Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

The Influence of Alkyl Chain Length on Extraction Equilibria of Ni(II) Complexes with 1-Alkylimidazoles in Aqueous Solution/Organic Solvent Systems

Beniamin Lenarcik[a]; Teresa Rauckyte[a]
[a] Department of Technology and Chemical Engineering, University of Technology and Agriculture, Bydgoszcz, Poland

To cite this Article Lenarcik, Beniamin and Rauckyte, Teresa(2004) 'The Influence of Alkyl Chain Length on Extraction Equilibria of Ni(II) Complexes with 1-Alkylimidazoles in Aqueous Solution/Organic Solvent Systems', Separation Science and Technology, 39: 14, 3353 — 3372

To link to this Article: DOI: 10.1081/SS-200028915

URL: http://dx.doi.org/10.1081/SS-200028915

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 39, No. 14, pp. 3353–3372, 2004

The Influence of Alkyl Chain Length on Extraction Equilibria of Ni(II) Complexes with 1-Alkylimidazoles in Aqueous Solution/Organic Solvent Systems

Beniamin Lenarcik* **and Teresa Rauckyte**

University of Technology and Agriculture, Department of Technology
and Chemical Engineering, Bydgoszcz, Poland

ABSTRACT

Extraction process has been studied of Ni(II) complexes with 1-alkylimidazoles (with alkyl $= C_4H_9$ through $C_{14}H_{29}$) from aqueous solutions at 25°C, at a fixed ionic strength (0.5; KNO_3). Toluene, p-xylene, dichloromethane and 2-ethyl-1-hexanol were used as diluents. Stability constants of the complexes formed in the aqueous phase, β_n, were determined as well as the composition and partition constants, P_c, of the extracted species. It was demonstrated that stability constants of the Ni(II) complexes with the 1-alkylimidazoles as well as their partition constants increased with increasing chain length of the alkyl substituent. The larger stability constants were received for dichloromethane. The highest

---

*Correspondence: Beniamin Lenarcik, University of Technology and Agriculture, Department of Technology and Chemical Engineering, 3 Seminaryjna Street, 85-326, Bydgoszcz, Poland; E-mail: beniamin.lenarcik@atr.bydgoszcz.pl.

DOI: 10.1081/SS-200028915 0149-6395 (Print); 1520-5754 (Online)

www.dekker.com

values of the partition constants of Ni(II) complexes were received for the system water/2-ethyl-1-hexanol. On the basis of the UV-VIS spectra it was found that during all experiments the basic structure of the coordination polyhedron of Ni(II) has been retained.

Key Words: Ni(II) complexes; 1-Alkylimidazoles; Solvent extraction; Stability constants; Partition constants.

INTRODUCTION

Nickel is a strategic metal and its production and application show an increasing tendency.[1] Hence, its recovery from lean ores, industrial effluent waters, and other wastes is one of the fundamental problems of modern hydrometallurgy.

For solvent extraction of Ni(II) ions and their separation from Co(II), various extractants have been used such as LIX 84,[2,3] LIX 54,[4] and LIX 973N.[5]

The alkylimidazole derivatives as effective extractants for divalent metals extraction were patented 30 years ago.[6] 1-Alkylimidazoles are the weakest bases among substituted 1,3-diazoles[7,8] which, however, form highly stable complexes with Ni(II) ions in solution.[9–11] At a satisfactory ligand concentration, the complexes of this metal are extractable with benzyl alcohol, isoamyl alcohol, cyclohexanol, cyclohexanone,[12,13] and 2-methyl-1-propanol.[13]

The solubility of 1-alkylimidazoles declines sharply with the increase of the alkyl chain length as in the case of analogous pyridine derivatives. The first three derivatives ($R{=}CH_3-$, C_2H_5-, C_3H_7-) are well soluble in the water. However 1-butylimidazole solubility in the water is limited. All the following members of homologous series are sparingly soluble.[14,18,26] The solubility of metal complexes with homologous series of 1,3-diazoles change in a similar way.[6] Thus providing favorable conditions for utilizing them for extraction of metal ions such as those of Co(II), Ni(II), Cu(II), and Zn(II). Hence, it is necessary to determine stability constants of their complexes with sparingly soluble imidazoles and characterization of their extraction potential.

To date, the influence of the alkyl chain length in 1-alkylimidazoles on complexing capacity and extractability of Co(II)[15] and Zn(II)[16] has been determined. The results have shown that knowledge of the partition constants of the 1-alkylimidazole complexes offers the possibility for selective separation of the metals through selection of either optimal pH of solution or appropriate diluents.

The purpose of this work was to investigate the influence of alkyl chain length on the stability constants of the Ni(II) complexes with 1-alkylimidazoles (where alkyl = C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, C_8H_{17}, C_9H_{19}, $C_{10}H_{21}$, $C_{11}H_{23}$, $C_{12}H_{25}$, and $C_{14}H_{29}$). Toluene, p-xylene (both nonpolar), dichloromethane, and 2-ethyl-1-hexanol (both polar) were used as diluents. Their dipole moments are, respectively, 0.31; 0; 1.14, and 1.74 D.[17]

The results of our studies can be useful for characterization of other extractants such as alkyl derivatives of 8-hydroxyquinoline, pyridine, 2-hydroxy-5-acetophenone, and 5-salicylaldoxime, frequently employed as extractants.

EXPERIMENTAL

Materials

The 1-alkylimidazoles were provided by Dr A. Skrzypczak (Technical University, Poznan, Poland).[18] The remaining details relating to the research of structure and purity of compounds were given in the preceding work.[7]

The potassium and nickel (II) nitrates, both of analytical reagent grade (POCh Poland), were crystallized twice from double-distilled water. The concentration of Ni(II) salt was determined by titration with EDTA and by atomic absorption spectrophotometry (AAS). The concentration of potassium nitrate was determined gravimetrically as potassium sulfate. Nitric acid (analytical reagent; produced by POCh in Poland) was standardized against anhydrous sodium carbonate.

Both toluene and dichloromethane (POCh Poland), p-xylene (Fluka), and 2-ethyl-1-hexanol (Aldrich), all analytical reagent grade, are used without purification.

