Separation Science and Technology
Publication details, including instructions for authors and subscription information:
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To cite this Article Lenarcik, Beniamin and Ojczenasz, Piotr(2005) 'Investigation of the Stability of Co(II) Complexes with a Homologous Series of 1-Alkylimidazoles in Aqueous Solution by Using a Partition Method with Several Solvents', Separation Science and Technology, 39: 1, 199 — 226

To link to this Article: DOI: 10.1081/SS-120027409

URL: http://dx.doi.org/10.1081/SS-120027409

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 1, pp. 199–226, 2004

Investigation of the Stability of Co(II) Complexes with a Homologous Series of 1-Alkylimidazoles in Aqueous Solution by Using a Partition Method with Several Solvents

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ABSTRACT

Extraction of Co(II) complexes of nine 1-alkylimidazoles (with $R = C_4H_9$ to $C_{14}H_{29}$) from aqueous solution ($I = 0.5$, KNO_3, at 25°C) with toluene, *o*-xylene, dichloromethane, and 2-ethyl-1-hexanol was studied. Stability constants of the complexes formed in the aqueous phase and partition constants of the extracted species were determined. Both the stability constants (β_n) and partition constants (P_n) of the complexes increase with increasing length of the alkyl chain. The more soluble

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DOI: 10.1081/SS-120027409
0149-6395 (Print); 1520-5754 (Online)

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1-alkylimidazoles was found to form tetrahedral and octahedral complexes at the third and fourth step of complexation. The appearance of the octahedron ⇆ tetrahedron configuration equilibrium was found to depend on the nature of the solvent used.

Key Words: Co(II) complexes; Stability; 1-Alkylimidazoles; Hydrophobicity; Tetrahedral complexes.

INTRODUCTION

To solvent extraction of metals from aqueous solutions, those ligands (extractants) are used that are sparingly soluble in water. These are, for instance, alpha-hydroxy oximes,[1,2] 8-hydroxyquinolines,[1] substituted pyridines,[3] and the like. To strengthen their hydrophobic properties, long-chain aliphatic substituents are attached to the aromatic ring. In this connection, a problem arises as to how the alkyl chain length influences parameters characterizing the extraction process.

To describe the quantity of these systems, knowledge of dissociation constants of protonated extractant, K_a, stability constants of complexes with extracted metal ion, β_n, and partition constants of complex compounds passing into the organic phase, P_n, are needed.[4,5]

Alkylimidazoles are a class of organic bases, which owing to their relatively strong complexation capacity[6–9] and limited solubility in water, constitute potential extractants likely to find application in solvent extraction of transition metal ions.[10] However, stability constants of complexes for all types of the alkylimidazoles with Co(II), Ni(II), Cu(II), and Zn(II) have been determined only for ligands containing no more than four carbon atoms in one or more alkyl substituents of the 1,3-diazole ring.[11–19]

Recently, dissociation constants of the protonated forms HL^+ for four different of homologous series of the alkylimidazoles containing up to 12 carbon atoms in the hydrocarbon group were reported.[20] Knowledge of basicities of these compounds paves the way to investigation of complexation capacity of a particular homologous series of the alkylimidazoles.

The purpose of this work was to investigate the influence of the alkyl chain length on the stability, structure of the coordination sphere, and extraction capacity of the Co(II) complexes with the 1-alkylimidazoles. Co(II) ion was purposely chosen for our investigations because it forms colorful complexes, which facilitates observation of the extraction process. However, the choice of this ion can imply additional phenomena, because Co(II) with some derivatives of imidazoles form octahedral complexes and also tetrahedral complexes.[11–19] This phenomena can be increased values of stability constants of complexes and their partition constants.

The objects of our investigations were the Co(II) complexes with nine 1-alkylimidazoles with the following *n*-substituents: butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, and tetradecyl.

The bases are sparingly soluble in water, therefore, a partition method in the liquid–liquid system was used.[3–5] Toluene, *o*-xylene, dichloromethane, and 2-ethyl-1-hexanol were used as water-immiscible solvents. This study was a continuation of our earlier works, which concerned of complex-forming properties of the first four alkyl derivatives of homologous series studied by the potentiometric method.[6–9,11–19]

EXPERIMENTAL

The 1-alkylimidazoles were synthesized at the Institute of Chemistry and Technology, Technical University, Poznań (Poland).[21] Purity and structure of these compounds was checked as described elsewhere.[20] The solution of Co(II) nitrate was prepared from recrystallized salt and determined by titration with EDTA and by using atomic absorption spectroscopy method. Potassium nitrate was determined gravimetrically as potassium sulphate. Nitric acid was standardized against anhydrous Na_2CO_3 or $Na_2B_4O_7 \cdot 10H_2O$. Organic solvents toluene, *o*-xylene, dichloromethane, and 2-ethyl-1-hexanol were purified by distillation.

Potentiometric measurements were run on PHM-250 pH meter (Radiometer, Copenhagen) equipped with combination electrode (glass-calomel) GK C2401-8 (Radiometer, Copenhagen). The extraction of Co(II) complexes was additionally monitored spectrophotometrically by recording the spectra on UV-VIS 8452A spectrophotometer (Hewlett Packard, USA). The low concentrations of cobalt in aqueous solution were measured on spectrometer of atomic absorption AAS BUCK Scientific 210VGP.

The measurements were run at 25°C at a fixed ionic strength ($I = 0.5$) maintained in the aqueous phase with KNO_3. Before extraction, the concentrations of the metal ions and nitric acid in the aqueous phase were constant (0.01 M and 0.02 M, respectively) and the ligand concentrations were varied. Six cm^3 of the aqueous phase were placed in a graduated test tube and an equal volume of an alkylimidazole solution in the organic solvent was added. The test tubes were then shaken for 1 to 2 h. After attaining the partition equilibrium, the difference in the phase volume was read out, the phases were separated. The pH of the aqueous phase was measured to determine the free azole concentration at equilibrium, as well as the metal ion concentration by titration with a standardized EDTA solution and by using atomic absorption spectroscopy method. With colored complexes, absorption spectra over the visible range were taken in organic phase.

The extraction process was characterized by inspecting the dependence between distribution ratio D_M and pH. The free ligand molar concentration in the water phase $[L]$ was calculated from the pH values using:

$$[L] = \frac{K_a \cdot [\mathrm{HL}^+]}{\mathrm{H_3O^+}} \tag{1}$$

where K_a—is the dissociation constant of the protonated ligand over a particular concentration range; and $[\mathrm{HL}^+]$—is the concentration of protonated ligand, equal to the analytical concentration of nitric acid in the aqueous phase. The dissociation constants of the protonated ligand of the 1-alkylimidazoles were taken from literature[20] and listed in the Table 1.

The distribution ratio (D_M) of Co(II) between the aqueous and organic phases was found from the measured concentrations and calculated from:

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

where $C_M{}^o$ and C_M denote analytical concentrations of the metal ion in the aqueous phase before and after reaching distribution equilibrium, respectively. The pooled D_M values and the corresponding sets of the independent variable, $[L]$, were then used for the determination of stability constants β_1 of Co(II) complexes with all studied 1-alkylimidazoles.

RESULTS AND DISCUSSION

Results of the extraction experiments are presented as plots of the logarithm of the distribution ratio of Co(II) as a function of pH of the aqueous phase, separately for toluene (Fig. 1), *o*-xylene (Fig. 2), dichloromethane (Fig. 3), and 2-ethyl-1-hexanol (Fig. 4). The plots differ in shape, location in the coordinate system, and slopes for different alkyl derivatives of imidazole. Some of the plots are straight lines, while others are curvilinear. In all of the systems studied, the distribution ratio of central ion, D_M, increases with increasing values of pH of the aqueous phase.

Figure 1 shows distribution curves of the Co(II) complexes with 1-alkylimidazoles for toluene as the solvent. The curves for level $\log D_M = 0$ are widely separated in range from pH ≈ 4.5 up to 7.5. With the exception of 1-octylimidazole, slopes of the curves are similar. In the case of partition of Co(II) complexes with 1-octylimidazole, the $\log D_M$ vs. pH curve has the

Table 1. Stability constants $\log \beta_n$ and partition constants $\log P_n$ of Co(II) complexes with 1-alkylimidazoles in aqueous solution at 25°C and constant ionic strength $I = 0.5$ (KNO_3).

