ● -1-pentyl-4(5)-methylimidazole; □-1-hexyl-4(5)-methylimidazole; △-1-heptyl-4(5)-methylimidazole; ◇-1-octyl-4(5)-methylimidazole; ○-1-nonyl-4(5)-methylimidazole; ∗-1-decyl-4(5)-methylimidazole.

the case of the most sparingly soluble derivatives of imidazoles (i.e. 1-nonyl- and 1-decyl-4[5]-methylimidazoles) the angles of slopes of straight lines are definitely smaller than for readier soluble 1,3-diazoles. So, one can presume that species extracted into the organic phase contain a smaller number of molecules of 1,3-diazole bounded to the co-ordination sphere of central ion. The Co(II) complexes with derivatives containing up to four carbon atoms in the 1-alkyl chain are not extracted into 2-ethyl-1-hexanol, similarly as by using toluene (Fig. 1).

In the same conditions, the extraction of Zn(II) complexes with 1-alkyl-4(5)-methylimidazoles in toluene and 2-ethyl-1-hexanol (26) were previously executed. Table 1 summarizes our results of pH values of extraction curves ($\log D_M = f(pH)$) at the $\log D_M = 0$ level ($pH_{1/2}$) with those for Zn(II). As seen, the values of $pH_{1/2}$ for all the systems with Zn(II) are lower as compared to those with Co(II).

Figures 4 and 5 represent the influence of the bulkiness of the 1-alkyl group on subtracting $pH_{1/2Zn}$-$pH_{1/2Co}$ ($\Delta pH_{1/2}$) for extraction with toluene and 2-ethyl-1-hexanol, respectively. The efficiency of separation Zn(II) from Co(II) by using toluene as a solvent (Fig. 4) increase with an increasing alkyl chain length attaining a maximum for 1-octyl-4(5)-methylimidazole, whereas for the long-chained derivatives (those with the nonyl and decyl substituents) definitely drops. For extraction with 2-ethyl-1-hexanol (Fig. 5), the relations between the $\Delta pH_{1/2}$ and the number of carbon atoms in the azole molecule are essentially similar as before. The most suitable selective extractant to the separation Zn(II) from Co(II) of the investigated imidazole bases is 1-octyl-4(5)-methylimidazole.

Table 1. The $pH_{1/2}$ values of extraction curves ($\log D_M = f(pH)$) of complexes Co(II) and Zn(II) with 1-alkyl-4(5)-methylimidazoles in aqueous solution ($I = 0.5$ KNO_3) at 25°C

Ligand	$pH_{1/2Zn(II)}$(26)	$pH_{1/2Co(II)}$	$pH_{1/2Zn} - pH_{1/2Co(II)}$	Solvent
1-Pentyl-4(5)-	6.50	6.60	0.10	Toluene
methylimidazole	6.43	7.70	1.27	2-Ethyl-1-hexanol
1-Hexyl-4(5)-	6.04	7.50	1.46	Toluene
methylimidazole	6.14	7.88	1.74	2-Ethyl-1-hexanol
1-Heptyl-4(5)-	5.85	8.06	2.21	Toluene
methylimidazole	6.68	7.95	1.27	2-Ethyl-1-hexanol
1-Octyl-4(5)-	5.22	7.75	2.53	Toluene
methylimidazole	5.39	7.98	2.59	2-Ethyl-1-hexanol
1-Nonyl-4(5)-	4.59	5.37	0.78	toluene
methylimidazole	5.32	6.83	1.51	2-Ethyl-1-hexanol
1-Decyl-4(5)-	4.44	4.93	0.49	Toluene
methylimidazole	5.24	5.98	0.74	2-Ethyl-1-hexanol

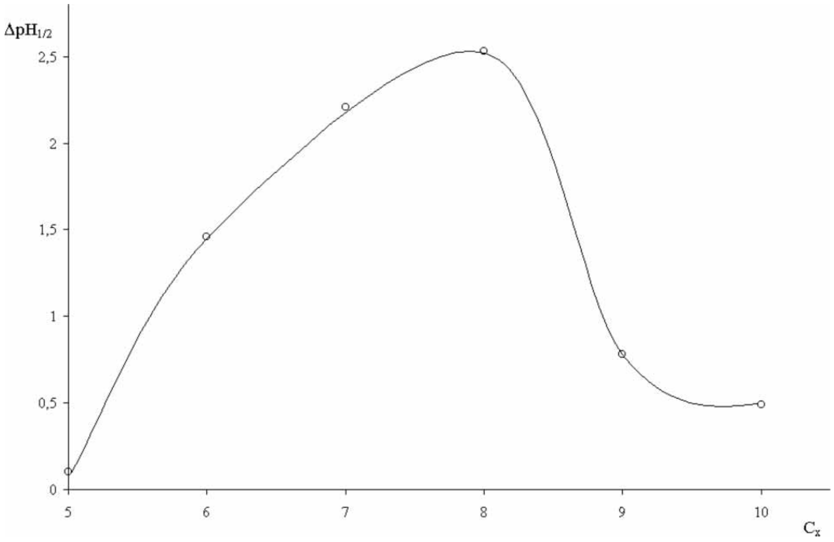

Figure 4. Influence of the hydrocarbon chain length in position “1” on the subtracting of $pH_{1/2}$ values of plots $\log D_M$ vs. pH between Zn(II) and Co(II) complexes with 1-alkyl-4(5)-methylimidazoles by using toluene as a solvent.

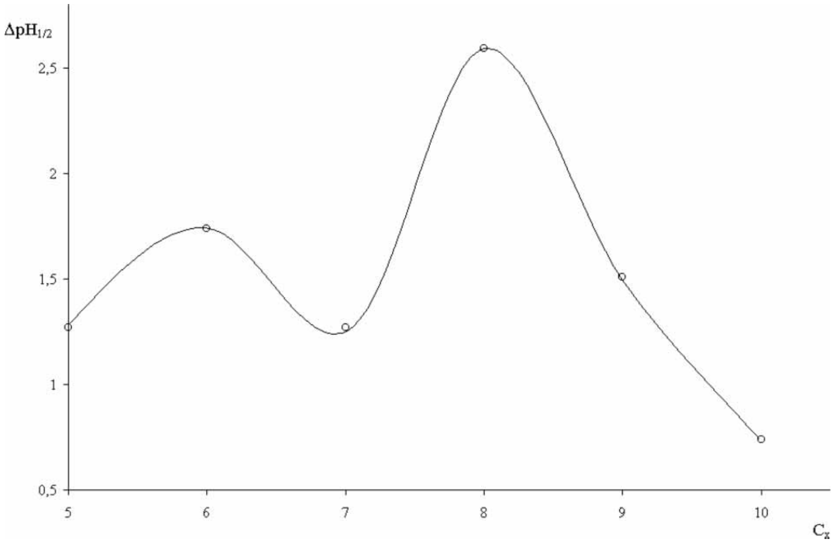

Figure 5. Influence of the hydrocarbon chain length in position “1” on the subtracting of $pH_{1/2}$ values of plots $\log D_M$ vs. pH between Zn(II) and Co(II) complexes with 1-alkyl-4(5)-methylimidazoles by using 2-ethyl-1-hexanol as a solvent.

The distribution ratios D_M, and consequently the shape, the location, as well as slopes in plots of $\log D_M$ *vs* pH of the systems studied depend on cumulative stability constants of the complexes being formed in aqueous solution (β_c) [Eq. (5)], the number and composition of extracted compounds into organic phase and their partition constants (P_c) Eq. (6) (31–33).

The alkylimidazoles form both octahedral and tetrahedral complexes with Co(II) in the aqueous solution. The complexation process is described by the equations (3) and (4).

$$^{\mathrm{okt}}[\mathrm{Co(H_2O)_6}]^{2+} + \mathrm{cL} \rightleftharpoons {}^{\mathrm{okt}}[\mathrm{Co(H_2O)_{6-c}L_c}]^{2+} + \mathrm{cH_2O} \tag{3}$$

$$^{\mathrm{okt}}[\mathrm{Co(H_2O)_6}]^{2+} + \mathrm{cL} \rightleftharpoons {}^{\mathrm{tet}}[\mathrm{Co(H_2O)_{4-c}L_c}]^{2+} + (\mathrm{c}+2)\mathrm{H_2O} \tag{4}$$

The stability constants of these complexes is defined as below:

$$\beta_c = \frac{^{\mathrm{okt}}[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}} + {}^{\mathrm{tet}}[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}}}{[\mathrm{Co^{2+}}]_{\mathrm{aq}} \cdot [\mathrm{L}]_{\mathrm{aq}}^{\mathrm{c}}} = \frac{[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}}}{[\mathrm{Co^{2+}}]_{\mathrm{aq}} \cdot [\mathrm{L}]_{\mathrm{aq}}^{\mathrm{c}}} \tag{5}$$

All the complexes pass into the organic phase together with two nitrate ions $\mathrm{NO_3^-}$. In the case of solvents, which have strong donor proprieties, the water molecules are substituted by the solvent molecules.

$$\mathrm{P_c} = \frac{^{\mathrm{okt}}[\mathrm{CoL_c^{2+}}]_{\mathrm{org}} + {}^{\mathrm{tet}}[\mathrm{CoL_c^{2+}}]_{\mathrm{org}}}{^{\mathrm{okt}}[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}} + {}^{\mathrm{tet}}[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}}} = \frac{[\mathrm{CoL_c^{2+}}]_{\mathrm{org}}}{[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}}} \tag{6}$$

where $[\mathrm{CoL_c^{2+}}]_{\mathrm{org}}$ and $[\mathrm{CoL_c^{2+}}]_{\mathrm{aq}}$ are molar concentrations of Co(II) complexes in the organic phase and aqueous solution, respectively.