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

Equipment

Potentiometric measurements were carried out on a computer-aided multifunctional pH-meter (ELMETRON CX-741) equipped with a combination electrode C2401-8 (Radiometer). The atomic absorption spectrophotometer — BUCK Scientific 210 VGP instrument with a hallow cathode lamp Ni 232.0 was used for the determination of Ni(II) concentration. Hewlett Packard 8452A Diode Array Spectrophotometer was used for the registration of absorption spectra of the Ni(II) complexes in the organic phase.

Extraction Procedure

The measurements were run at a fixed ionic strength of the aqueous phase ($I = 0.5$; $HNO_3 + KNO_3$), at 25°C. The experiments were carried out in 15–20-mL graduated test tubes. Before extraction, the concentration of nitric acid (0.01 M) and Ni(II) nitrate (0.01 M) in the aqueous phase was constant, and the ligand concentration from 0.01 to 0.28 mol/L in the organic phase was varied. Six milliliters of the aqueous phase and an equal volume of an alkylimidazole solution in organic diluent were placed in a test tube. The test tube was then shaken for 20 to 30 min at 25°C. The equilibrium was established after a few minutes, however, no longer than 30 min. After that the phases were separated and the pH of the aqueous layer was measured. The Ni(II) concentration was determined by titration with a standardized EDTA solution and by atomic absorption spectrophotometry. Visible absorption spectra of the organic layer were subsequently recorded.

RESULTS AND DISCUSSION

To describe quantitatively the process of extraction, we used a D_M parameter referred to as the distribution ratio of metal ions between the organic and the aqueous phases and defined as follows:

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

where C_M^0 is the metal concentration in the aqueous phase before extraction, and C_M is the concentration after reaching partition equilibrium.

Most of the extraction experiments are presented separately for particular diluents as a dependence of $\log D_M$ vs. pH. Figures 1 through 4 show the results of extraction with toluene, p-xylene, dichloromethane, and 2-ethyl-1-hexanol, respectively. To make the figures more communicative, several of interfering and crossing curves were removed.

Data in Fig. 1 show that the extraction process with toluene runs at different pH ranges for particular imidazoles. The difference in $pH_{1/2}$ values (for $\log D_M = 0$) for the curve of 1-pentyl and 1-tetradecylimidazoles equals almost 3 pH units.

The extraction curves for p-xylene as diluent (Fig. 2) are similar to those presented in Fig. 1. The difference in $pH_{1/2}$ between extreme curves is as high as almost 3.2 pH units.

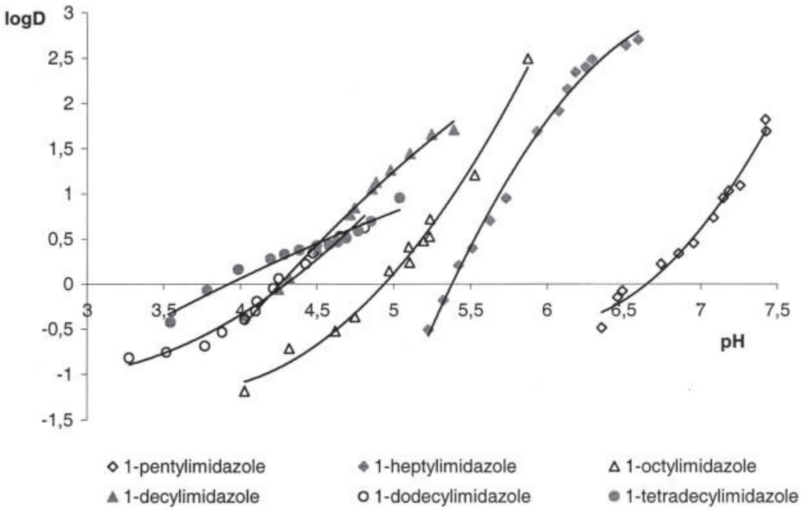

Figure 1. Influence of the alkyl chain length of 1-alkylimidazoles on the extraction process of Ni(II) complexes with these extractants which use toluene as a diluent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5(KNO_3)$]. Analytical concentration of 1-alkylimidazoles in the organic phase was varied from 0.01 mol/L (corresponding to the lowest pH) to 0.28 mol/L (the highest pH, respectively).

The curves for dichloromethane as diluent (Fig. 3) differ from those described above in that, first, the difference between the 1-butylimidazole and 1-heptylimidazole curves is considerably smaller, amounting to 1.25 pH unit only. Second, the $\log D_M = f(pH)$ curves form a compact bunch of curves (cf. 1-hexyl-, 1-octyl-, 1-nonyl-, 1-decylimidazole). The effectiveness of extraction for 1-dodecylimidazole is lower than has been expected.

The results for 2-ethyl-1-hexanol (Fig. 4) are in principle similar to those described previously for the hydrocarbon diluents, toluene and p-xylene. The only exception is 1-dodecylimidazole, for which the extraction efficiency is low (similar to that of dichloromethane as diluent). The difference in $pH_{1/2}$ between extreme curves (1-butylimidazole-1-octylimidazole) is 1.4.

The shapes of curves in Figs. 1–4 show that generally more than one complex undergoes extraction. In the case of the most sparingly soluble 1-alkylimidazoles, slopes of the plots of log D vs. pH are smaller than those for the readily soluble bases, this indicating that species containing smaller number of ligands are being extracted. In all cases, with the increase of the alkyl chain length in position 1 of the imidazole molecule, the extraction curves move gradually toward lower pH values. As seen in equation (2) this might be caused by elevated stability constants of the Ni (II) complexes,

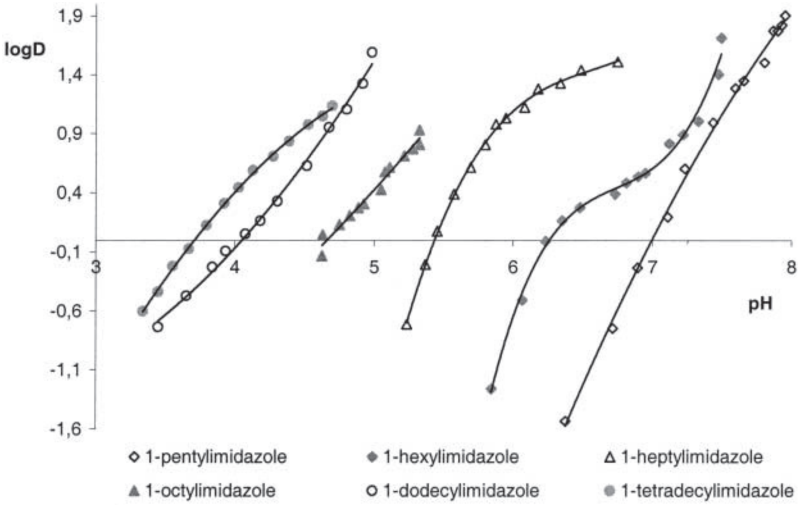

Figure 2. Influence of the alkyl chain length of 1-alkylimidazoles on the extraction process of Ni(II) complexes with these extractants which use p-xylene as a diluent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5(KNO_3)$]. Analytical concentration of 1-alkylimidazoles, the same as given in Fig. 1.

by increased partition constants of the extracted species, or by interplay of both.