Ligand	Solvent	pK_a[20]	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6
1-MethylIm	[7]	7.19	2.40	4.40	5.85	6.95		
1-PropylIm	[8]	7.23	2.38	4.20	5.44	6.90	7.88	8.40
	[6]		2.44	4.75	6.00	6.54		
1-ButylIm	Toluene	7.21	2.84 ± 0.30	4.80 ± 0.50	6.40 ± 0.60	7.54 ± 0.75	8.48 ± 0.90	8.60 ± 0.85
	Dichloromethane		2.60 ± 0.25	4.70 ± 0.50	6.27 ± 0.60	7.36 ± 0.75	7.95 ± 0.80	
	2-Ethyl-1-hexanol		2.48 ± 0.25	4.29 ± 0.45	5.52 ± 0.55	7.20 ± 0.70	8.17 ± 0.80	8.98 ± 0.90
1-PentylIm	Toluene		3.00 ± 0.30	5.10 ± 0.50	6.60 ± 0.66	7.88 ± 0.80	8.68 ± 0.87	9.02 ± 0.90
	o-Xylene	7.27	2.97 ± 0.30	5.03 ± 0.50	6.56 ± 0.66	7.88 ± 0.80	8.80 ± 0.88	9.79 ± 0.97
	Dichloromethane		3.33 ± 0.35	5.60 ± 0.55	6.80 ± 0.70			
	2-Ethyl-1-hexanol		2.54 ± 0.25	4.72 ± 0.48	6.28 ± 0.63	8.50 ± 0.85		
1-HexylIm	Toluene		3.28 ± 0.30	5.67 ± 0.56	7.28 ± 0.75	8.26 ± 0.85		
	o-Xylene	7.30	3.78 ± 0.40	5.90 ± 0.60	7.45 ± 0.75	8.40 ± 0.84		
	Dichloromethane		4.05 ± 0.40	6.10 ± 0.60	7.67 ± 0.75			
	2-Ethyl-1-hexanol		2.50 ± 0.25	5.05 ± 0.50	6.96 ± 0.70	8.60 ± 0.86		
1-HeptylIm	Toluene		3.80 ± 0.40	6.14 ± 0.60	8.06 ± 0.80			
	o-Xylene	7.32	4.00 ± 0.40	6.25 ± 0.60	8.00 ± 0.80	8.84 ± 0.90		
	Dichloromethane		4.46 ± 0.45	6.31 ± 0.60	8.06 ± 0.80	8.70 ± 0.90		
	2-Ethyl-1-hexanol		3.00 ± 0.30	5.52 ± 0.55	7.35 ± 0.75	9.05 ± 0.90	10.09 ± 1.00	
1-OctylIm	Toluene		4.02 ± 0.40	6.80 ± 0.70	8.29 ± 0.83			
	o-Xylene	7.36	4.70 ± 0.50	6.80 ± 0.70	8.64 ± 0.86			
	Dichloromethane		4.89 ± 0.50	6.80 ± 0.70	8.54 ± 0.86			
	2-Ethyl-1-hexanol		2.98 ± 0.30	5.85 ± 0.60	7.89 ± 0.80	9.64 ± 0.96		

(*continued*)

Table 1. Continued.

Ligand	Solvent	pK_a[20]	log β_1	log β_2	log β_3	log β_4	log β_5	log β_6
1-NonylIm	Dichloromethane	7.43	4.98 ± 0.50	7.35 ± 0.75				
1-DecylIm	Toluene		4.82 ± 0.50	7.43 ± 0.75	9.20 ± 0.90			
	o-Xylene	7.39	5.53 ± 0.55	7.69 ± 0.77	9.35 ± 0.95			
	Dichloromethane		5.34 ± 0.55	7.38 ± 0.75	9.06 ± 0.90	9.85 ± 0.99		
	2-Ethyl-1-hexanol		3.79 ± 0.40	6.15 ± 0.60	8.44 ± 0.85	10.22 ± 1.00	11.57 ± 1.00	12.12 ± 1.00
1-DodecylIm	Toluene		5.20 ± 0.50	7.94 ± 0.80				
	o-Xylene	7.43	6.35 ± 0.60	8.27 ± 0.80				
	Dichloromethane		5.64 ± 0.60	7.85 ± 0.80	9.41 ± 0.95			
	2-Ethyl-1-hexanol		4.25 ± 0.40	6.65 ± 0.67	8.85 ± 0.90			
1-TetradecylIm	Toluene		5.60 ± 0.60	8.05 ± 0.80	9.89 ± 0.90			
	Dichloromethane	7.48	6.15 ± 0.60	8.45 ± 0.85				
	2-Ethyl-1-hexanol		4.69 ± 0.47	7.42 ± 0.75	10.07 ± 1.00	11.93 ± 1.00		

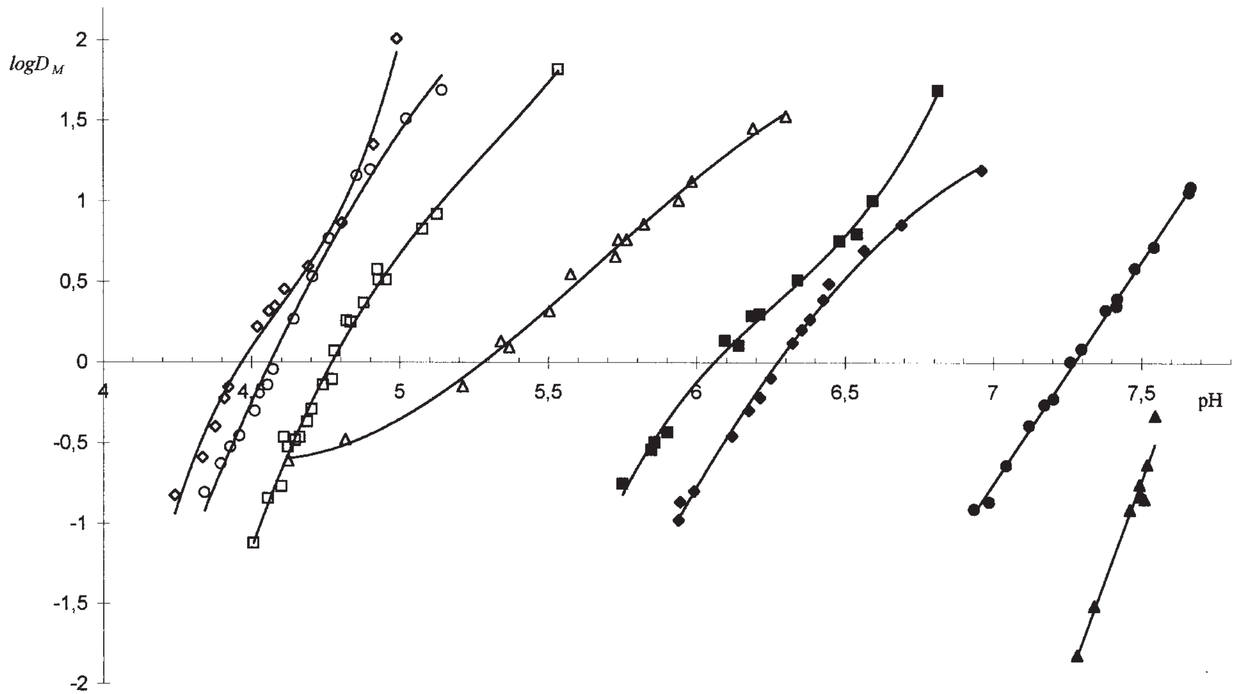

Figure 1. Influence of the alkyl chain length in the molecules of 1-alkylimidazoles on the process of extraction Co(II) by using toluene as a solvent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5(KNO_3)$]. ▲, 1-butylimidazole; ●, 1-pentylimidazole; ◆, 1-hexylimidazole; ■, 1-heptylimidazole; △, 1-octylimidazole; ◇, 1-decylimidazole; □, 1-dodecylimidazole; ○, 1-tetradecylimidazole.