The approximate stability constants β_c for each system were determined by the numerical method using Rydberg's equation 7 (32).

$$\frac{[\mathrm{L}]^{\mathrm{c}}}{\mathrm{D_M}} = \frac{\beta_1}{\mathrm{P_c} \cdot \beta_c}[L] + \frac{1}{\mathrm{P_c} \cdot \beta_c} \tag{7}$$

The molar concentration of the free ligand in the aqueous phase [L] was calculated from the pH measurements of the aqueous solution and from the dissociation constant of the protonated azole base [Eq. (8)]. The dissociation constants of the protonated ligand of the 1-alkyl-4(5)-methylimidazoles, summarized in Table 2, were taken from previous work (22).

$$[\mathrm{L}] = \frac{K_a \cdot [\mathrm{HL^+}]}{\mathrm{H_3O^+}} \tag{8}$$

where: K_a is the dissociation constant of the protonated ligand over a particular concentration range; $[\mathrm{HL^+}]$ is the concentration of protonated ligand, equal to the analytical concentration of nitric acid in the aqueous phase.

In this procedure, a relationship of $[\mathrm{L}]^{\mathrm{c}}/\mathrm{D_M}$ as a function [L] was tested numerically by searching of the straight line as described by equation

Table 2. The pKa values of alkylimidazoles and the stability constants log β_c of Co(II) complexes with 1-alkyl-4(5)-methylimidazoles in aqueous solution at 25°C and constant ionic strength ($I = 0.5$ KNO_3)

Ligand	pKa	log β_1	log β_2	log β_3	log β_4	Solvent
1,4(5)−Dimethylimidazole	7.75 (34)	1.40	2.25	2.60	4.78	
1-Ethyl-4(5)-methylimidazole	7.87 (22)	0.95	1.44	1.73		Trichlorometane
1-Propyl-4(5)-methylimidazole	7.88 (22)	2.51	2.74			Trichlorometane
1-Butyl-4(5)-methylimidazole	7.93 (22)	3.11	3.54	3.82	3.97	Trichlorometane
1-Pentyl-4(5)-methylimidazole	7.97 (22)	3.46	3.88	4.32		Toluene
		3.30	3.72	4.20		2-Ethyl-1-hexanol
		3.62	3.97			Trichloromethane
1-Hexyl-4(5)-methylimidazole	8.01 (22)	3.83	4.17			Toluene
		3.69	4.24	4.66	5.18	2-Ethyl-1-hexanol
		3.74	4.17	4.49	4.77	Trichloromethane
1-Heptyl-4(5)-methylimidazole	8.05 (22)	4.02	4.53			Toluene
		4.07	4.57	5.00	5.46	2-Ethyl-1-hexanol
		3.87	4.33			Trichloromethane
1-Octyl-4(5)-methylimidazole	8.1 (22)	4.43	4.76			Toluene
		4.25	4.76	5.11	5.63	2-Ethyl-1-hexanol
		4.07	4.60	4.85		Trichloromethane
1-Nonyl-4(5)-methylimidazole	8.11 (22)	4.60	4.97	5.56		Toluene
		4.42	4.94	5.42		2-Ethyl-1-hexanol
		4.11	4.69			Trichloromethane
1-Decyl-4(5)-methylimidazole	8.15 (22)	4.74	5.07	5.70	6.10	Toluene
		4.52	5.01	5.53		2-Ethyl-1-hexanol
		4.31	4.85	5.15		Trichloromethane

The given values of the constants β_c carry 10% tolerance.

$y = ax + b$ for the smallest c values starting from 1 up to 6. The stability constant of the first complex, β_1, formed in the aqueous phase was obtained by dividing coefficients *a* and *b* of the determined straight line. Then, using equation (9) and the method of curve fitting, precise β_c and P_c values were found. The results, verified in this way, are collected in Table 2 (stability constants) and Table 3 (partition constants).

$$D_M = \frac{\begin{array}{c} P_c \cdot \beta_c \cdot [L]^c + P_{c+1} \cdot \beta_{c+1} \cdot [L]^{c+1} \\ + P_{c+2} \cdot \beta_{c+2} \cdot [L]^{c+2} + \cdots + P_N \cdot \beta_N \cdot [L]^N \end{array}}{1 + \beta_1 \cdot [L] + \beta_2 \cdot [L]^2 + \cdots + \beta_N \cdot [L]^N} \qquad (9)$$

On the basis of the obtained values of β_c and P_c the simulations of experimental points were made by using equation (9). For example Fig. 6 presents the points on extraction curve ($\log D_M$ vs. pH), determined from the experimental part and from calculations. Their distribution on experimental line is fully satisfactory. The good agreement of the experimental with calculated points was obtained for all investigated extraction systems.

The stability constants presented in Table 2 are compatible with those obtained from potentiometric measurements carried out earlier for 1,4-dimethylimidazole (34). At all the complexation steps, the β_c constants increase with an increasing 1-alkyl chain length.

Figures 7–9 represent the influence of solvent on respective stability constants $\log \beta_1$, $\log \beta_2$ and $\log \beta_3$. At all the three complexation steps up to 1-hexyl-4(5)-methylimidazole the results for all solvent used are comparable. With the next homologous series of the 1-alkyl-4(5)-methylimidazoles, the smallest and fairly divergent values were obtained for trichloromethane.

Figure 10 shows stability constants of the Co(II) complexes with 1-alkylimidazoles (23) and 1-alkyl-4(5)-methylimidazoles averaged for all solvents used. The results for 4(5)-methyl derivatives, excepting the first complexation step, are distinctly lower as compared to those with derivatives carrying 1-alkyl group only. This phenomenon is due to the steric hindrance of the methyl substituent atoms at position "4" or "5" in imidazole ring, which prevent the penetration of the heterocyclic ligand into the coordination sphere of the central ion. Simultaneously, in the aqueous solution the octahedron $\leftrightarrows$ tetrahedron configuration, equilibrium displaces towards tetrahedral species, which are less stable as compared to those substituted at position "1" but more readily pass into the organic phase owing to smaller number of co-ordinated water molecules.

The next three Figures (11–13) present relationships between partition constants of the complexes, $\log P_c$, and the number of carbon atoms in the alkyl substituent in position "1" (C_x) of the investigated 1-alkyl-4(5)-methylimidazoles.

Figure 11 shows the relationship of the water–toluene system. All the partition constants for the first complexes [ML] are very low ($P_1 < 1$) and

Table 3. The partition constants $\log P_c$ of Co(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	$\log P_1$	$\log P_2$	$\log P_3$	$\log P_4$	Solvent
1-Ethyl-4(5)-methylimidazole	−1.70	1.85	2.15		Trichlorometane
1-Propyl-4(5)-methylimidazole	−1.40	1.86			Trichlorometane
1-Butyl-4(5)-methylimidazole	−1.22	0.60	2.18	2.88	Trichlorometane
1-Pentyl-4(5)-methylimidazole	−2.00	0.30	3.90		Toluene
	−2.70	0.11	1.59		2-Ethyl-1-hexanol
	−1.10	2.08			Trichloromethane
1-Hexyl-4(5)-methylimidazole	−1.70	1.88			Toluene
	−2.30	0.20	2.08	3.88	2-Ethyl-1-hexanol
	−1.00	0.85	2.48	3.98	Trichloromethane
1-Heptyl-4(5)-methylimidazole	−0.82	1.18			Toluene
	−2.00	0.28	2.20	3.70	2-Ethyl-1-hexanol
	−0.92	1.87			Trichloromethane
1-Octyl-4(5)-methylimidazole	−1.40	1.70			Toluene
	−1.92	0.30	2.30	3.78	2-Ethyl-1-hexanol
	−0.85	1.88	7.00		Trichloromethane
1-Nonyl-4(5)-methylimidazole	−1.22	3.85	7.36		Toluene
	−1.82	2.30	4.70		2-Ethyl-1-hexanol
	−0.82	3.26			Trichloromethane
1-Decyl-4(5)-methylimidazole	−1.10	4.48	7.96	18.90	Toluene
	−1.40	3.30	6.30		2-Ethyl-1-hexanol
	−0.75	2.30	7.52		Trichloromethane

The given values of the constants P_c carry 10% tolerance.