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

where c is the number of particles in the first Ni(II) complex, which is so hydrophobic that it passes into the organic phase, β_1, β_2, ..., β_N are the consecutive stability constants of the complexes formed in the aqueous solution, β_c are the stability constants of Ni(II) complexes in the aqueous phase which pass into the organic phase, [L] is the concentration of the free imidazole base in the aqueous phase, and P_c is the partition constant of metal complexes $[ML_n]$ transferred into the organic phase.

To interpret in quantitative terms the influence of these parameters on the extraction process, we determined stability constants (β_n) of the Ni(II) complexes and their partition constants (P_c) between the organic and the aqueous phases. P_c is determined as a ratio of molar concentrations of complex ML_n in the organic and the aqueous phase.

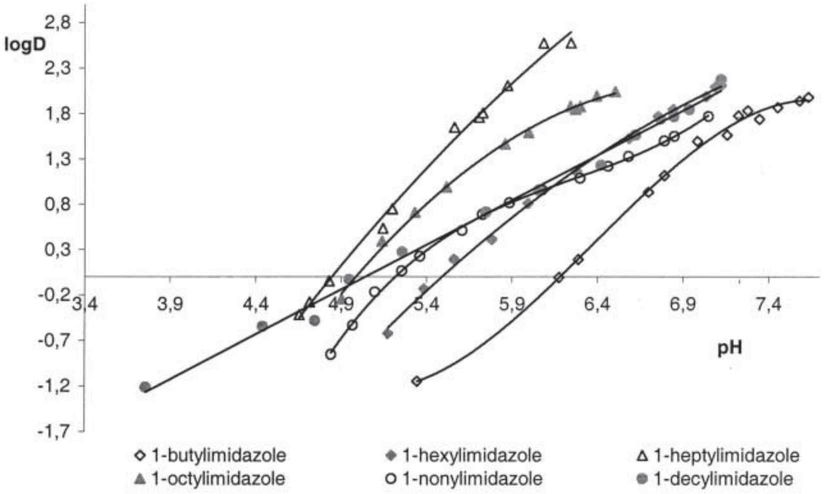

Figure 3. Influence of the alkyl chain length of 1-alkylimidazoles on the extraction process of Ni(II) complexes with these extractants which use dichloromethane as a diluent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5\,(KNO_3)$]. Analytical concentration of 1-alkylimidazoles, the same as given in Fig. 1.

The stability constants β_1 and the composition of extracted complexes were determined using Rydberg's equations, Eq. (3) obtained by rearrangement of Eq. (2) under assumption that only one complex is being extracted.

$$\frac{[L]^c}{D_M} = \frac{\sum_{n=0}^{n=N} \beta_n [L]^n}{P_c \beta_c} \tag{3}$$

The Rydberg's equation was extended by our methodology whereby we assume that Eq. (3) may be used for the determination of the probable composition of the first complex being extracted and its first stability constant, β_1. By this computer-aided procedure we were able to investigate the $[L]^c/D = f([L])$ function by varying exponent c from 1 to 6. In this way a bundle of curves was obtained, of which only one was a straight line with positive slope and b value. It is assumed that the c value is equal to the number of ligand molecules attached to the central ion in the first complex being extracted. The molar concentration of the free ligand in the aqueous phase was found from the equation:

$$[L] = \frac{K_a \cdot [HL^+]}{[H_3O^+]} \tag{4}$$

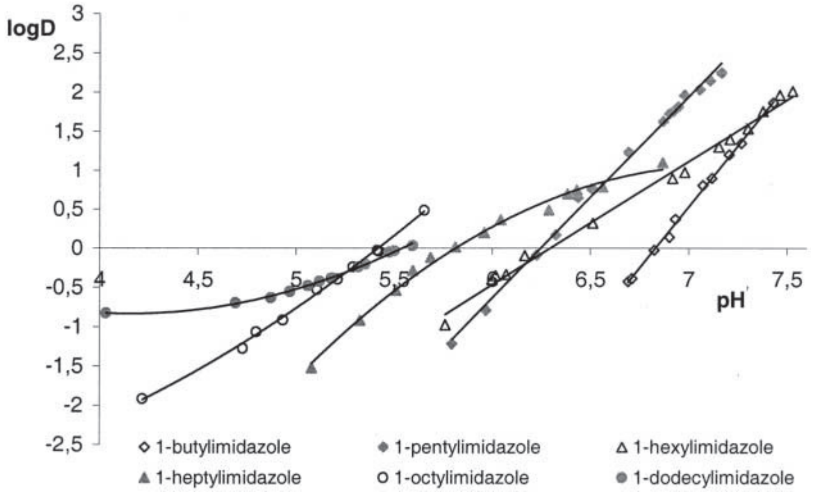

Figure 4. Influence of the alkyl chain length of 1-alkylimidazoles on the extraction process of Ni(II) complexes with these extractants which use 2-ethyl-1-hexanol as a diluent [at 25°C and constant ionic strength of the aqueous solution $I = 0.5\,(KNO_3)$]. Analytical concentration of 1-alkylimidazoles, the same as given in Fig. 1.

where K_a is the acidity constant of the protonated ligand, and $[HL^+]$ is the concentration of the conjugate acid equal to analytical concentration of nitric acid in aqueous solution.