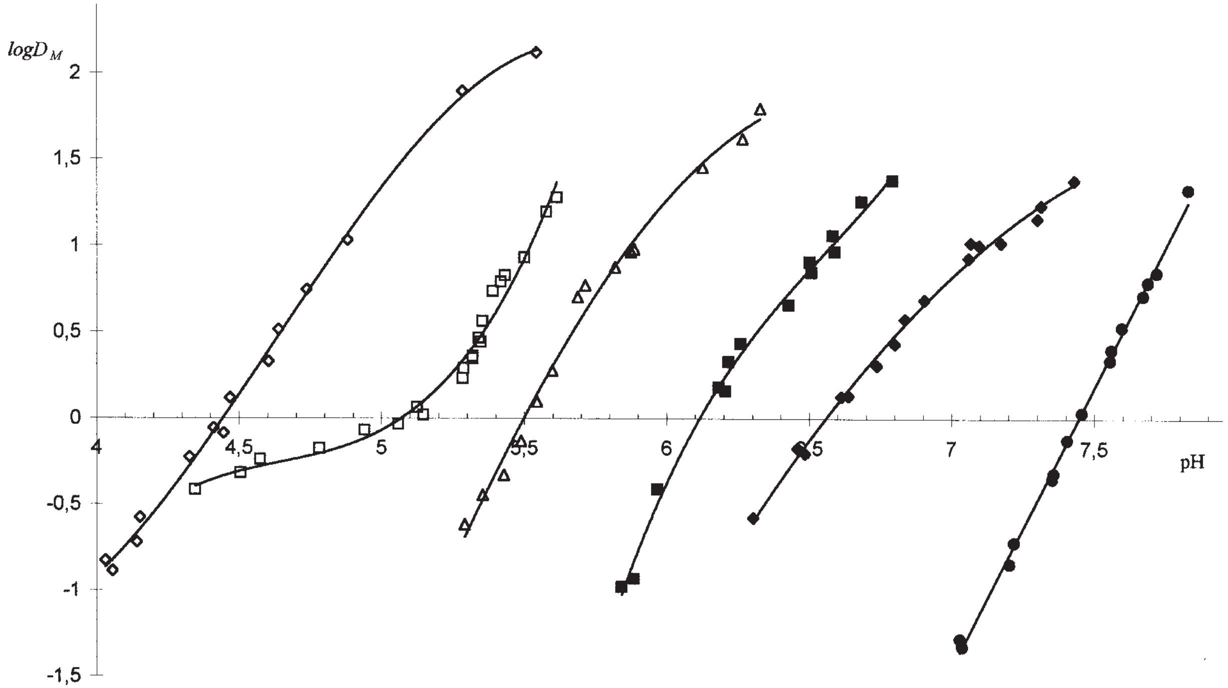

Figure 2. Influence of the alkyl chain length in the molecules of 1-alkylimidazoles on the process of extraction Co(II) by using *o*-xylene as a solvent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5(KNO_3)$]. ●, 1-pentylimidazole; ◆, 1-hexylimidazole; ■, 1-heptylimidazole; △, 1-octylimidazole; ◇, 1-decylimidazole; □, 1-dodecylimidazole.

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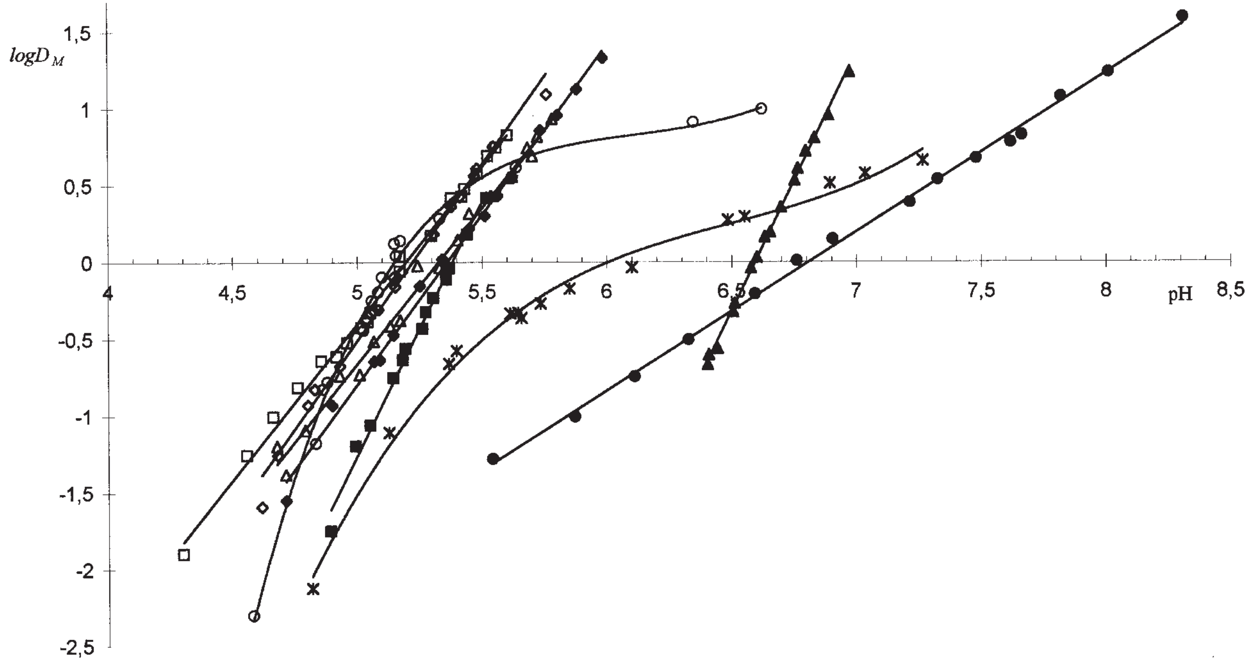

Figure 3. Influence of the alkyl chain length in the molecules of 1-alkylimidazoles on the process of extraction Co(II) by using dichloromethane as a solvent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5(KNO_3)$]. ▲, 1-butylimidazole; ●, 1-pentylimidazole; ◆, 1-hexyl-imidazole; ■, 1-heptylimidazole; △, 1-octylimidazole; ∗, 1-nonylimidazole; ◇, 1-decylimidazole; □, 1-dodecylimidazole; ○, 1- tetradecylimidazole.

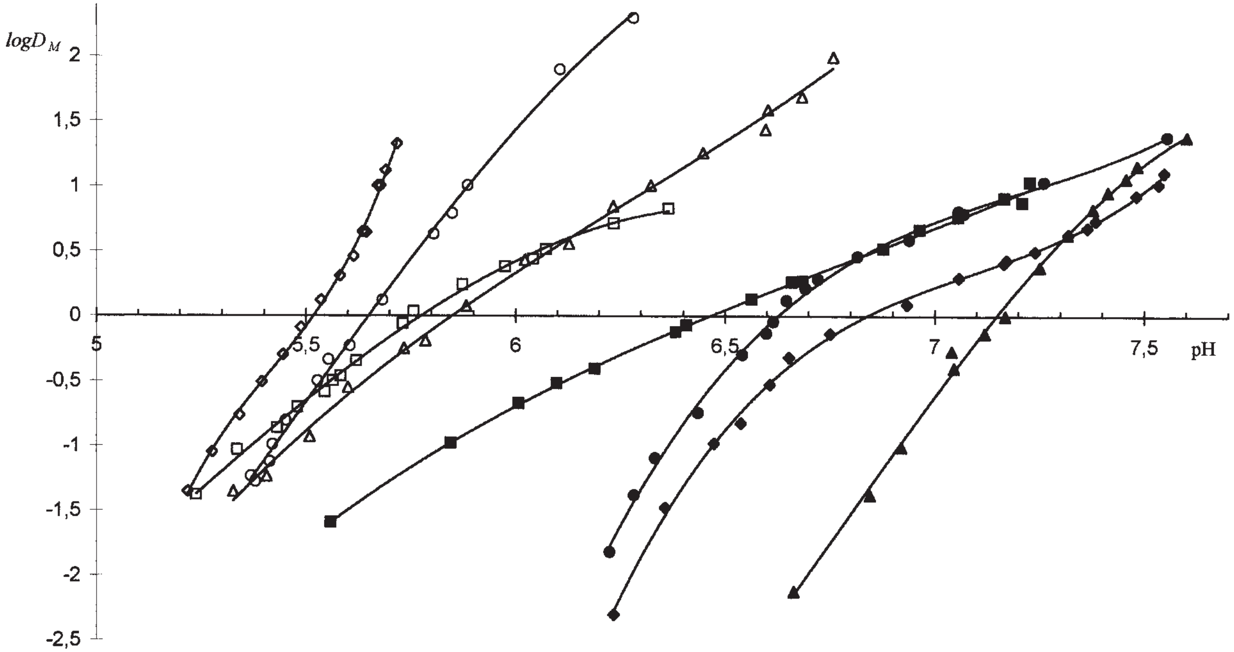

Figure 4. Influence of the alkyl chain length in the molecules of 1-alkylimidazoles on the process of extraction Co(II) by using 2-ethyl-1-hexanol as a solvent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5$ (KNO_3)]. ▲, 1-butylimidazole; ●, 1-pentylimidazole; ◆, 1-hexylimidazole; ■, 1-heptylimidazole; △, 1-octylimidazole; ◇, 1-decylimidazole; □, 1-dodecylimidazole; ○, 1-tetradecylimidazole.

smallest slope. Thus, it reveals that Co(II) complex passing into the organic phase contains the lowest number of the ligand molecules.