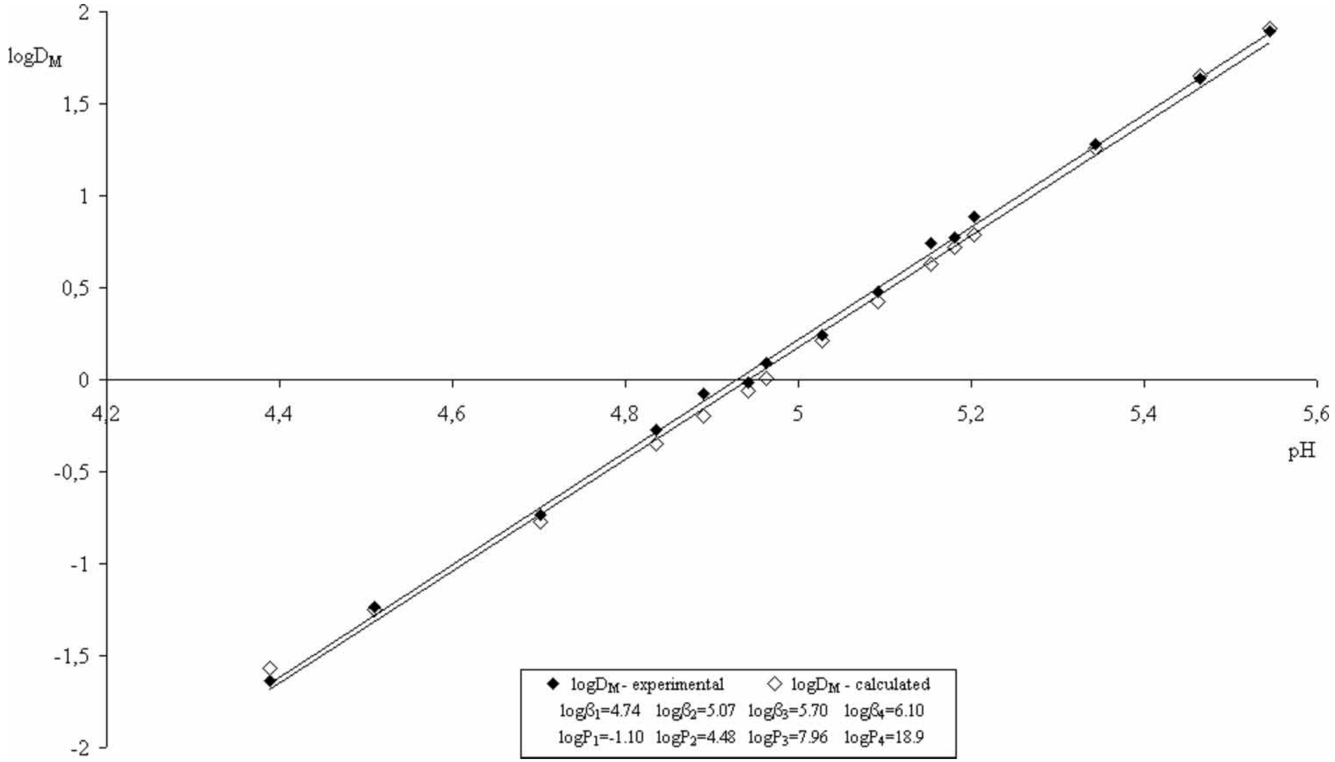

Figure 6. Comparison of obtained experimental and calculated values log D_M vs. pH on the extraction of Co(II) complexes with 1-decyl-4(5)-methylimidazole by using toluene as solvent.

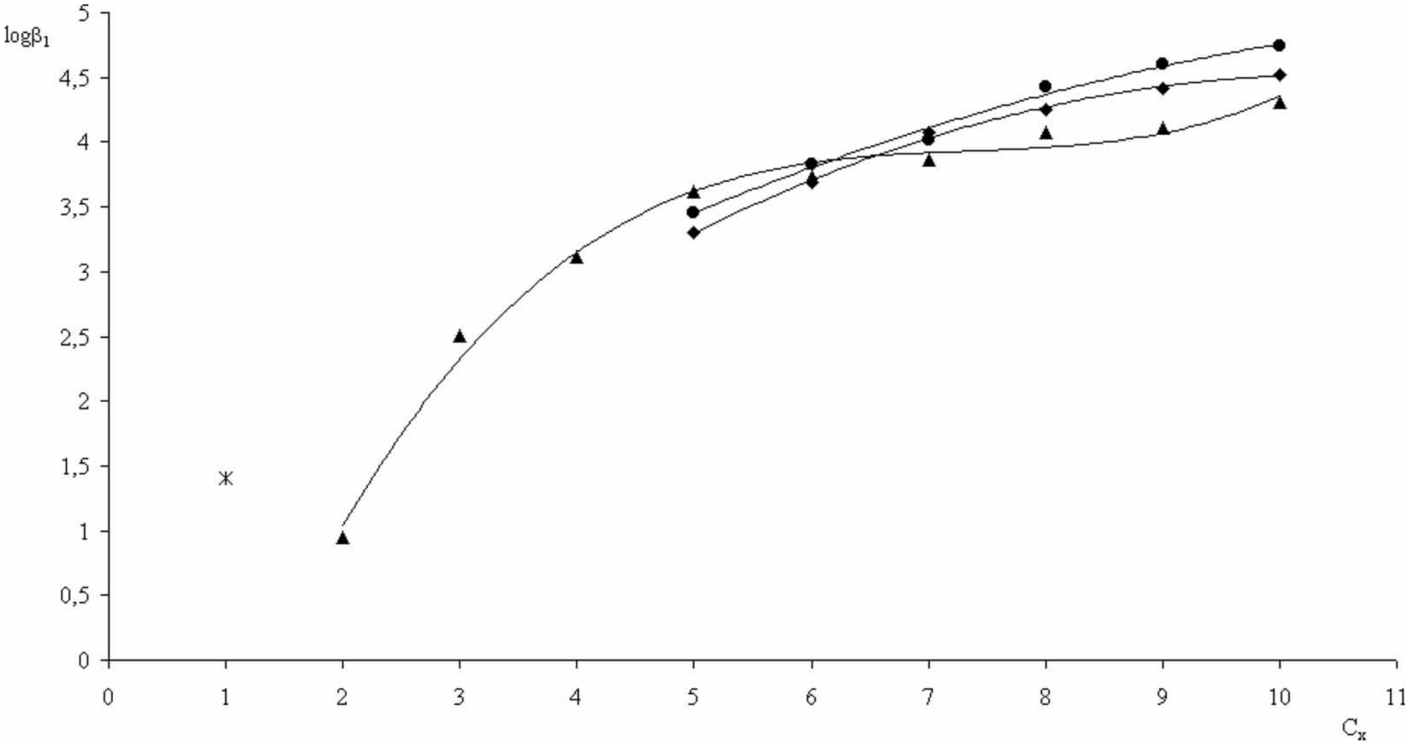

Figure 7. Influence of solvent on the stability constants β_1 of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles. ● -toluene; ▲-trichloromethane; ◆-2-ethyl-1-hexanol; ∗-potentiometric results.