Necessary pK_a values were taken from.[7] The pK_a values for the 1-alkylimidazoles with more than 10 methylene units in the alkyl chain were assumed to be the same as that of 1-decylimidazole. The β_1 values obtained in this way are collected in Table 1. In the table included are also β_n values previously determined by the potentiometric method for the readily soluble 1-alkylimidazoles.[9,10] As seen, the β_n values determined by both methods are in very good agreement, thus indicating that the data of the extraction method obtained on the basis of the Rydberg's equation are reliable. Because the constants obtained for dichloromethane appear to be overestimated, for calculation of the mean values of the stability constants, the data for toluene, p-xylene, and 2-ethyl-1-hexanol were taken.

Distribution ratio values (D_M) corresponding to the experimentally measured pH values, calculated on the basis of Eqs. (2) and (4), were counted in order to test the determined stability and partition constants (β_n and P_c). Figure 5 presents the points on the extraction curve (log D vs. pH), determined from the experimental part and from the calculations, based on

Table 1. Stability constants* and partition constants* of 1-alkylimidazoles–Ni(II) complexes in aqueous solutions at 25°C and constant ionic strength I = 0.5 (KNO_3).

Extractant	$pK_a^{[7]}$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log P_1$	$\log P_2$	$\log P_3$	$\log P_4$	Solvent
1-methylimidazole	7.19	3.05	5.95	7.61	9.13					
1-ethylimidazole	7.20	3.04	5.54	7.52	8.97					
1-propylimidazole	7.23	3.06	5.56	7.60	9.18					
1-butylimidazole	7.25	3.30	5.88	7.96						
1-pentylimidazole	7.27	3.00	5.50	7.60	9.10	0.48	1.18	1.78	2.48	toluene
		2.86	5.90	7.60	9.20	−1.30	−0.30	0.00	1.48	p-xylene
		3.70	6.05	8.20	9.50	0.90	1.48	1.95	2.54	dichloromethane
		3.30	6.00	8.10	9.70	1.00	2.70	3.48	4.30	2-ethyl-1-hexanol
1-hexylimidazole	7.3	3.30	5.80	7.90	9.30	0.70	1.25	1.90	2.54	toluene
		3.16	6.00	7.80	9.40	−0.30	0.00	1.18	2.72	p-xylene
		3.80	6.25	8.50	9.80	1.18	1.74	2.18	2.78	dichloromethane
		3.35	6.10	8.20	9.80	1.18	2.81	3.60	4.48	2-ethyl-1-hexanol
1-heptylimidazole	7.32	3.60	6.00	8.00	9.30	0.78	1.30	2.00	2.60	toluene
		3.70	6.20	8.00	9.60	0.00	1.00	2.30	3.76	p-xylene
		4.12	6.53	8.85	10.0	1.30	1.84	2.25	2.95	dichloromethane
		3.40	6.10	8.30	9.90	1.30	2.90	3.78	4.60	2-ethyl-1-hexanol
1-octylimidazole	7.34	3.90	6.20	8.10	9.50	0.90	1.32	2.00	2.65	toluene
		3.70	6.20	8.00	9.60	0.48	1.70	3.04	4.50	p-xylene
		4.40	6.80	9.00	10.2	1.40	1.90	2.32	3.04	dichloromethane
		3.50	6.15	8.30	9.90	1.40	3.00	3.90	4.60	2-ethyl-1-hexanol
1-nonylimidazole	7.36	4.20	6.60	8.60	10.1	0.95	1.36	2.04	2.70	toluene
		4.17	6.60	8.50	10.1	0.60	1.78	3.08	4.76	p-xylene

(*continued*)

Table 1. Continued.

Extractant	$pK_a^{[7]}$	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$	$\log P_1$	$\log P_2$	$\log P_3$	$\log P_4$	Solvent
		4.64	7.00	9.30	10.4	1.48	1.93	2.36	3.04	dichloromethane
		3.55	6.20	8.30	10.0	1.48	3.04	4.00	4.48	2-ethyl-1-hexanol
1-decylimidazole	7.39	4.40	6.90	8.80	10.2	1.00	1.43	2.04	2.74	toluene
		4.22	6.40	8.30	9.60	0.60	1.90	3.11	4.86	p-xylene
		4.90	7.30	9.60	10.7	1.54	1.95	2.40	3.04	dichloromethane
		3.60	6.30	8.30	9.90	1.54	3.08	4.08	4.60	2-ethyl-1-hexanol
1-undecylimidazole	7.41	4.50	6.90	8.90	10.3	1.00	1.48	2.04	2.78	toluene
		4.70	6.90	8.70	10.3	0.60	1.84	3.11	4.88	p-xylene
		5.20	7.50	9.90	10.9	1.57	1.98	2.43	3.04	dichloromethane
		3.90	6.50	8.60	10.2	1.60	3.11	4.11	4.48	2-ethyl-1-hexanol
1-dodecylimidazole	7.43	4.55	6.95	8.90	10.2	1.08	1.50	2.04	2.81	toluene
		5.27	7.20	9.00	10.5	0.60	1.84	3.11	4.89	p-xylene
		5.50	7.80	10.1	11.0	1.60	2.00	2.46	3.11	dichloromethane
		4.10	6.80	8.80	10.4	1.70	3.15	4.15	4.60	2-ethyl-1-hexanol
1-tetradecylimidazole	7.48	5.08	7.50	9.40	10.8	1.18	1.54	2.06	2.84	toluene
		6.00	7.80	9.60	10.9	0.70	1.84	3.08	4.90	p-xylene
		5.80	8.00	10.3	11.3	1.62	2.02	2.49	3.11	dichloromethane

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

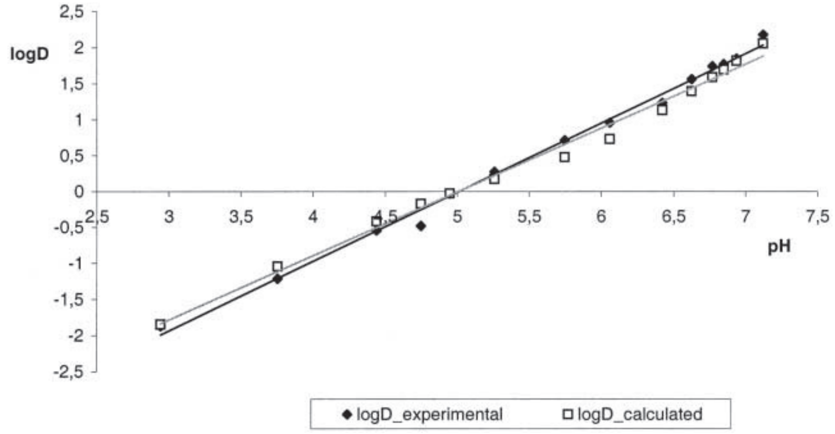

Figure 5. Comparison of the obtained experimental and calculated values log D vs. pH on the extraction of Ni(II) complexes with 1-decylimidazole for dichloromethane as a diluent.

the assumed β_n and P_c values. Their distribution on the experimental line may be declared as fully satisfactory.