In Fig. 2, distribution of the Co(II) complexes between aqueous solution and *o*-xylene is presented. Extraction of the Co(II) complexes with 1-butylimidazole does not run by using this solvent. The $\log D_M$ vs. pH curves are generally shifted toward lower pH values with increasing hydrocarbon chain length. But the $\mathrm{pH}_{1/2}$ value (pH for $\log D_M = 0$) for the Co(II) complexes of 1-dodecylimidazole (5.17) is greater than that for the 1-decylimidazole compounds (4.43).

Extreme extraction curves on Fig. 3 (with dichloromethane) are separated from one another by ca. 1.6 pH units at $\log D_M = 0$. The values of $\mathrm{pH}_{1/2}$ decrease from 1-pentyl- to 1-tetradecylimidazole. Generally, the variations are consistent with increasing length of the alkyl substituent. There is a distinct differentiation in extractability of the Co(II) complexes between easily and sparingly water-soluble 1-alkylimidazoles formed in aqueous phase. The most suitable extractants for Co(II) with dichloromethane are 1-hexyl, 1-octyl, 1-decyl, 1-dodecyl, and 1-tetradecylimidazole. Extraction curves for the five first-named 1-alkylimidazoles constitute a common set of curves that are roughly parallel and distanced from one another by no more than 0.2 pH unit. Consequently, they extract a Co(II) complex that has the same number of connected molecules of 1,3-diazole.

The most effective extractants in this group are 1-decyl ($\mathrm{pH}_{1/2} = 5.22$), 1-dodecyl ($\mathrm{pH}_{1/2} = 5.20$), and 1-tetradecylimidazole ($\mathrm{pH}_{1/2} = 5.14$), while the worst extractant is 1-pentylimdazole ($\mathrm{pH}_{1/2} = 6.82$).

Most of the extraction curves of the Co(II) complexes in 2-ethyl-1-hexanol (see Fig. 4) have different slopes. The curves are also more widely separated from one another along the pH axis as those previously discussed. This indicates that the hydrophobic properties of the molecule play an important role in differentiating the extractability of the Co(II) complexes. The most distinct differences are seen in the shapes of the curves between sparingly soluble and easier water-soluble alkylimidazoles.

The plots of $\log D_M$ vs. pH for 1-tetradecyl, 1-dodecyl, 1-decyl, and 1-octylimidazole on one hand, and those of 1-heptyl, 1-hexyl, 1-pentyl, and 1-butylimidazole on the other hand, constitute two set of curves.

Within the first set, the curves are separated for $\log D_M = 0$ in a range from 5.5 up to 5.8 of pH values. They do not overlap. Within the second set, the curves for $\log D_M = 0$ are separated in a range from pH 6.41 up to 7.14.

Shapes of the curves of the 1-pentyl and 1-hexylimidazole complexes are similar and for $\log D_M = 0$ they are displaced from each other by 0.3 pH unit.

The location of extraction curves in plots of $\log D_M$ vs. pH has been known to be dependent on cumulative stability constants of the complexes being formed in aqueous solution (β_n), the number and composition of extracted compounds into organic phase, and their partition constants (P_n).[1,3–6]

$$D_M = \frac{P_n \cdot \beta_n \cdot [L]^n + P_{n+1} \cdot \beta_{n+1} \cdot [L]^{n+1} + P_{n+2} \cdot \beta_{n+2} \cdot [L]^{n+2} + \cdots + P_N \cdot \beta_N \cdot [L]^N}{1 + \beta_1 \cdot [L] + \beta_2 \cdot [L]^2 + \cdots + \beta_N \cdot [L]^N} \tag{3}$$

β_n-denotes cumulative concentrations stability constants of Co(II) complexes in the aqueous phase with investigated imidazoles.

$$\beta_n = \frac{[\mathrm{Co}L_n{}^{2+}]}{[\mathrm{Co}^{2+}] \cdot [L]^n} \tag{4}$$

All of the concentrations presented in Eqs. (3) and (4) refer to aqueous phase. The probability of passing of any of the successive complexes into the organic phase is determined by its partition constant, P_n, defined as:

$$P_n = \frac{[ML_n]_{(o)}}{[ML_n]_{(w)}} \tag{5}$$

where $[ML_n]_{(o)}$ and $[ML_n]_{(w)}$ denote molar concentrations of complex ML_n in the organic and aqueous phase, respectively. All complexes $[ML_n]_{(o)}$ pass into the organic phase together with two nitrate ions ($NO_3{}^-$).

To determine stability constants of the complexes, Rydberg's equation was first used:[4]

$$\frac{[L]^n}{D_M} = \frac{\beta_1}{P_n \cdot \beta_n}[L] + \frac{1}{P_n \cdot \beta_n} \tag{6}$$

where β_1 is the stability constant of the $[CoL]^{2+}$ complex and P_n is the distribution constant of $[ML_n]$ complex between the organic and aqueous phase.

Then, the shape of relationship of $[L]^n/D_M$ as a function of the free ligand concentration in the aqueous phase $[L]$ was tested. In this procedure, a straight line for the smallest n was searched for with successive n values starting from 1 up to 6. Parameter n denotes the number of alkylimidazole molecules bounded in the first complex of Co(II) extracted into the organic phase. Stability constant of the first complex, β_1, formed in the aqueous phase, $[\mathrm{CoL}(\mathrm{H_2O})_5]^{2+}$, was obtained by dividing parameters of the determined straight line (a/b).

Then, using Eq. (3), quantities β_n and P_n were refined by the curve-fitting procedure. The quantities of β_n verified in this way are collected in Table 1 together with the previously determined potentiometrically stability constants for the more readily water-soluble 1-alkylimidazoles.

Stability constants presented in Table 1 show perfect agreement with the potentiometric data. The stability constants obtained by the partition method are comparable for a particular complexation step independent of the kind of solvent used but only for three solvents, namely, toluene, *o*-xylene, and dichloromethane. The differences do not exceed experimental error. The values of stability constants β_n obtained for 2-ethyl-1-hexanol as solvent are lowest.

In this case, molecules of solvent by reason of more strong donor proprieties are bounded to the coordination sphere of Co(II). The models used by us for calculations of stability constants β_n and partition constants P_n proved too simplified. We are going to investigate this problem in the future.

Consequently, average stability constants of a particular complex, β_n, can be calculated from experiments where three different solvents (toluene, *o*-xylene, and dichloromethane) were used. Results of these calculations are presented in Fig. 5 as plots of log β_n vs. the number of carbon atoms in the alkyl chain. In Fig. 6, analogous plots for 2-ethyl-1-hexanol are presented. The plots correspond, respectively, to $\beta_1, \beta_2, \ldots, \beta_6$. Before the plots, results of the potentiometric measurements are also shown.

As is seen, the stability constants of the Co(II) complexes with 1-alkylimidazoles (with $R = CH_3$ up to $C_{14}H_{29}$) increase with increasing alkyl chain length. Data in Table 2 show that two to six complexes are extracted in each extraction system. The partition constants depend on the nature of solvent and size of the 1-alkylimidazole molecule.

Figures 7 through 10 present relationships between partition constants of the complexes, log P_n, and the number of carbon atoms in the alkyl chain (C_x) of the investigated 1,3-diazoles.

Figure 7 shows the relationship for the water–toluene system. All the partition constants of the extracted complexes increase with increasing alkyl chain length. Over the range C_4 to C_8, they increase linearly for all the partition constants. The slope of the log $P_n = f(C_x)$ function increases with increasing the number of the ligand molecules, (n) bounded in the complexes of Co(II). In the case of Co(II) complexes of the type [*ML*], the relationship is linear for all the alkylimidazoles studied and can be written as:

$$\log P_1 = 0.17 \cdot C_x - 2.72$$

All extracted complexes of the type [*ML*] have the similar coordination number, most likely 6, and are characterized by very low the values of partition constants $P_n < 1$ (see Table 2).

The composition of this species can be determined as follows: $[CoL(H_2O)_3(NO_3)_2]$. One cannot exclude that the part of extracted compounds contains in coordination sphere the solvent molecules. It is especially probable for dichloromethane and 2-ethyl-1-hexanol.

