

Search for the possibility of utilizing the differences in complex-forming capacities of alkyimidazoles for selective extraction of some metal ions from aqueous solutions

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Alkyl substituents in position 1 of the imidazole ring distinctly affect the hydrophobic properties of the molecule and strengthen its basicity. Hence, 1-alkylimidazoles have been used as extractants of a number of metal ions. Again, a methyl substituent in position 2 of the imidazole ring raises by an order of magnitude the basicity. At the same time, the substituent impedes the formation of the 2-alkylimidazole complexes with metal ions due to the steric effect.

By the substitution of alkyl groups in position 1 or 2 of the imidazole ring it is possible to program the extraction properties of extractants and to control the selectivity of extraction.

Keywords: selective extraction, alkyl imidazole derivatives, transition metals ions.

INTRODUCTION

Imidazole (Fig. 1) belongs to the family of 5-membered heterocyclic bases known also as azoles. Its molecule is planar, of aromatic character, and fairly stable thermally.

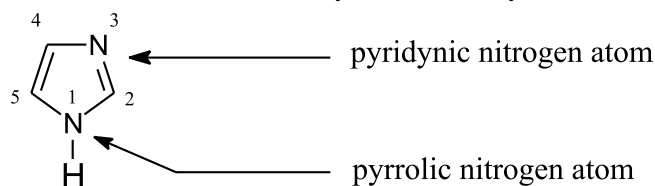


Figure 1. Structure of imidazole

Owing to the presence of the nitrogen atom in position 3, imidazole is a base (pK_a 7.12) stronger than pyridine (pK_a 5.31) but weaker than ammonia (pK_a 9.63).¹

According to Pearson's classification, imidazole is a base of intermediate strength. Accordingly, it can form stable complexes with either similar in strength or soft Lewis acids.² Substitution of an alkyl in position 1 strengthens the basicity of the nitrogen atom only slightly. 1-Alkylimidazoles are the weakest bases among all the 1-, 2-, 4-, and 5-monoalkyl derivatives of 1,3-diazole.³ The water solubility of these bases and their complexes decreases sharply with increasing the alkyl chain length. Sparingly water-soluble alkyimidazoles have been suggested as the extractants for the solvent extraction of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II).^{4,5} The 1-alkylimidazole (alkyl ranging from CH₃ through C₄H₉) complexes with d-electron metals were studied by Lenarcik and co-workers.⁶⁻⁸ Du Preez utilized 1-decylimidazole to extract Co(II), Ni(II) and Cu(II) from their perchlorate, chloride and thiocyanate solutions.⁹ Recently, formation of the Co(II), Ni(II), Cu(II), and Zn(II) complexes with homologous series of 1-alkylimidazoles (with alkyl ranging from C₄H₉ through C₁₄H₂₉) has been studied by the partition method.¹⁰⁻¹³ Stability constants of the metal complexes in water have been determined as well as the partition ratios of species, which passed to the organic phase.

COMPOUNDS WITH 1-ALKYLIMIDAZOLES

The purpose of this contribution was to establish the conditions for selective extraction of the Co(II), Zn(II), Ni(II), and Cu(II) ions from aqueous solutions using alkyimidazoles as extractants.

All the studies were carried out at 298 K at constant ionic strength of the aqueous phase equal to 0,5 kept by KNO₃ and HNO₃. The extraction measurements were carried out after adding an equal volume of organic solution of variable concentrations of 1-alkyl- or 1,2-dialkylimidazoles to the water phase containing 1 mM investigated metal ions (Co(II), Ni(II), Cu(II), Zn(II)). After the equilibrium was achieved, both phases were separated and the pH and metal ions concentration (by atomic absorption spectrophotometry) in the aqueous solution were measured.

To elaborate these conditions for the selective extraction of Co(II), Zn(II), and Cu(II) an attempt has been made to carefully scrutinize our results of investigations into the stability and extraction capacity of transition metal complexes with alkyimidazoles.