A maximum *c* value previously determined by the Rydberg's method did not exceed 4. Accordingly, we assumed that no more than four complexes occurred in the aqueous phase. Having the β_1 values for the Ni(II) complexes with all 1-alkylimidazoles as well as the β_2, β_3, and β_4 constants determined potentiometrically for the first members of the homologous series of 1-alkylimidazoles, we calculated β_2, β_3, and β_4 by the curve-fitting method based on Eq. (2). These constants increase for each diluent with the increase in the number of carbon atoms in the substituent. Similarly, partition constants P_1, P_2, P_3, and P_4 were obtained.

Figure 6 shows the dependence between the mean stability constants, β_n, and the number of carbon atoms in the alkyl chain of 1-alkylimidazoles for three organic diluents. Initial points of the curves refer to the data for readily soluble 1-alkylimidazoles (1-methyl to 1-butyl) determined previously by the potentiometric method.[9,10]

In an analogous way, stability constants of the Co(II)[14] and Zn (II)[15] complexes with homologuous series of 1-alkylimidazoles were previously determined. In order to compare our results with those previously reported, summarized in Table 2 are straight line parameters illustrating the dependence of the logarithms of the stability constants of Co(II), Ni (II), and Zn (II) complexes with 1-alkylimidazoles as a function of the carbon atoms (x) in the

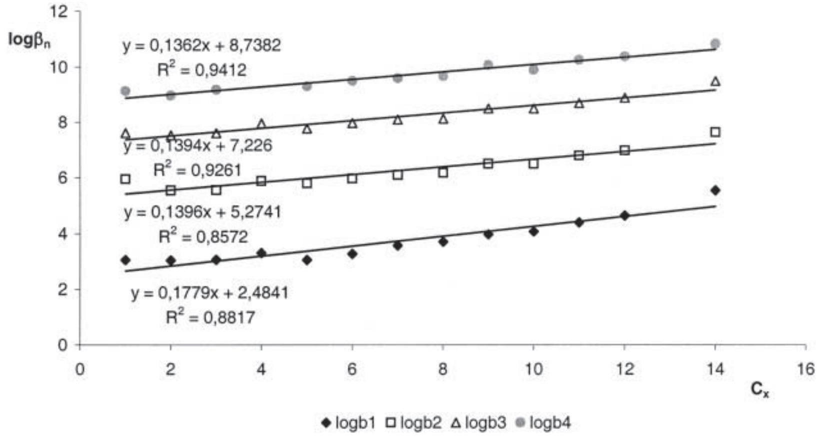

Figure 6. Influence of the alkyl chain length on the values of stability constants ($\log \beta_n$) of Ni(II) complexes with 1-alkylimidazoles (average results for toluene, p-xylene, and 2-ethyl-1-hexanol).

group of alkyl ligand. Slopes *a* of the straight lines of the y = ax + b equation are greater than 0. This means that the stability of the complexes increases with an increasing number of the carbon atoms. Again, parameter *b* reveals that at all the stages of complexation Ni(II) complexes are more stable in comparison with analogous complexes of Co(II) and Zn(II).

In Figs. 7–10, partition constants are presented for the Ni(II) complexes with the sparingly soluble 1-alkylimidazoles. They increase more or

Table 2. Comparison of the stability constants (average from Results for toluene, p-xylene, dichloromethane, and 2-ethyl-1-hexanol) of Co(II), Ni(II), and Zn(II) complexes with 1-alkylimidazoles.

$\log \beta_n$	Co(II)[15]	Ni(II)	Zn(II)[16]
β_1	$y = 0.3016x + 1.65316$ $R^2 = 0.9317$	$y = 0.1608x + 2.6314$ $R^2 = 0.9042$	$y = 0.2291x + 1.9858$ $R^2 = 0.9232$
β_2	$y = 0.3423x + 3.5924$ $R^2 = 0.9355$	$y = 0.1638x + 5.2895$ $R^2 = 0.8947$	$y = 0.2291x + 4.5$
β_3	$y = 0.377x + 4.8808$ $R^2 = 0.9346$	$y = 0.1642x + 7.2331$ $R^2 = 0.9535$	$y = 0.2291x + 6.7$
β_4	$y = 0.4344x + 5.78$ $R^2 = 0.9328$	$y = 0.1658x + 8.6531$ $R^2 = 0.9263$	

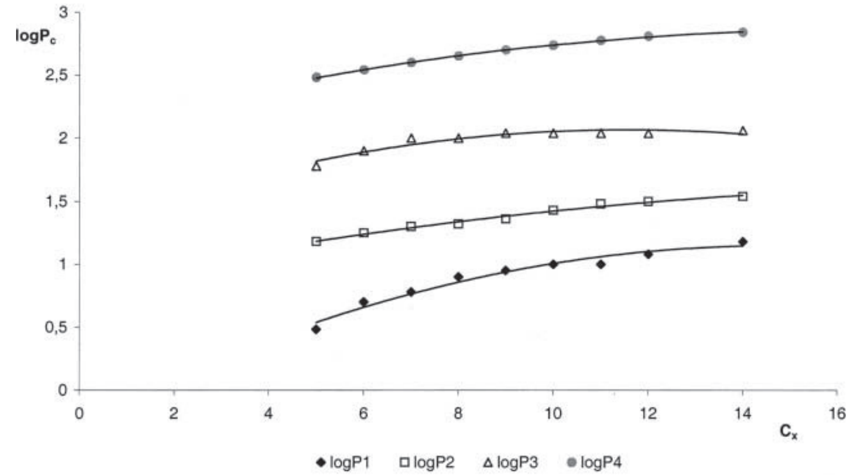

Figure 7. Influence of the alkyl chain length on the partition constants ($\log P_c$) of Ni(II) complexes with 1-alkylimidazoles by using toluene as a diluent.

less sharply for different diluents and stabilize themselves beginning from 1-decylimidazole onwards.