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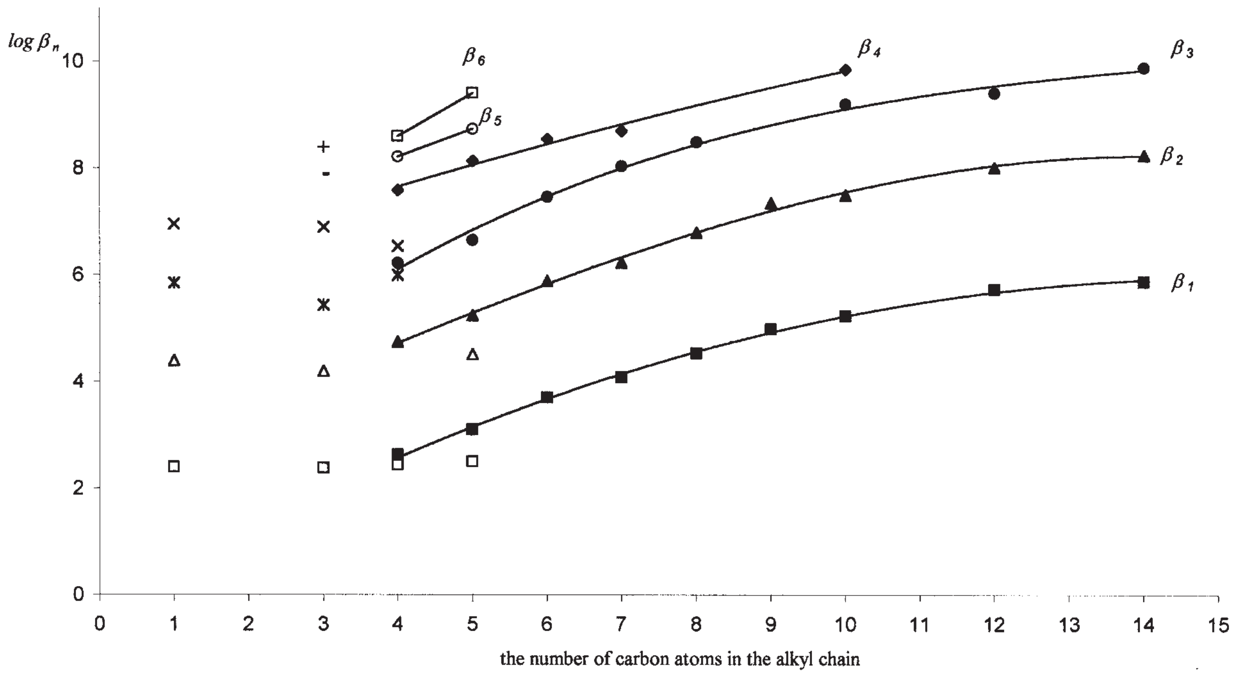

Figure 5. Influence of the alkyl chain length on the stability constants (log β_n) of Co(II) complexes with 1-alkylimidazoles (average from results for toluene, *o*-xylene, and dichloromethane); □, △, $*$, ×, —, + adequately β_1, β_2, β_3, …—results of potentiometric measurements.

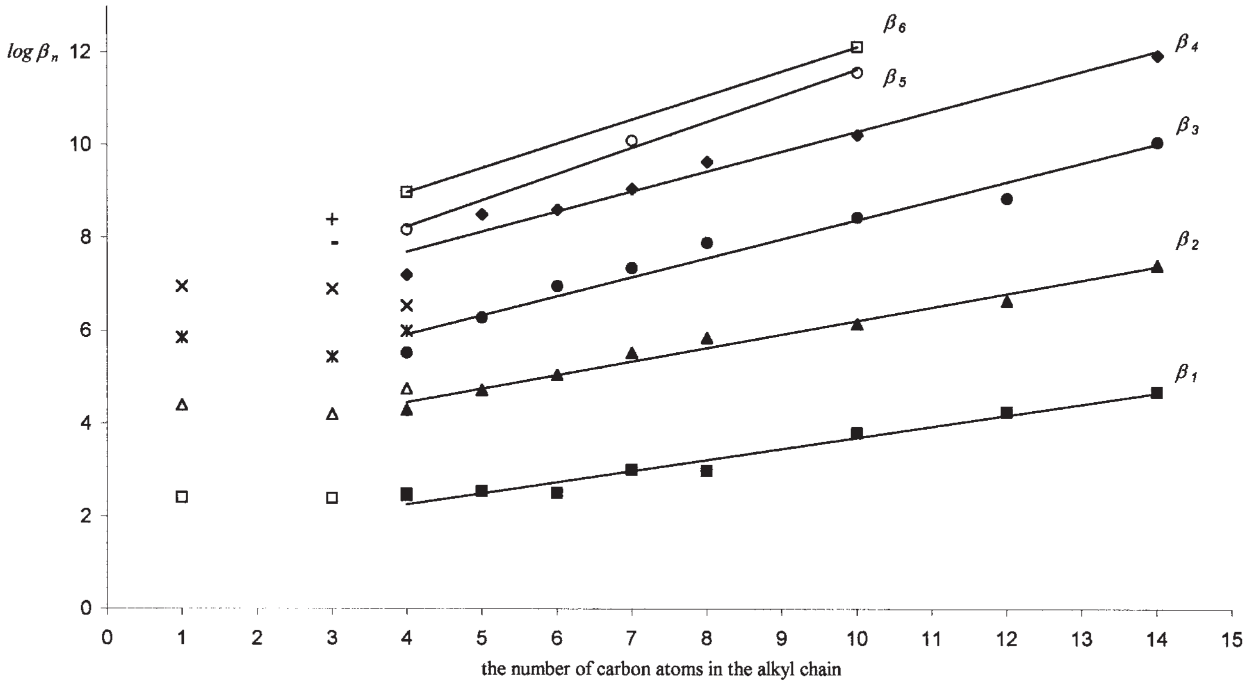

Figure 6. Influence of the alkyl chain length on the stability constants (log β_n) of Co(II) complexes with 1-alkylimidazoles by using 2-ethyl-1-hexanol as a solvent; □, △, ∗, ×, —, + adequatly β_1, β_2, β_3, . . .—results of potentiometric measurements.

Table 2. Partition constants log P_n of Co(II) complexes with 1-alkylimidazoles passing from water phase (constant ionic strength $I = 0.5$ (KNO_3)) into organic solvents at 25°C.

Ligand	Solvent	pK_a[20]	log P_1	log P_2	log P_3	log P_4	log P_5	log P_6
1-ButylIm	Toluene	7.21	−2.12	−2.12	−1.82	−1.00	0.30	0.58
	Dichloromethane		−1.58	−0.15	0.00	0.30	4.18	
	2-Ethyl-1-hexanol		−2.10	−1.82	0.00	0.08	0.48	2.69
1-PentylIm	Toluene		−1.89	−1.40	−1.00	1.16	2.56	2.81
	o-Xylene	7.27	−1.52	−1.44	−0.22	0.18	1.18	2.74
	Dichloromethane		−1.55	0.08	1.38			
	2-Ethyl-1-hexanol		−1.70	−0.92	0.48	1.30		
1-HexylIm	Toluene		−1.70	−0.60	0.48	3.36		
	o-xylene	7.30	−1.40	−0.96	1.70	3.15		
	Dichloromethane		−1.52	0.34	3.81			
	2-Ethyl-1-hexanol		−1.40	−0.30	0.85	1.00		
1-HeptylIm	Toluene		−1.52	0.08	2.34			
	o-Xylene	7.32	−1.26	−0.55	2.48	4.13		
	Dichloromethane		−1.49	0.48	3.70	7.54		
	2-Ethyl-1-hexanol		−1.00	0.48	1.15	1.48	2.30	

1-OctylIm	Toluene		−1.40	1.15	3.72			
	o-Xylene	7.36	−1.15	0.00	3.99			
	Dichloromethane		−1.48	0.78	4.46			
	2-Ethyl-1-hexanol		−0.70	0.78	2.30	3.45		
1-NonylIm	Dichloromethane	7.43	−1.44	1.04				
1-DecylIm	Toluene		−1.07	1.86	5.81			
	o-Xylene	7.39	−0.82	1.08	6.30			
	Dichloromethane		−1.42	1.26	4.93	8.51		
	2-Ethyl-1-hexanol		−0.60	0.85	2.48	5.00	6.30	10.77
1-DodecylIm	Toluene		−0.70	2.41				
	o-Xylene	7.43	−0.52	2.18				
	Dichloromethane		−1.39	1.60	5.04			
	2-Ethyl-1-hexanol		−0.59	0.90	2.54			
1-TetradecylIm	Toluene		−0.46	2.48	6.08			
	Dichloromethane	7.48	−1.35	2.00				
	2-Ethyl-1-hexanol		−0.52	0.95	2.78	4.70		