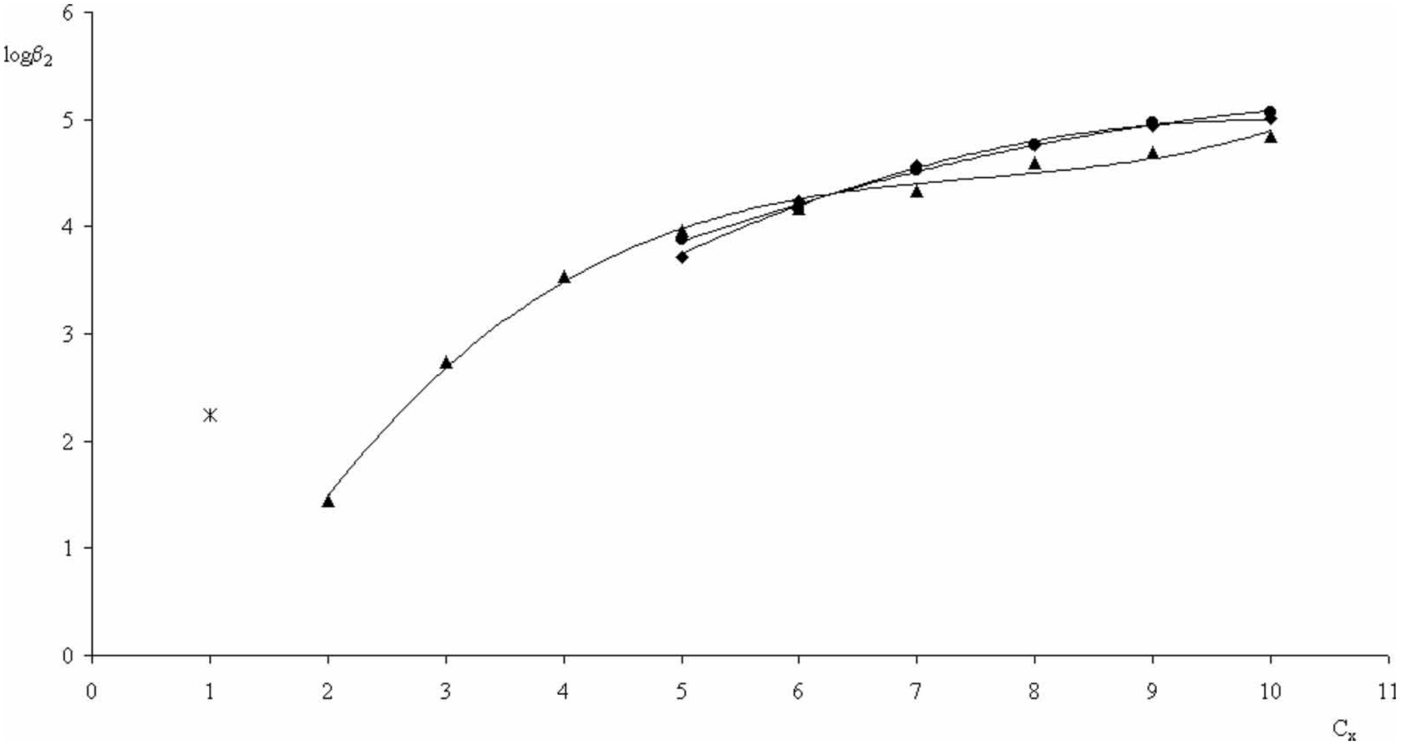

Figure 8. Influence of solvent on the stability constants β_2 of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles. ● -toluene; ▲-trichloromethane; ◆-2-ethyl-1-hexanol; ∗-potentiometric results.

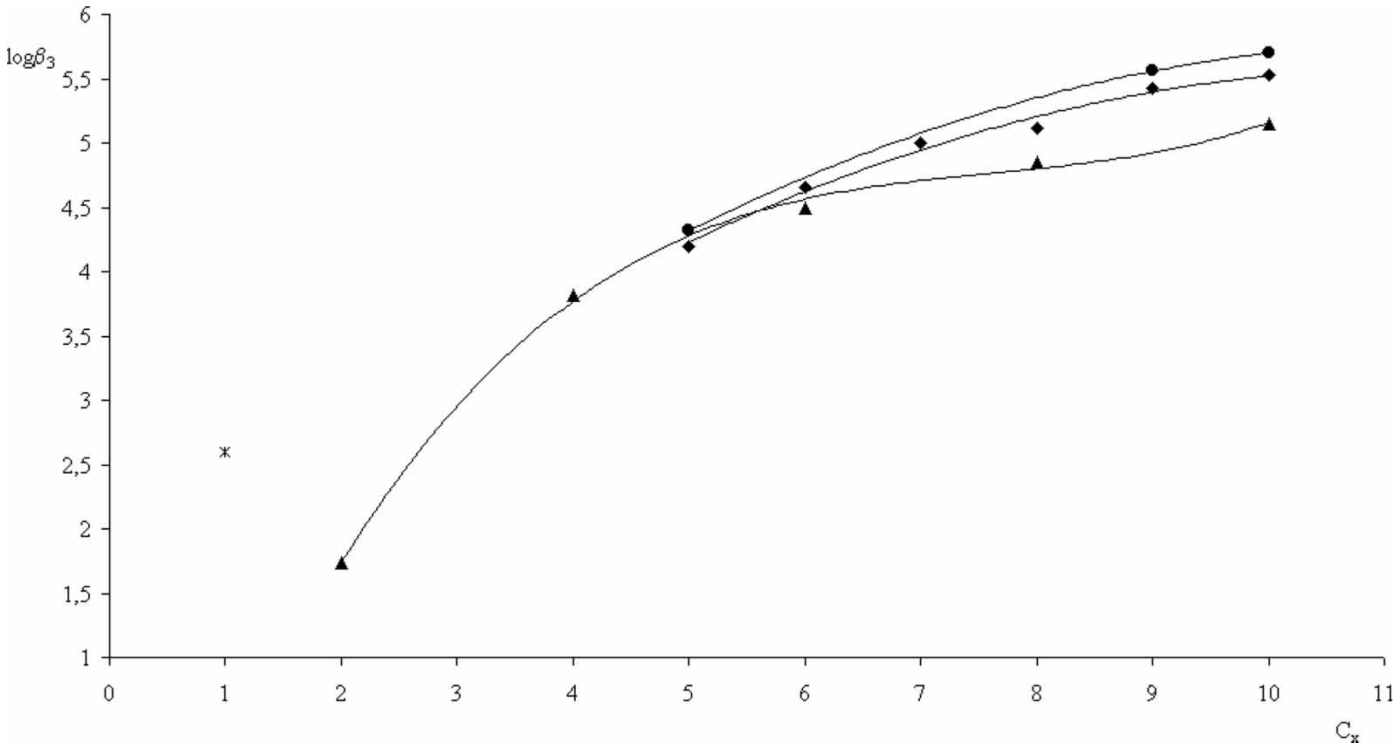

Figure 9. Influence of solvent on the stability constants β_3 of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles. ● -toluene; ▲-trichloromethane; ◆-2-ethyl-1-hexanol; ∗-potentiometric results.

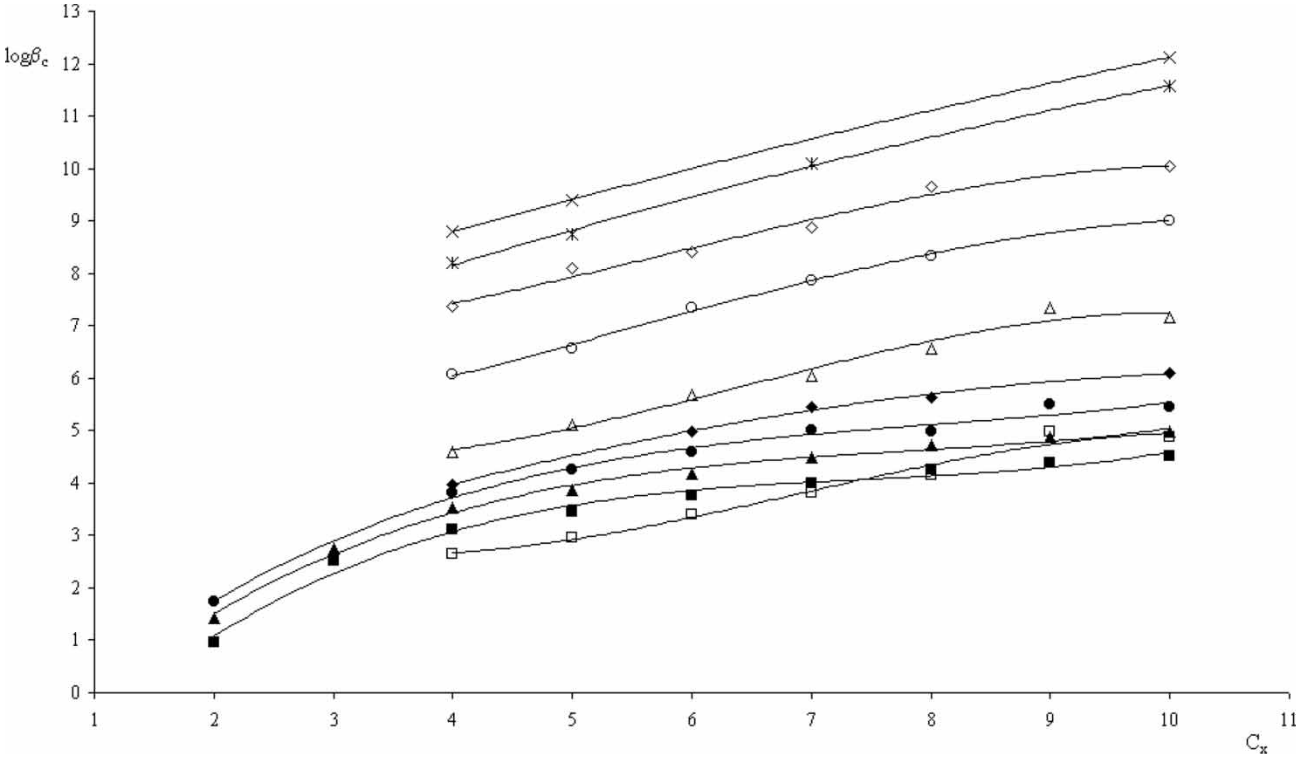

Figure 10. Plots of log β_c vs. the number of carbon atoms in 1-alkyl chain for the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles: ■-log β_1; ▲-log β_2; ● -log β_3; ◆-log β_4 and 1-alkylimidazoles; □-log β_1; △-log β_2; ○-log β_3 ◇-log β_4; ✱-log β_5 ×-log β_6.