In order to determine coordination numbers and the contents of the complexes being extracted, we examined visible absorption spectra for all

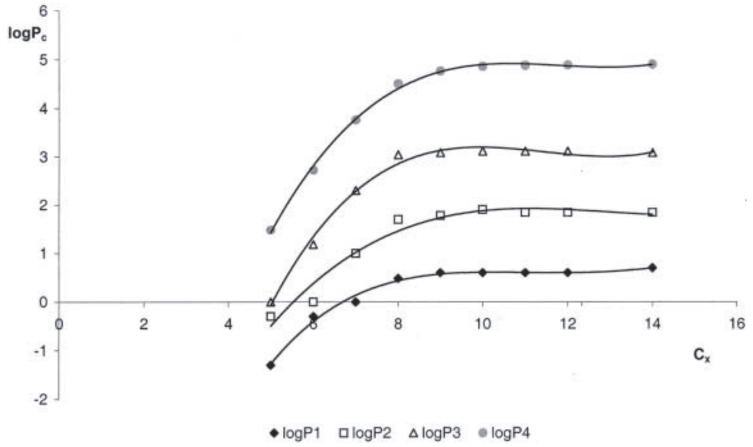

Figure 8. Influence of the alkyl chain length on the partition constants ($\log P_c$) of Ni(II) complexes with 1-alkylimidazoles by using p-xylene as a diluent.

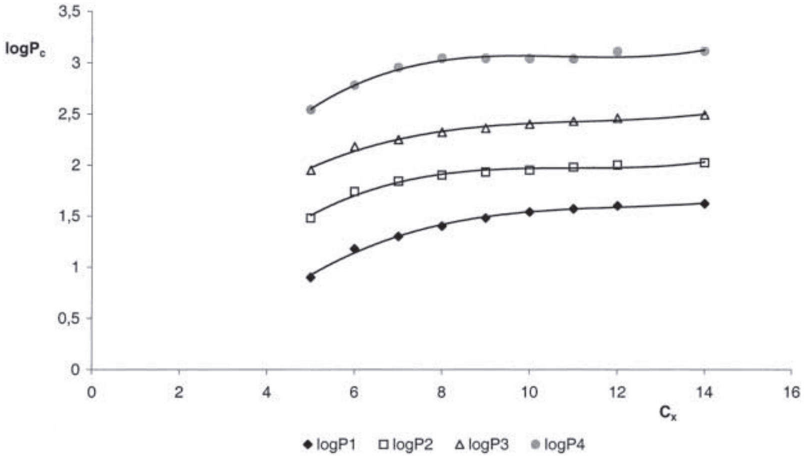

Figure 9. Influence of the alkyl chain length on the partition constants (log P$_c$) of Ni(II) complexes with 1-alkylimidazoles by using dichloromethane as a diluent.

the solvents used. All the solutions were more or less blue colored. In their spectra there were two maxima at 370 nm and 600 nm. The absorption band corresponding to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transition is characterized by maximum 600 nm and the transition $^3A_{2g}$ (F) $\rightarrow {}^3T_{1g}$ (P) is replied for

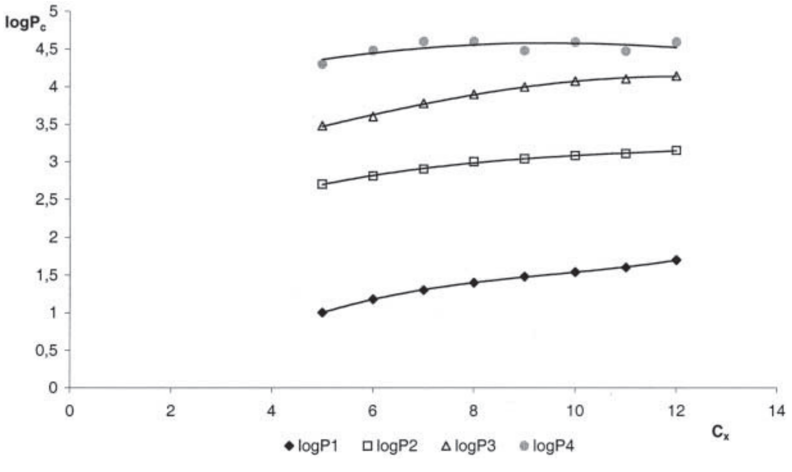

Figure 10. Influence of the alkyl chain length on the partition constants (log P$_c$) of Ni(II) complexes with 1-alkylimidazoles by using 2-ethyl-1-hexanol as a diluent.

maximum 370 nm.[20–25] This indicates that in both phases only the complexes with coordination number 6 occur (octahedral or pseudo-octahedral). Accordingly, the complexation process in the aqueous solution can be described by the equation

$$[\mathrm{Ni(H_2O)_6}]^{2+} + \mathrm{nL} \longleftrightarrow [\mathrm{Ni(H_2O)_{6-n}L_n}]^{2+} + \mathrm{nH_2O}$$

$$[\mathrm{Ni(H_2O)_{6-n}L_n}]^{2+}_{\mathrm{aq}} + \mathrm{xS} + 2\mathrm{NO_3^-} \longleftrightarrow [\mathrm{Ni\ L_nS_x}](\mathrm{NO_3})_{2\,\mathrm{org}}$$

where S stands for the diluent molecules.