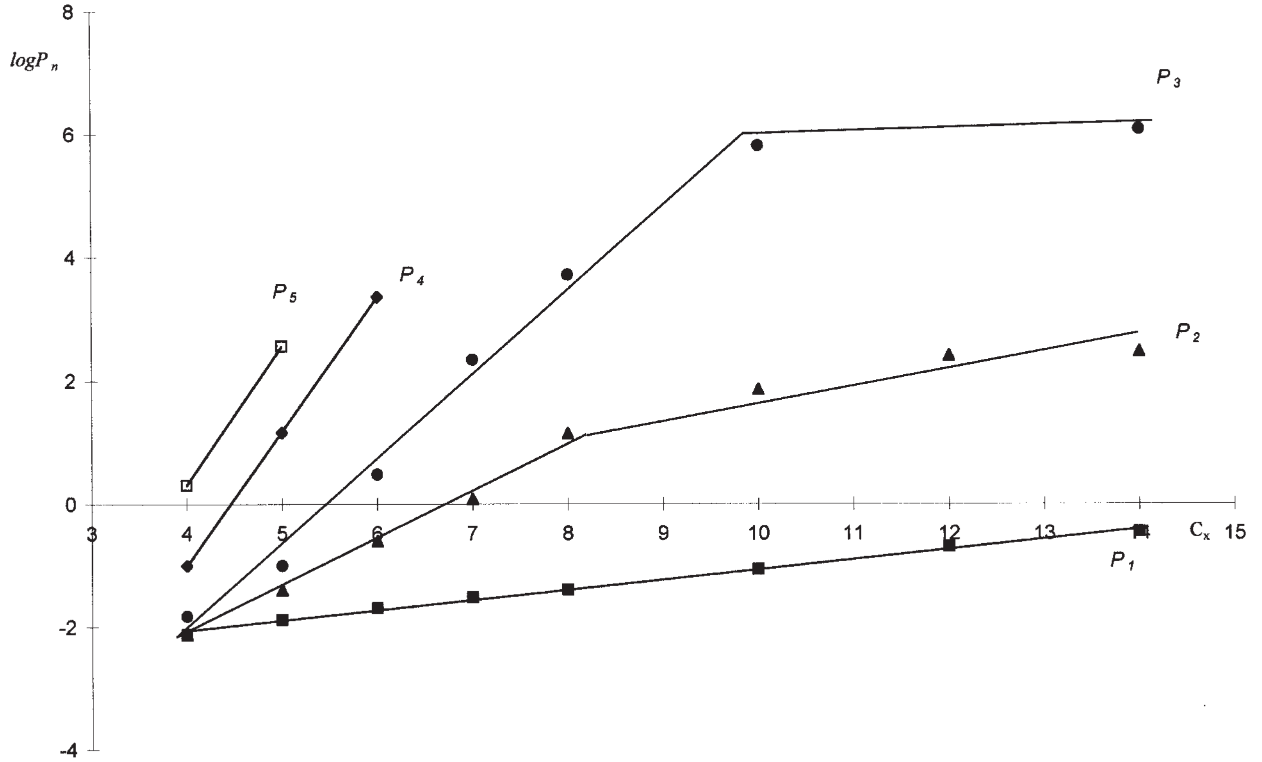

Figure 7. Influence of the alkyl chain length on partition constants (log P_n) of Co(II) complexes with 1-alkylimidazoles (adequately P_1, P_2, P_3, ...) by using toluene as a solvent.

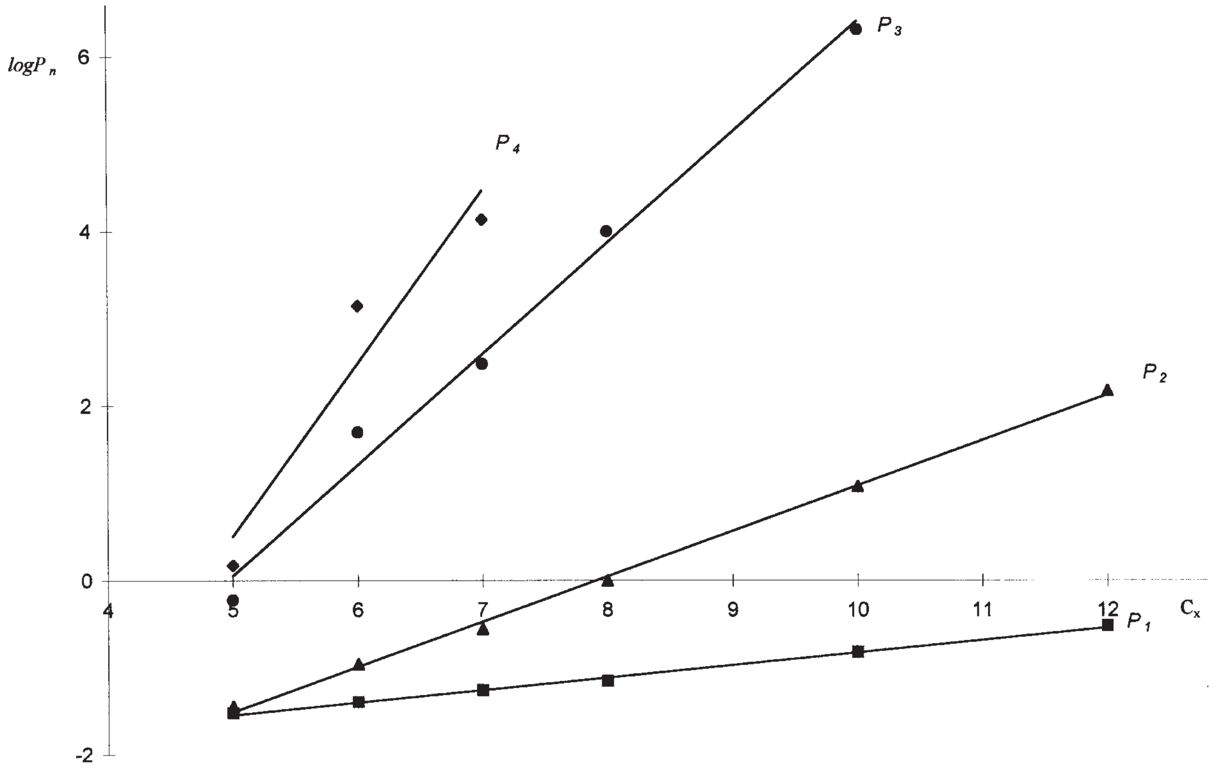

Figure 8. Influence of the alkyl chain length on partition constants (log P_n) of Co(II) complexes with 1-alkylimidazoles (adequately P_1, P_2, P_3, . . .) by using *o*-xylene as a solvent.

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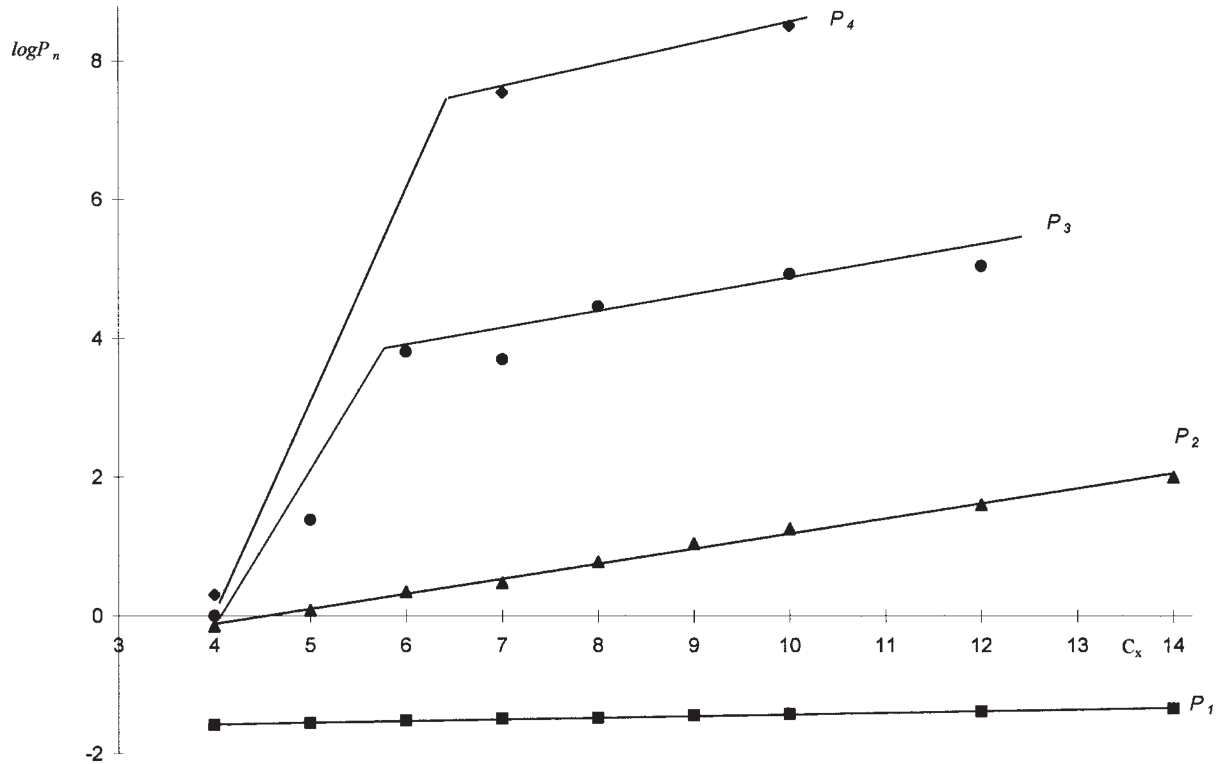

Figure 9. Influence of the alkyl chain length on partition constants (log P_n) of Co(II) complexes with 1-alkylimidazoles (adequately P_1, P_2, P_3, . . .) by using dichloromethane as a solvent.