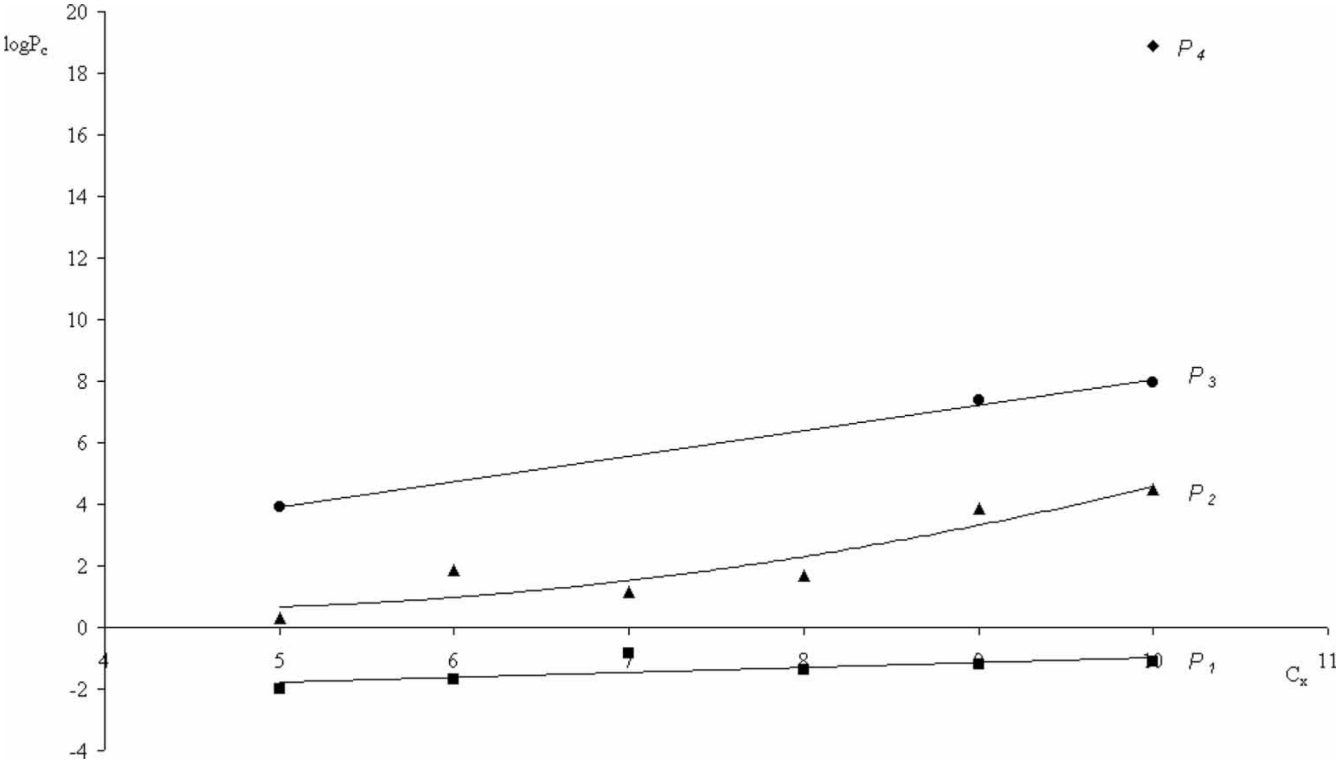

Figure 11. Influence of the alkyl chain length in the position "1" on the partition constant (log P$_c$) for Co(II) complexes with 1-alkyl-4(5)-methylimidazoles by using toluene as a solvent.

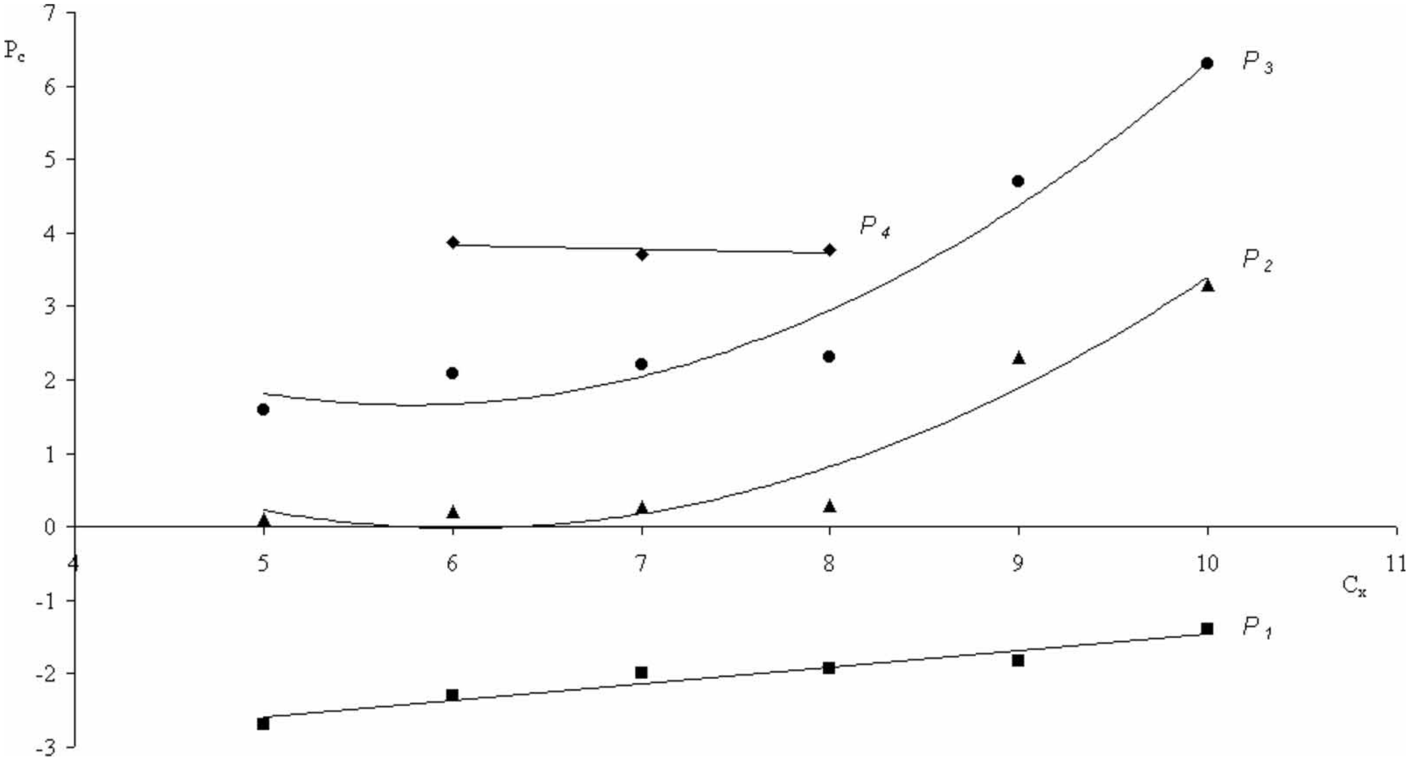

Figure 12. Influence of the alkyl chain length in the position "1" on the partition constant (log P_c) for Co(II) complexes with 1-alkyl-4(5)-methylimidazoles by using 2-ethyl-1-hexanol as a solvent.