Of the complexes formed in the aqueous phase, those with coordination imidazole number of 1 up to ≤ 4 were extracted. As seen in Table 1 and curves 6–9, the partition constants of the first and second partition steps ($c = 1$ and $c = 2$, respectively) are small. This means that the process of extraction of the complexes is controlled by the stability and partition constants of the third ($c = 3$) and fourth ($c = 4$) complex. Table 3 summarizes the partition constants of the Co(II), Ni(II), and Zn(II) complexes with 1-heptylimidazoles, 1-decylimidazoles, and 1-tetradecylimidazoles for toluene and dichloromethane. As seen, the partition constants for the Ni(II) complexes are higher than those of their Zn(II) and Co(II) counterparts in the absence of tetrahedral species in aqueous solution. Readily extractable tetrahedral complexes ($N = 4$) of Co(II) occur in the second, third, and fourth complexation steps. Thus, in this case, the partition constants, in particular P_3 and P_4, are higher than those of analogous Ni(II) compounds. With Zn(II), the tetrahedral complexes occur at the lower stages of the complexation process (beginning from $n = 2$ onwards). Consequently, the partition constants of the complexes with 2 and 3 ligands (P_2 and P_3, respectively) are higher than those of the Ni(II) counterparts.

Another problem to be tackled was to examine the influence of the diluent on the extraction process. Seemingly, the diluent molecules might enter the coordination sphere of the central ion together with those of the extractant. This would result in enhanced hydrophobicity of the complexes, causing a shift of extraction curves toward lower pH values. In Figs. 11 and 12 extraction curves are presented for two sparingly soluble 1-alkylimidazoles and four diluents. As seen, the influence of dichloromethane predominates, in particular for the first member of the homologous series of 1-alkylimidazoles (1-pentylimidazole). The curves for this diluent are distinctly displaced toward lower pH values. With increasing alkyl chain length, this influence becomes progressively weaker and with 1-undecylimidazole the curves for toluene, p-xylene, and dichloromethane are close to one another. It seems likely that for sparingly soluble imidazoles, with more than eight carbon

Table 3. Comparison of the partition constants of Co(II), Ni(II), and Zn(II) complexes with 1-alkylimidazoles between aqueous phase and organic phase [at 25°C and constant ionic strength of the aqueous solution $I = 0.5$ (KNO_3)].

	Co(II)[15]				Ni(II)				Zn(II)[16]				
Extractant	log P_1	log P_2	log P_3	log P_4	log P_1	log P_2	log P_3	log P_4	log P_1	log P_2	log P_3	log P_4	Solvent
1-heptylimidazole	−1.52	0.08	2.34		0.78	1.30	2.00	2.60	0.30	2.35	3.37		toluene
	−1.49	0.48	3.70	7.54	1.30	1.84	2.25	2.95	0.08	3.2	5.12		dichloromethane
1-decylimidazole	−1.07	1.86	5.81		1.00	1.43	2.04	2.74	0.78	3.3			toluene
	−1.42	1.26	4.93	8.51	1.54	1.95	2.40	3.04	0.48	2.57			dichloromethane
1-tetradecylimidazole	−0.46	2.48	6.08		1.18	1.54	2.06	2.84					toluene
	−1.35	2.00			1.62	2.02	2.49	3.11	0.40	1.08	2.39		dichloromethane

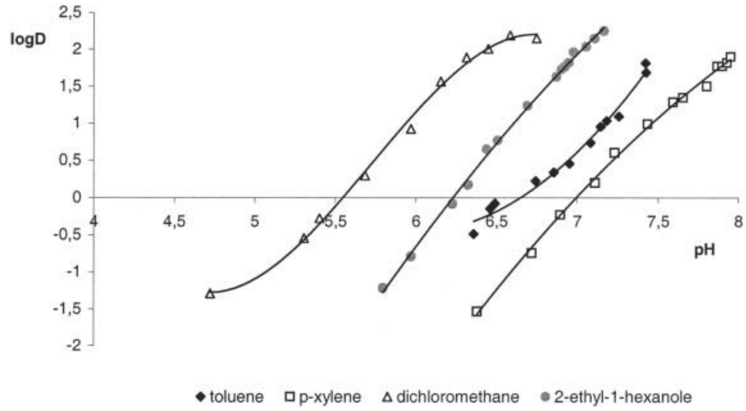

Figure 11. Plots of log D vs. pH of the aqueous phase of extraction of Ni(II) complexes with 1-pentylimidazole (concentration from 0.01 mol/L to 0.23 mol/L) for various diluents.

atoms in the alkyl chain, only the difference in solubility of the complexes affects the position of the curves on the pH axis.

It was surprising to note that the extraction curves for 2-ethyl-1-hexanol appeared at higher pH values. Most probably, the 2-ethyl-1-hexanol molecules do not enter to the coordination sphere of the Ni(II) complexes.

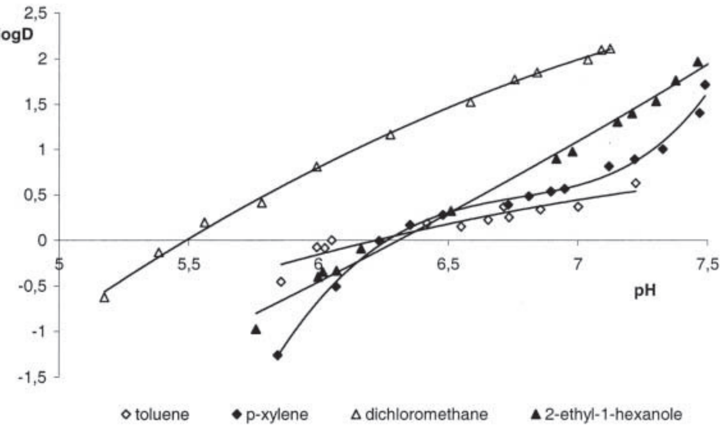

Figure 12. Plots of log D vs. pH of the aqueous phase of extraction of Ni(II) complexes with 1-undecylimidazole (concentation from 0.01 mol/L to 0.26 mol/L) for various diluents.

CONCLUSIONS

All 1-alkylimidazole, even those sparingly soluble, form complexes with Ni(II) in aqueous solution, containing 1 to 4 azole molecules in the coordination sphere. The stability constants of these complexes increase lineary with the increase of the length of the imidazoles ligand alkyl chain.

The partition constants of the extracted complexes in the system organic solvent/water initially increase with increasing alkyl chain length, and then the influence of the chain length decreases. For the chains longer than 1-decyl, the partition constants virtually do not change. The highest values of partition constants $\log P_c$ for Ni(II) complexes are found for system water/2-ethyl-1-hexanol. The values of partition constants of Ni(II) complexes with 1-alkylimidazoles show certain correlation with the solubility of 1-alkylimidazoles in the investigated diluents.[26] The values of partition constants P_c of nickel (II) complexes change as follows: 2-ethyl-1-hexanol $\geq$ dichloromethane $>$ toluene $>$ p-xylene.