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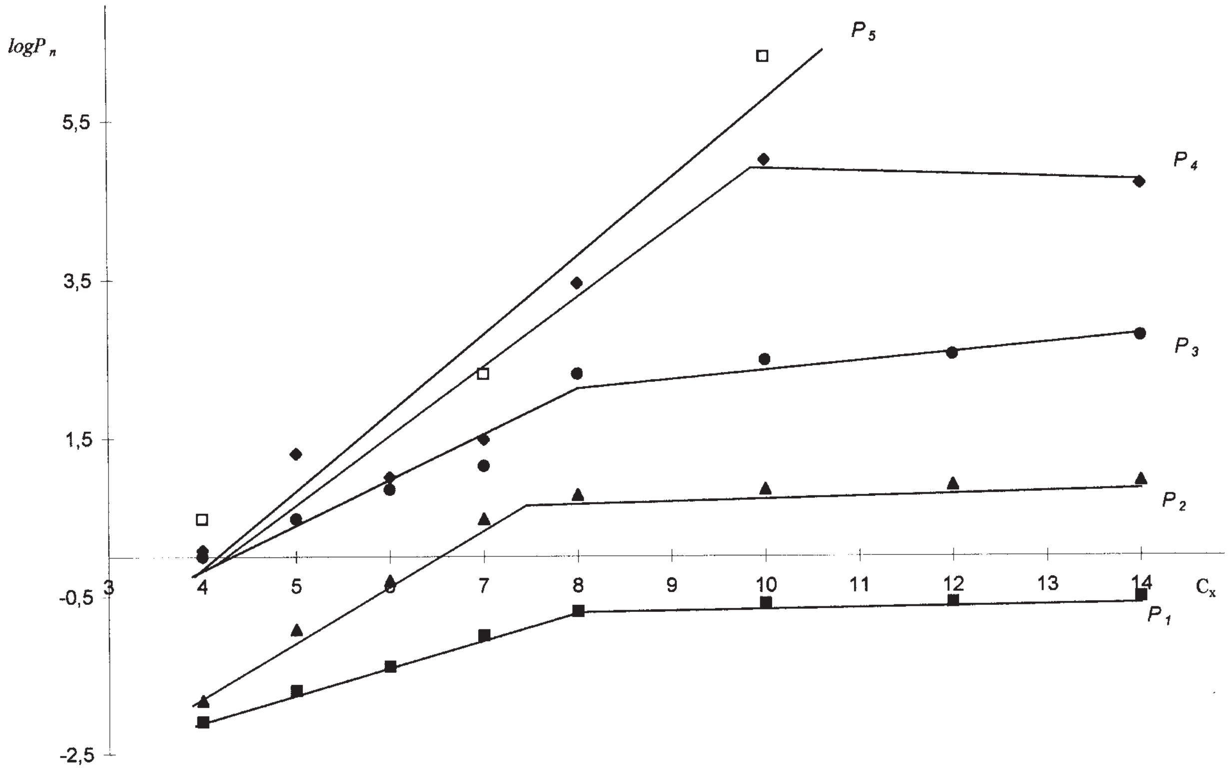

Figure 10. Influence of the alkyl chain length on partition constants (log P_n) of Co(II) complexes with 1-alkylimidazoles (adequately P_1, P_2, P_3, . . .) by using 2-ethyl-1-hexanol as a solvent.

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The angle of the slopes of straight lines log P_n vs. C_x certainly characterizes the extraction capacity of complexes (hydrophobicity). It enlarges with an increase in the number molecules of ligand (extractant) bounded in the coordination sphere of the Co(II). The angle also increases, when hexaco-ordinate complexes, e.g., $[CoL_4(H_2O)_2](NO_3)_2$ or $[CoL_4(NO_3)_2]$ change in tetraco-ordinate $[CoL_4](NO_3)_2$.

The P_2 quantities increase steeply starting from $R = C_4H_9$ up to C_8H_{17} and then less so. The relationship for P_3 has a similar shape. It means that for five of the first of investigated 1-alkylimidazoles pass into the organic phase tetrahedral compounds ($[CoL_2(NO_3)_2]$). For more sparingly soluble in water of derivatives of alkylimidazoles coordination number of extracted complexes is 6 ($[CoL_2(H_2O)_2(NO_3)_2]$). Similarly, one can explain the break on the graph $\log P_3 = f(C_x)$.

However, more meaningful are the relationships between log P_n and C_x with *o*-xylene as the main constituent of the organic phase (see Fig. 8). In this case, all relationships are linear with an increase in the number of alkylimidazole molecules bounded in coordination sphere in the Co(II) complexes enlarging the slopes of the straight lines.

It proves that coordination number of extracted complexes is constant for determined complexation step. Probably for two first complexation steps the coordination number is 6 and for the other two, 4. Hence, in the range of homologous series of the 1-alkylimidazoles, the values P_n values are relative only to the number of 1-alkylimidazole molecules bounded in coordination sphere in the Co(II).

$$\log P_1 = 0.14 \cdot C_x - 2.26$$
$$\log P_2 = 0.52 \cdot C_x - 4.11$$
$$\log P_3 = 1.27 \cdot C_x - 6.29$$
$$\log P_4 = 1.98 \cdot C_x - 9.38$$

The plots in Fig. 9 (for dichloromethane) are similar to those in Fig. 8, but for P_1 and P_2 only:

$$\log P_1 = 0.02 \cdot C_x - 1.67$$
$$\log P_2 = 0.22 \cdot C_x - 0.99$$

Whereas the P_3 and P_4 quantities increase steeply over the range 1-butyl–1-hexylimidazole:

$$\log P_3 = 1.90 \cdot C_x - 7.79$$
$$\log P_4 = 2.41 \cdot C_x - 9.36$$

With the next homologues, the straight lines are almost parallel to those of P_2:

$$\log P_3 = 0.24 \cdot C_x + 2.33 \text{ (for } C_6 \text{ to } C_{12})$$
$$\log P_4 = 0.32 \cdot C_x + 5.30 \text{ (for } C_6 \text{ to } C_{10})$$

By using dichloromethane in the organic phase pass complexes probably solvated by the solvent molecules. On the first complexation steps passes compound: $[CoS_3L(NO_3)_2]$, and on the second: $[CoS_2L_2(NO_3)_2]$.

On the third and fourth step of complexation at first the tetrahedral are extracted: $[CoSL_3](NO_3)_2$, $[CoL_4](NO_3)_2$ and for more sparingly water-soluble of 1-alkylimidazoles hexaco-ordinate compounds: $[CoSL_3(NO_3)_2]$, $[CoL_4(NO_3)_2]$. S denotes solvent molecule.

Figure 10 presents a plot of log P_n vs. C_x for 2-ethyl-1-hexanol. The P_1, P_2, and P_3 quantities increase gradually for the whole homologous series. Up to 1-heptylimidazole, the plots are linear with the tendency of the slopes to increase upon raising n [the number molecules of alkylimidazole in coordination sphere Co(II)].

$$\log P_1 = 0.36 \cdot C_x - 3.52 \text{ (for } C_4 \text{ to } C_8)$$
$$\log P_2 = 0.75 \cdot C_x - 4.78 \text{ (for } C_4 \text{ to } C_7)$$
$$\log P_3 = 0.53 \cdot C_x - 2.21 \text{ (for } C_4 \text{ to } C_8)$$

Upon further increase of the molecular weight of the ligands, the plots are almost parallel, with smaller slopes than those previously discussed:

$$\log P_1 = 0.03 \cdot C_x - 0.90$$
$$\log P_2 = 0.03 \cdot C_x - 0.55$$
$$\log P_3 = 0.08 \cdot C_x + 1.70$$

The breaks on the graphs log P_1, log P_2, and log P_3 vs. C_x (see Fig. 10) similar to those on Figs. 7 and 9 are due to the increase of coordination number extracted complexes with 4 on 6 and simultaneously the change of coordination structure from tetrahedral to octahedral. It happens because hexaco-ordinate complexes of the Co(II) with more sparingly water-soluble are sufficiently hydrophobic to pass into the organic phase.