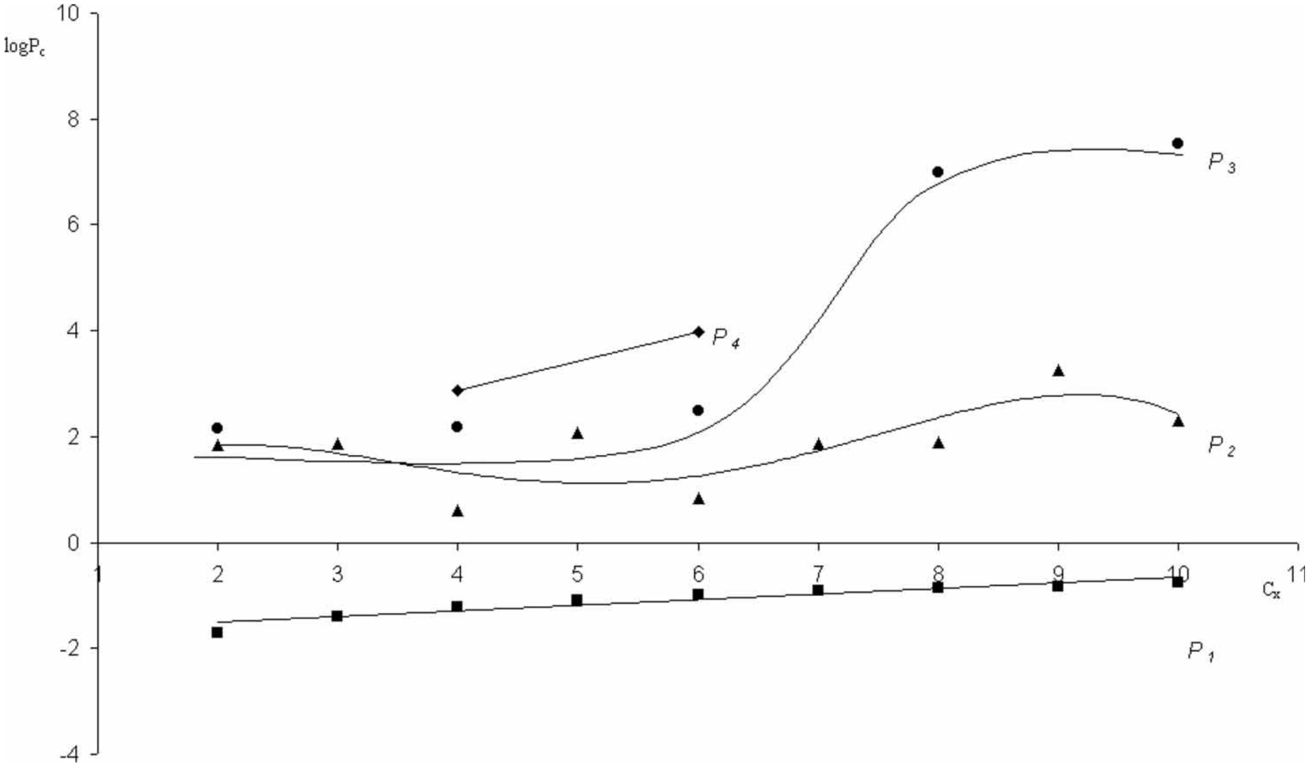

Figure 13. Influence of the alkyl chain length in the position “1” on the partition constant (log P_c) for Co(II) complexes with 1-alkyl-4(5)-methylimidazoles by using trichloromethane as a solvent.

increase only slightly with an increasing of the bulkiness of the 1-alkyl group. It can be assumed that co-ordination number of all extracted first complexes is most likely 6. The distinct increase is seen for higher co-ordinated complexes, [ML_2] (P_2), [ML_3] (P_3) and [ML_4] (P_4). In comparison with the first complexes their partition constants are several orders of magnitude higher. It means, that beginning from the second complexation step into the organic phase pass more readily extractable tetrahedral species.

In case of the complexes extracted with trichloromethane and 2-ethyl-1-hexanol (Figs.12,13), respectively, the relationships between $\log P_c$ and C_x are similar as before. At the first complexation steps the partition constants increase only slightly. On higher complexation steps form the tetraco-ordinate compounds of much higher partition constants. The special tendency to form the tetrahedral octahedral complexes together show the most hydrophobic derivatives: 1-octyl-, 1-nonyl-, and 1-decyl-4(5)-methylimidazole (exceptionally high values of P_c).

Figure 14 illustrates differences in the partition constants (P_c) of the Co(II) complexes with 1-alkylimidazole (23) and 1-alkyl-4(5)-metylimidazoles between aqueous solution and toluene. The partition constants of Co(II) complexes at first complexation step are practically the same for both types of the ligands. It means, that all complexes of the type [ML], independently of the structure of the alkylimidazoles have the same co-ordination number, most likely 6. On higher complexation steps ($1 < c \leq 4$), the steric hindrance by the methyl group in position "4" or "5" favors the formation of the tetrahedral complexes Co(II), thus resulting in an enhancement of partition constants as compared to those obtained for the 1-alkylimidazole complexes. These occurrences found the confirmation in UV-VIS spectra of the organic phase. All the solutions of investigated complexes with organic solvents were more or less violet colored.

Figures 15 and 16 present the absorption spectra of the organic phase after extraction of the Co(II) complexes with earlier reported 1-decylimidazole (23) and 1-decyl-4(5)-methylimidazole in toluene, respectively. The specters of the organic phase for 1-alkylimidazoles have strong maximum of octahedral complexes ($\lambda_{max} = 500\,nm$) and two weakly formed maxima in range of longer waves ($\lambda_{max} = 540$ and $585\,nm$) corresponding with tetrahedral compounds. In the case of Co(II) the octahedral band is due to the ${}^4T_{1\,g}(F) \rightarrow {}^4T_{1\,g}(P)$ electronic transition, while the tetrahedral band is due to the electronic transition ${}^4A_2(F) \rightarrow {}^4T_1(P)$. The specters of the organic phase for 1-alkyl-4(5)-methylimidazoles show a very high absorbancy in the wide range from 500 to 600 nm ($\lambda_{max} = 540$ and $570\,nm$). They are characterized as more weak absorption maximum ($\lambda_{max} = 490\,nm$). For both these types of imidazole derivatives pass into the organic phase in both octahedral and tetrahedral species. The intensity of tetrahedral bands in the 1-alkyl-4(5)-methylimidazoles is definitely higher than that of the 1-alkylimidazoles. It indicates that the steric hindrance facilitates the formation of tetrahedral species in aqueous

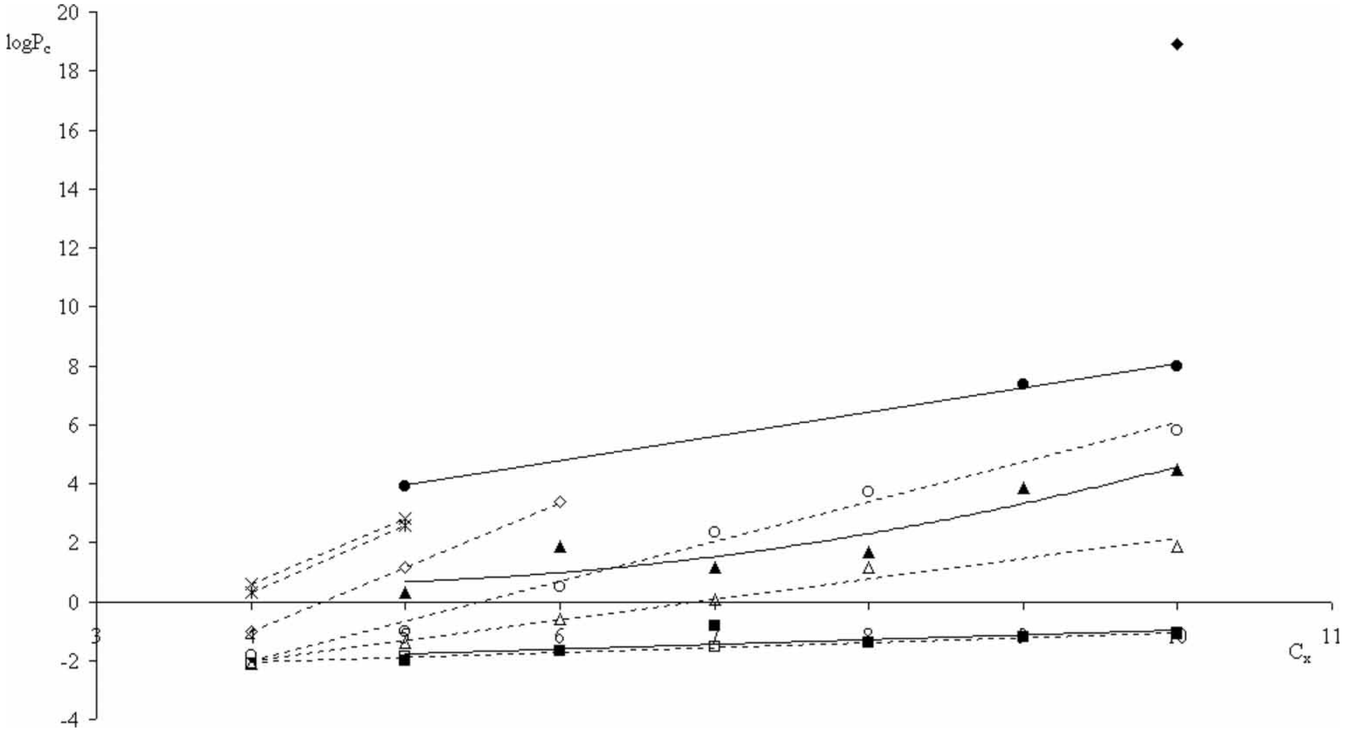

Figure 14. Influence of the alkyl chain length in the position "1" on the partition constants (log P_c) for Co(II) complexes with 1-alkyl-4(5)-methylimidazol: ■-logP_1; ▲-logP_2; ● -logP_3; ◆-logP_4 and 1-alkylimidazoles; □-logP_1; △-logP_2; ○-logP_3 ◇-logP_4; ∗-logP_5 × -logP_6 by using toluene as a solvent.