The absorption spectra show that the coordination number of the Ni(II) complexes is 6. Consequently they were formed by replacement of the water molecules in the coordination sphere of Ni(II) by the azole molecules. Ni(II) complexes with 1 to 4 imidazole molecules pass to the organic phase. These are solvated either by organic diluent or by water molecules.

For the extracted species with dichloromethane diluent the following composition, $[\mathrm{Ni\ L_3\ S_3}](\mathrm{NO_3})_2$ and $[\mathrm{Ni\ L_4\ S_2}](\mathrm{NO_3})_2$, can be proposed. With hydrocarbon diluents (toluene, p-xylene) and probably 2-ethyl-1-hexanol, similar compounds are extracted, but in place of diluent molecules they probably coordinate water molecules.

REFERENCES

1. Cote, G. Hydrometallurgy of strategic metals. Solvent Extr. Ion Exc. **2000**, *18* (4), 703–727.
2. Price, M.J.; Reid, J.G. Ammoniacal solvent extraction at Queensland nickel process installation and operation. Proceedings of International Solvent Extraction Conference, 1993; Logsdail, D.H., Slater, M.J., Eds.; Elsevier Applied Science: London, 1993; 225.
3. Price, M.J.; Reid, J.G. Separation and recovery of nickel and cobalt in ammoniacal systems-process development. Proceedings of International Solvent Extraction Conference, York, 1993; Logsdail, D.H., Slater, M.J., Eds.; Elsevier Applied Science: London, 1993; 159.

4. Alguacil, F.J.; Alonso, M.; Lopez, F.A. Influence of ammonium salts on solvent extraction of nickel using LIX 54. J. Chem. Eng. Jpn. **2001**, *34* (1), 83.
5. Alguacil, F.J.; Cobo, A. Solvent extraction with LIX 973N for the selective separation of copper and nickel. J. Chem. Technol. Biot. **1999**, *74*, 467–471.
6. Cupery, M.E. N-Imidazole Compounds and Their Complex Metal Derivatives. US Patent 3,843,667, October 22, 1974.
7. Lenarcik, B.; Ojczenasz, P. The influence of the size and position of the alkyl groups in alkylimidazole molecules on their acid–base properties. J. Heterocyclic Chem. **2002**, *39*, 287–290.
8. Catalan, J.; Abboud, J.L.M.; Elguero, J. Basicity and acidity of azoles. Adv. Heterocycl. Chem. **1987**, *41*, 241.
9. Lenarcik, B.; Barszcz, B. 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). Rocz. Chem. **1977**, *51*, 1849–1855.
10. Lenarcik, B.; Barszcz, B. 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-ethyl- and 1-propylimidazoles. Pol. J. Chem. **1979**, *53*, 963–971.
11. Lenarcik, B.; Barszcz, B.; Kulig, J. 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). Rocz. Chem. **1977**, *51*, 1315–1322.
12. Lenarcik, B.; Głowacki, J.; Rzepka, M. 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. Separ. Sci. Technol. **1979**, *14* (1), 37–54.
13. Lenarcik, B.; Głowacki, J. Search for optimum conditions of extraction of transition metal complexes with alkylimidazoles. II. Extraction of the Co(II), Ni(II), and Zn(II) complexes of 1-ethylimidazole and 1-butylimidazole. Separ. Sci. Technol. **1979**, *14* (8), 721–734.
14. Khabnadideh, S.; Rezaei, Z.; Khalafi-Nezhad, A.; Bahrinajafi, R.; Mohamadi, R.; Farrokhroz, A.A. Synthesis of N-alkylated derivatives of imidazole as antibacterial agents. Bioorg. Med. Chem. Lett. **2003**, *13*, 2863–2865.
15. Lenarcik, B.; Ojczenasz, P. 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. Separ. Sci. Technol. **2004**, *39* (1), 199–226.

16. Lenarcik, B.; Kierzkowska, A. The influence of alkyl chain length on stability constants of Zn (II) complexes with 1-alkylimidazoles in aqueous solutions and their partition between aqueous phase and organic solvent. Solvent Extr. Ion Exc. **2004**, *22* (2), 1–24.
17. Rydberg, J.; Musikas, C.; Choppin, G.R. *Principles and Practices of Solvent Extraction*; Marcel Dekker, Inc.: New York, 1992; Vol. 1, 22–24.
18. Pernak, J.; Krysinski, J.; Skrzypczak, A. Bakterizide wirkung von iminiumverbindungen. A. Tenside Surfact. Det. **1987**, *24* (5), 276–279.
19. Braibanti, A.; Ostacoli, G.; Paoletti, P.; Pettit, L.D.; Sammartano, S. Potentiometric apparatus and technique for the pH-metric measurement of metal-complex equilibrium constants. Pure Appl. Chem. **1987**, *59*, 1721–1728.
20. Chiboub-Fellah, A.; Meullemeestre, J.; Spies, C.; Vierling, F.; Khan, M.A. Octahedral and tetrahedral configuration changes of nickel(II) chloro complexes from spectrophotometric studies in aprotic solvents. Transit. Metal. Chem. **1999**, *24*, 135–140.
21. Drago, R.S. *Physical Methods in Inorganic Chemistry*; Reinhold Publishing Corporation: New York, 1965.
22. Jørgensen, C.K. *Absorption Spectra and Chemical Bonding in Complexes*; Pergamon Press, Inc.: Oxford, London, 1962; 120.
23. Bartecki, A. *Vidma Elektronove Zviazkov Kompleksovych*; Vydavnictva Naukovo-Technicne: Varsava, 1987; 110–118.
24. Merriam, J.S.; Perumareddi, J.R. Polarised electronic spectra and electronic energy levels of some tetragonal nickel (II) complexes. J. Phys. Chem. **1975**, *79*, 142.
25. Rowley, D.A.; Drago, R.S. Crystal field analysis of the spectra of tetragonal nickel (II) pyridine complexes. Inorg. Chem. **1967**, *6*, 1092–1096.
26. ibmlc2.chem.uga.edu/sparc.