The stability constants of all the 1-alkylimidazole complexes with Cu(II) are constant and independent of the alkyl length and pK_a of the 1-alkylimidazole base.

Stabilities of the Co(II), Zn(II), and Ni(II) complexes have been found to increase with increasing the alkyl chain length of 1-alkylimidazoles.¹⁰⁻¹² These dependences are lineal. The straight line dependence of the $\log \beta_n$ of Co(II), Ni(II), and the Zn(II) complexes with 1-alkylimidazoles as a function of the carbon atoms (x) in the group of alkyl chain in 1-alkylimidazole are presented in Table 1.

Stability constants of the Cu(II) complexes are considerably higher than those of Co(II), Ni(II), and Zn(II). This may be explained in terms of a larger contribution of the $\pi_{M \rightarrow L}$ back donation to interaction of Cu(II) with the imidazole ring. The 1-alkyl substituent does not significantly affect either the polarization of the imidazole ring or the energy of its antibonding π orbitals.¹ It can thus be assumed that the contribution of the $\pi_{M \rightarrow L}$ bonding is invariable in the Cu(II) complexes with all the 1-alkylimidazoles. Partition of metal between the organic and aqueous phases was characterized by a ratio of metal partition as a function of the pH of the aqueous phase. The so-called distribution ratio, D_M , of the metal ion was derived from the measured concentrations and calculated from:

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

Table 1. Comparison of the stability constants β_n of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 1-alkylimidazoles

$\log \beta_n$	Co(II) ^[10]	Ni(II) ^[12]	Cu(II) ^[13]	Zn(II) ^[11]
$\log \beta_1$	$y=0.302x+1.653$	$y=0.161x+2.631$	4.15	$y=0.229x+1.986$
$\log \beta_2$	$y=0.342x+3.592$	$y=0.164x+5.290$	7.57	$y=0.229x+4.500$
$\log \beta_3$	$y=0.377x+4.881$	$y=0.164x+7.233$		$y=0.229x+6.700$
$\log \beta_4$	$y=0.434x+5.780$	$y=0.166x+8.653$		

where: C_M^0 and C_M denote analytical concentrations of the metal ions in the aqueous phase before and after attaining partition equilibrium, respectively.

The extraction process of the complexes is described by the equation (2):

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

where: β_n and β_c are cumulative stability constants of the complexes in the aqueous phase, P_c are organic solvent/water partition ratios of the complexes, ($P_c = [ML_c]_{(org)} / [ML_c]_{(aq)}$), $[L]$ is the free ligand concentration (mol/L) in the aqueous phase and c is the number of ligands molecules in the first complex that is so hydrophobic that it freely passes into the organic phase.^{14, 15}

The required free azole base concentrations in the aqueous phase at equilibrium, $[L]$, were found from the following equation:

$$[L] = \frac{K_a [HL^+]}{[H_3O^+]} \quad (3)$$

where K_a is the dissociation constant of the protonated ligand HL^+ , $[HL^+]$ is the concentration of the conjugate acid of the ligand equal to the analytical concentration of nitric acid (mol/L) in the aqueous phase. The pK_a values of the alkylimidazoles needed for the calculations were taken from reference.³