The composition of the extracted complexes before the break of graphs log P_n vs. C_x, adequately for 1, 2, and 3 complexation steps can be following:

$[CoLS_3](NO_3)_2$ $\quad$ $[CoL_2S_2](NO_3)_2$ $\quad$ $[CoL_3S](NO_3)_2$

Whereas for large molecules of 1-alkylimidazoles, into the organic phase pass compounds:

$$[CoLS_5](NO_3)_2, \quad [CoL_2S_4](NO_3)_2, \quad [CoL_3S_3](NO_3)_2$$

The organic phase with the investigated complexes is invariably pale-red colored with a violet tint. Figures 11 and 12 present some absorption spectra of the organic phase after extraction of the Co(II) complexes with 1-octyl and 1-nonylimidazole in dichloromethane together with the corresponding pH of the aqueous phase and logarithms of distribution ratio D_M.

The spectra of the organic phase reveal both octahedral (absorption maxima around 500 nm) and tetrahedral (540 nm) complexes. The second complexes appear at higher ligand concentrations in the aqueous phase. Tetrahedral complexes of Co(II) are formed, generally, at the third and fourth complexation steps. Prove about this higher of partition constants P_3 and P_4 with comparison with P_1 and P_2 values. It is known that the average molar coefficient of tetrahedral complexes Co(II) is at least tenfold higher than that for octahedral complexes Co(II).[11–13] All spectras of the organic phase of the investigated complexes of 1-alkylimidazoles weakly formed maximum in range of longer waves. It proves that in investigated solutions of the organic phase, concentration of tetrahedral Co(II) complexes was very low, about 1–2% or less.

CONCLUSION

1. Stability constants of the Co(II) complexes with 1-alkylimidazoles increase with increasing chain length of the alkyl substituent at all complexation steps.
2. An increase in the ligand hydrophobicity results in an increase in the water/solvent partition constants of the complexes.
3. Generally at the third and fourth complexation steps, both tetracoordinate and hexaco-ordinate species occur in the aqueous phase, especially for 1-butyl, 1-pentyl, and 1-hexylimidazole. This results in the following configurational octahedron ⇆ tetrahedron equilibria:

$$[CoL_3(H_2O)_3]^{2+} \leftrightarrows [CoL_3(H_2O)]^{2+} + 2H_2O$$

$$[CoL_4(H_2O)_2]^{2+} \leftrightarrows [CoL_4]^{2+} + 2H_2O$$

Formation of the tetrahedral complexes enhances the extraction of Co(II).

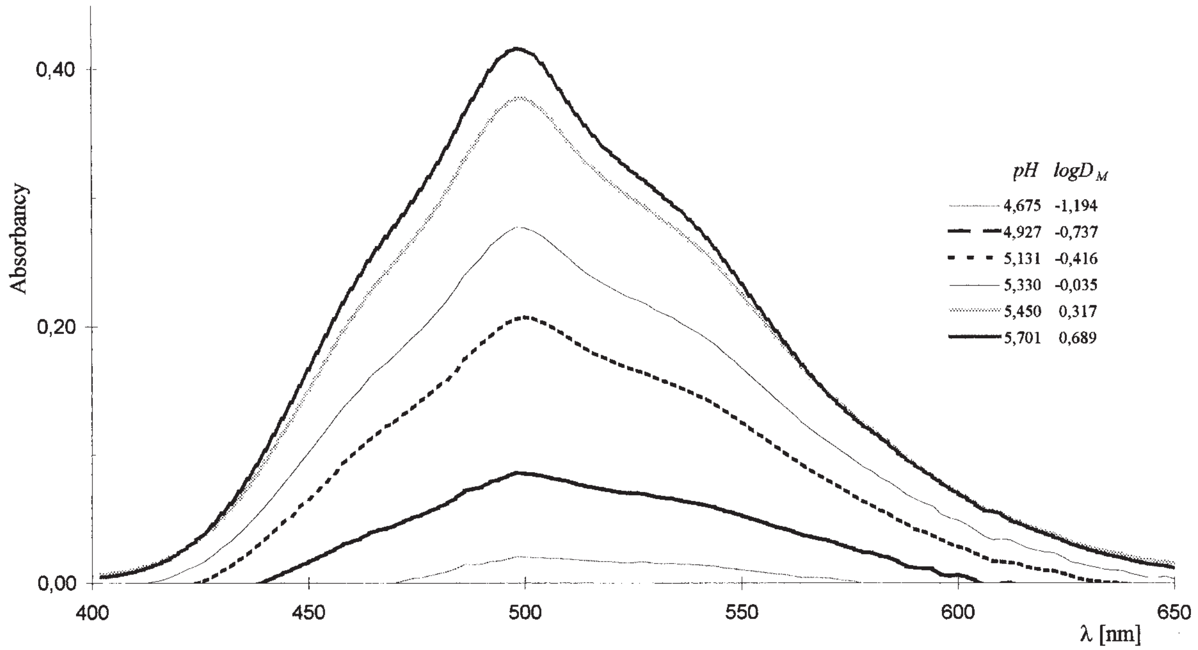

Figure 11. Absorbtion spectra of organic phase after extraction of the Co(II) complexes with 1-octyl-imidazole in dichloromethane together with the corresponding pH of the aqueous phase and logarithms of distribution ratio D_M.

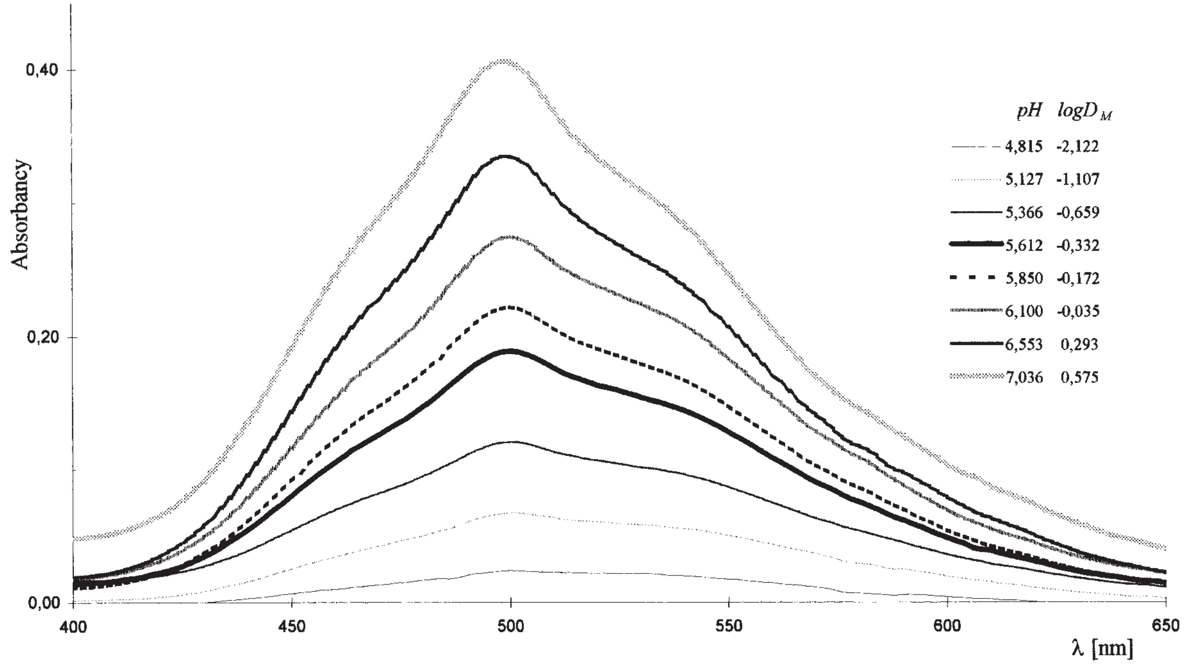

Figure 12. Absorbtion spectra of organic phase after extraction of the Co(II) complexes with 1-nonyl-imidazole in dichloromethane together with the corresponding pH of the aqueous phase and logarithms of distribution ratio D_M.

4. The extraction process depends less on the coordination number of complex with increasing of the alkyl chain length in 1-alkylimidazoles, so in these cases, the appearance of coordination equilibrium has little influence on the extraction process.

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Received February 2003
Revised July 2003

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