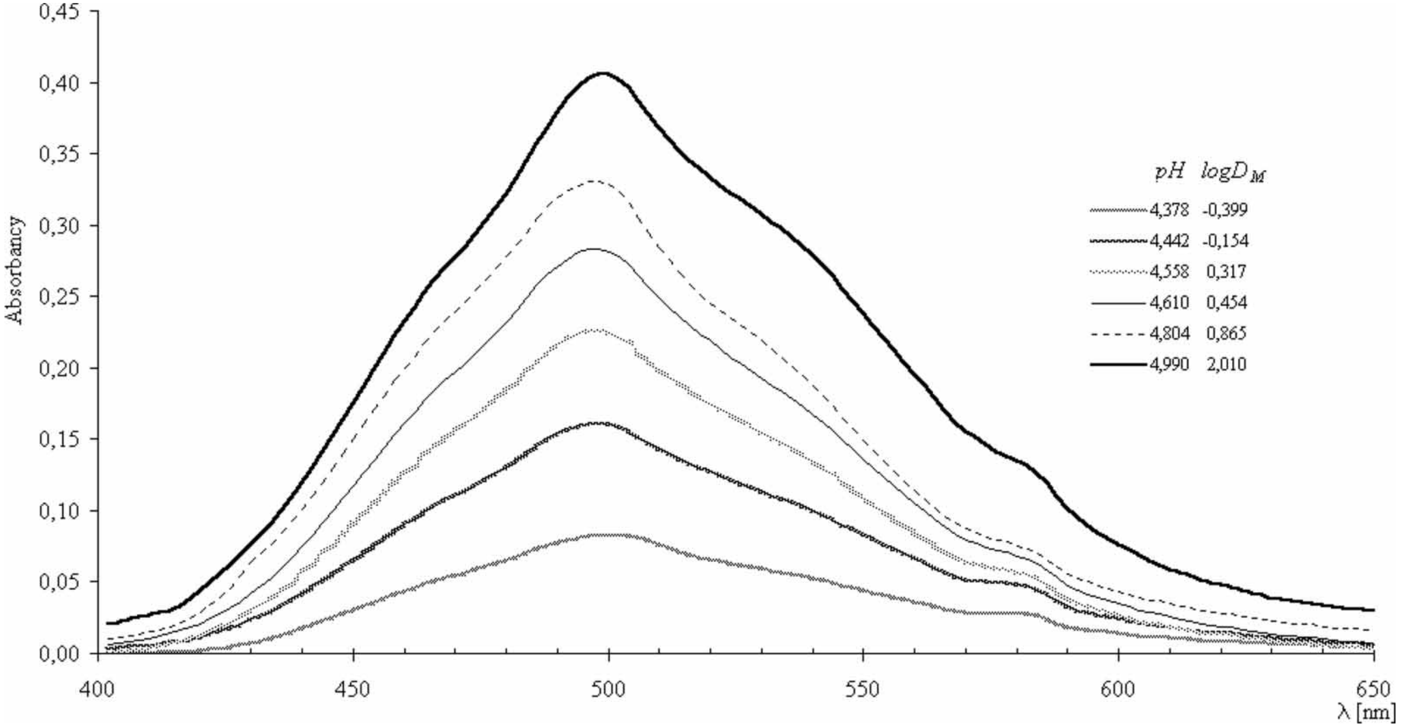

Figure 15. Absorption spectra of organic phase after extraction of the Co(II) complexes with 1-decylinidazole in toluene together with the corresponding pH's of the aqueous phase and logarithms of distribution ratio D_M.

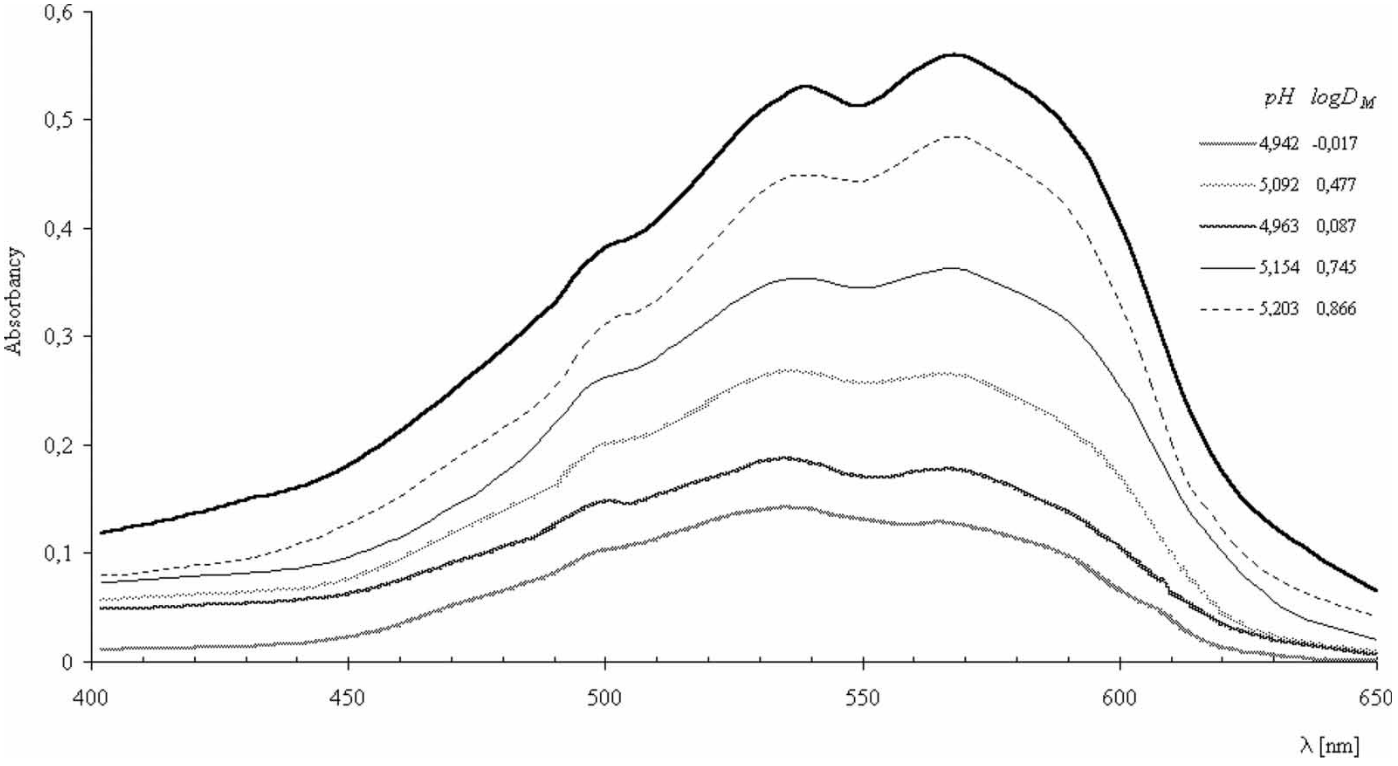

Figure 16. Absorption spectra of organic phase after extraction of the Co(II) complexes with 1-decyl-4(5)-methylimidazole in toluene together with the corresponding pH's of the aqueous phase and logarithms of distribution ratio D_M.

solution and consequently enlarges the probability of passing the successive complexes into the organic phase.

CONCLUSIONS

1. The two most hydrophobic derivatives (1-nonylo-, 1-decylo-4(5)-methylimidazole) can be used in practice in the extraction of Co(II) ions from aqueous solutions, as they warrant high value of distribution ratios D_M at low concentrations of the bases.
2. The Co(II) complexes with 1-alkyl-4(5)-methylimidazole are more reluctantly extractable into the organic phase than those with analogous systems with Zn(II) (26). Out of the azoles investigated by us, the most suitable selective extractant of Zn(II) from Co(II) ions is 1-octyl-4(5)-methylimidazole.
3. The stability constants of the Co(II) complexes with 1-alkyl-4(5)-methylimidazoles, at all complexation steps, slightly increase with an increasing 1-alkyl chain length. The steric effect due by the methyl group in position "4" or "5" considerably reduces the values of stability constants of the Co(II) complexes as compared to those with derivatives substituted at position "1" only. This effect does not permit the locating for more than four molecules of the imidazole ligand into the co-ordination sphere of the central ion.
4. The partition constants of the extracted complexes in the system organic solvent/water increase with 1-alkyl chain length. Additionally, the steric hindrance due to the presence of 4(5)-methyl substituent displaces the configurational equilibrium towards more readily extractable tetrahedral species, thus resulting in an increase in the partition constants as compared to those obtained for the 1-alkylimidazole complexes.

REFERENCES

1. Cote, G. (2000) Hydrometallurgy of Strategic Metals. *Solvent Extr. Ion Exc.*, 18 (4): 703–727.
2. Sarangi, K., Reddy, B.R., and Das, R.P. (1999) Extraction Studies of Cobalt(II) and Nickel(II) from Hydrochloric Acid Solutions using Na-Cyanex 272: Separation of Co(II)/Ni(II) by the Sodium Salts of D2EHPA, PC-88A and Cyanex 272 and their Mixtures. *Hydrometallurgy*, 52: 253–265.
3. Zhang, P. and Inoue, K. (1996) Extraction an Selective Stripping of Molybdenum(VI) and Vanadium(IV) from Sulfuric Acid Solution Containing Aluminium(II), Cobalt(II), Nickel(II) and Iron(II) by LIX 63 in Exxsol D80. *Hydrometallurgy*, 41: 45–53.
4. Przeszlakowski, S. and Wydra, H. (1982) Extraction of Nickel, Cobalt and Other Metals [Cu, Zn, Fe(III)] with a Commercial b-Diketone Extractant. *Hydrometallurgy*, 8: 49–64.

5. Wassink, B., Dreisinger, D., and Howard, J. (2000) Solvent Extraction Separation of Zinc and Cadmium From Nickel and Cobalt Using Aliquat 336, a Strong Base Anion Exchanger, in the Chloride and Thiocyanate Forms. *Hydrometallurgy*, 57: 235–252.
6. Zhou, T. and Pesic, B. (1997) A Pyridyne-based Chelating Solvent Extraction System for Selective Extraction of Nickel and Cobalt. *Hydrometallurgy*, 46: 37–53.
7. Cupery, M.E. N-Imidazole Compounds and Their Complex Metal Derivatives. U.S. Patent. 3,843,667, October 22.
8. Schaekers, J.M.; Dupreez, J.G.H. (2004) Solvent Extraction Mixture Comprising Substituted Imidazole or Benzimidazole for Purification of Groups of Base Metals. U.S. Patent. 2004/0208808 A1, October 21.
9. Lenarcik, B., Barszcz, B., and Kulig, J. (1977) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solution. Part XI. A Study on Complex Formation Between N-Butylimidazole and Co(II), Ni(II), Cu(II) and Zn(II). *Roczniki Chem.*, 51: 1315–1322.
10. Lenarcik, B. and Barszcz, B. (1977) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solution. Part XIV. Complex Formation Between N-Methylimidazole and Co(II), Ni(II), Cu(II) and Zn(II). *Roczniki Chem.*, 51: 1849–1855.
11. Lenarcik, B. and Barszcz, B. (1979) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solution. Part XIX. Structural Effects During Complexation of Co(II), Ni(II), Cu(II) and Zn(II) with 1-Ethylimidazole and 1-Propylimidazole. *Polish J. Chem.*, 53: 963–971.
12. Lenarcik, B. and Kurdziel, K. (1981) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solutions. Part XXIII. Effect of the Position of Methyl Substituents on the Complex-Forming Capacity of Imidazoles. *Polish J. Chem.*, 55: 737–745.
13. Lenarcik, B., Czopek, R., and Kurdziel, K. (1991) Research for Optimum Conditions for Extraction of Metal Complexes by Alkylimidazoles. Part IV. The Influence of Steric Effect on the Extraction of the Complexes of 2-Ethylimidazole with Co(II), Ni(II), Zn(II) and Cd(II). *Polish J. Chem.*, 65: 837–843.
14. Lenarcik, B., Głowacki, J., and Rzepka, M. (1979) Search for Optimum Conditions of Extraction of Transition Metal Complexes with Alkylimidazoles. I. Extraction of the Co(II), Ni(II) and Zn(II) Complexes of 1-Methylimidazole and of the Co(II) and Zn(II) Complexes of 2-Methylimidazole. *Sep. Sci. Technol.*, 14: 37–54.
15. Lenarcik, B., Adach, A., and Radzymińska-Lenarcik, E. (1999) The Influence of Steric Effect and Alkyl Chain Length on Extraction of the Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 1-alkyl-2-Methylimidazoles. *Polish J. Chem.*, 73: 1273–1281.
16. Lenarcik, B., Kulig, J., and Laidler, P. (1974) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solution. Part II. 2-Methylimidazole Complexes of Co(II), Cu(II) and Zn(II). *Roczniki Chem.*, 48: 1151–1157.
17. Lenarcik, B. and Obłąk, K. (1977) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solutions. Part XV. A Study on Complex Formation between 4-Methylimidazole and Co(II), Ni(II) and Zn(II). *Roczniki Chem.*, 51: 2079–2087.
18. Lenarcik, B. and Barszcz, B. (1980) Stability and Structure of Transition-Metal Complexes of Azoles in Aqueous Solution. Part 21. A Comparison of the Complex-Forming Capacity of 1,2-Dimethylimidazole with that of Other 1,3-Diazoles. *J. Chem. Soc. Dalton Trans*, 24–28.

19. Lenarcik, B., Kurdziel, K., and Czopek, R. (1991) Stability and Structure of Transition Metal Complexes of Azoles in Aqueous Solution. Part XXVIII. The Steric Effect in the Complex Formation of 2-n-Propylimidazole and 2-Isopropylimidazole. *Polish J. Chem.*, 65: 815–820.
20. Lenarcik, B., Kurdziel, K., and Czopek, R. (1991) Stability and Structure of Transition Metal Complexes with Azoles in Aqueous Solution. Part XXIX. The Influence of the Size and Structure of the Alkyl Group on the Formation of 2-Alkylimidazole Complexes. *Polish J. Chem.*, 65: 1235–1241.
21. Sigel, H., Saha, A., Saha, N., Carloni, P., Kapinos, L.E., and Griesser, R. (2000) Evaluation of Intramolecular Equilibria in Complexes Formed Between Substituted Imidazole Ligands and Nickel(II), Copper(II) or Zinc(II). *J. Inorg. Biochem.*, 78: 129–137.
22. Lenarcik, B. and Ojczenasz, P. (2002) The Influence of the Size and Position of the Alkyl Groups in Alkylimidazole Molecules on Their Acid ± Base Properties. *J. Heterocyclic Chem.*, 39: 287–290.
23. Lenarcik, B. and Ojczenasz, P. (2004) Investigation of the Stability of Co(II) Complexes with a Homologous Series of 1-alkylimidazoles in Aqueous Solutions by Using a Partition Method with Several Solvents. *Sep. Sci. Technol.*, 39: 199–226.
24. Lenarcik, B. and Kierzkowska, A. (2004) The Influence of Alkyl Chain Length and on Stability Constants of Zn(II) Complexes with 1-alkylimidazoles in Aqueous Solutions and Their Partition Between Aqueous Phase an Organic Solvent. *Solvent Extr. Ion Exch.*, 22 (4): 449–471.
25. Lenarcik, B. and Rauckyte, T. (2004) The Influence of Alkyl Chain Length on Extraction Equilibria of Ni(II) Complexes with 1-alkylimidazoles in Aqueous Solution/Organic Solvent System. *Sep. Sci. Technol.*, 14: 3353–3372.
26. Lenarcik, B. and Kierzkowska, A. (2004) The Influence of Alkyl Chain Length and Steric Effect on Stability Constants and Extractability of Zn(II) Complexes with 1-alkyl-4-methylimidazoles. *Sep. Sci. Technol.*, 39 (15): 3485–3508.
27. Marcus, Y. (1992) Principles of solubility and solutions. In *Principles and Practices of Solvent Extraction*; Rydberg, J., Musikas, C. and Choppin, G.R. (eds.), Marcel Dekker, Inc: New York; Vol. 1, 22–24.
28. Pernak, J., Krysinski, J., and Skrzypczak, A. (1987) Bakterizide Wirkung von Iminiumverbindungen. *A. Tenside, Surfactants Deter*; 24 (5): 276–279.
29. Scharlo, G. (1962) *Metody Analityceskoj Chimiji*. Kolicestvennyj Analiz Nieorganiceskich Sojedinenij: Chimija, Moskva; Vol. 27999,910; (a) Kolarov, N.Z.. *Anal. Chem.*, 1941, 22: 399.
30. Braibanti, A., Ostacoli, G., Paoletti, P., Pettit, L.D., and Sammartano, S. (1987) Potentiometric Apparatus and Technique for the pH-metric Measurement of Metal-Complex Equilibrium Constants. *Pure Applied Chem.*, 59: 1721–1728.
31. Alegret, S. (1988) *Developments in Solvent Extraction*; Horwood Ltd: Chichester, England.
32. Rydberg, J. (1950) On the Complex Formation Between Thorium and Acetylacetone. *Acta Chem.Scand.*, 4: 1503–1522.
33. Rossotti, F.J.C., Rossotti, H. (1961) *The Determination of Stability Constants*; McGraw-Hill: New York.
34. Lenarcik, B., Kurdziel, K., Czopek, R. (1986) Search for Optimum Conditions of Extraction of Metal Complexes with Alkylimidazoles. III. Structure-Extractability Relationship for 1,4-Dimethylimidazole Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II). *Solvent Extr. Ion Exch.*, 4: 165–182.