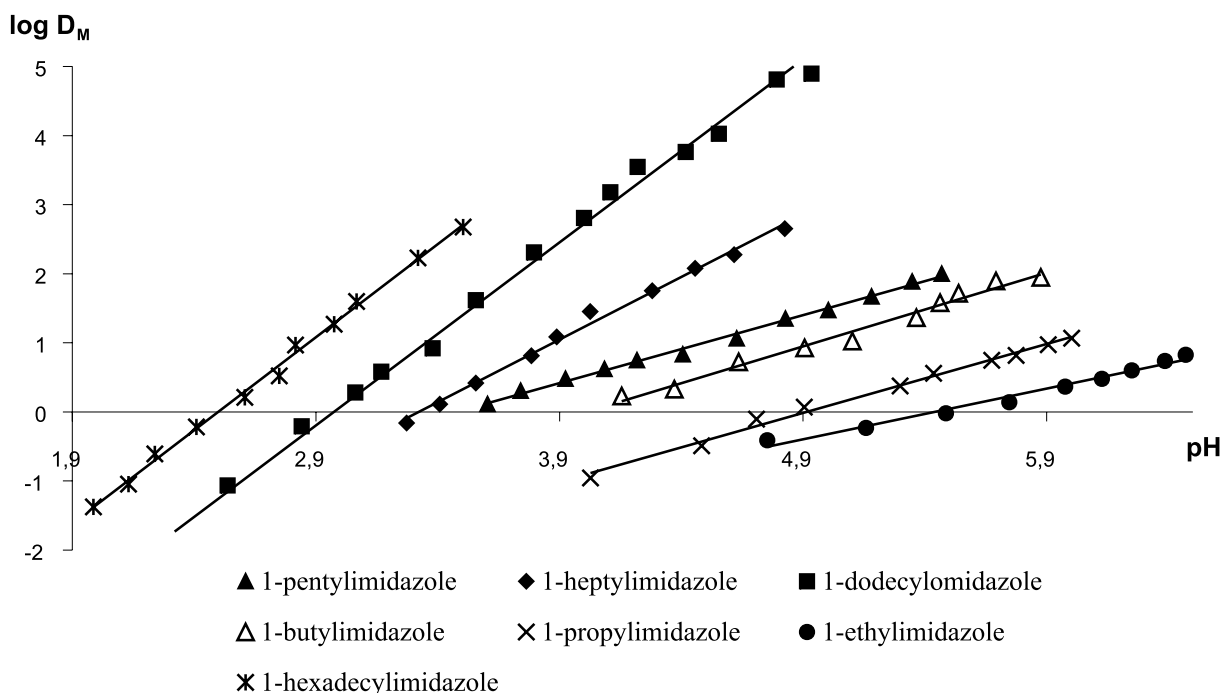
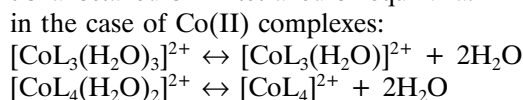
With each solvent the extraction curves ($\log D_M = f(pH)$) are distinctly displaced toward lower pH values with increasing the alkyl chain length of 1-alkylimidazole. In other words, the magnitude of $pH_{1/2}$ for the partition ratio of metal(II),

$\log D_M = 1$, decreases with increasing the number of methylene groups in 1-alkyl. An example of this type of shifting is presented in Fig. 2.

Partition ratio, P_n , of the metal complexes depends on the hydrophobic properties of an alkylimidazole and the nature of the solvent. The influence of the alkyl chain length of alkylimidazoles on partition ratios for methylene chloride and 2-ethylhexanol are presented in Fig.3 and Fig.4, respectively.

On the complexes formed in the aqueous phase, those with the coordination imidazole number of 1 up to ≤ 4 were extracted. As it can be seen in Figs 3 – 4, the partition ratios of the first and second partition steps are small for Co(II) and Zn(II). This means that the extraction process is controlled by the stability and the partition ratios of the third and fourth complex. The partition constants for the Ni(II) complexes are higher than those of their Co(II) and Zn(II) counterparts in the absence of tetrahedral species in the aqueous solution. Readily extractable tetrahedral complexes of Co(II) occur in the second, third, and fourth complexation steps. Thus, in this case, the partition ratios, 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. Consequently, the partition ratios of the complexes with 2 and 3 ligands (P_2 and P_3 , respectively) are higher than those of the Ni(II) counterparts.

In the case of Co(II) and Zn(II) complexes with 1-alkylimidazoles both tetra- and hexa-coordinate species occur in the aqueous phase. This results in the following configurational octahedron \leftrightarrow tetrahedron equilibria:

**Figure 2.** The influence of the alkyl chain length of 1-alkylimidazoles on the extraction of Cu(II) complexes into 2-ethylhexanol

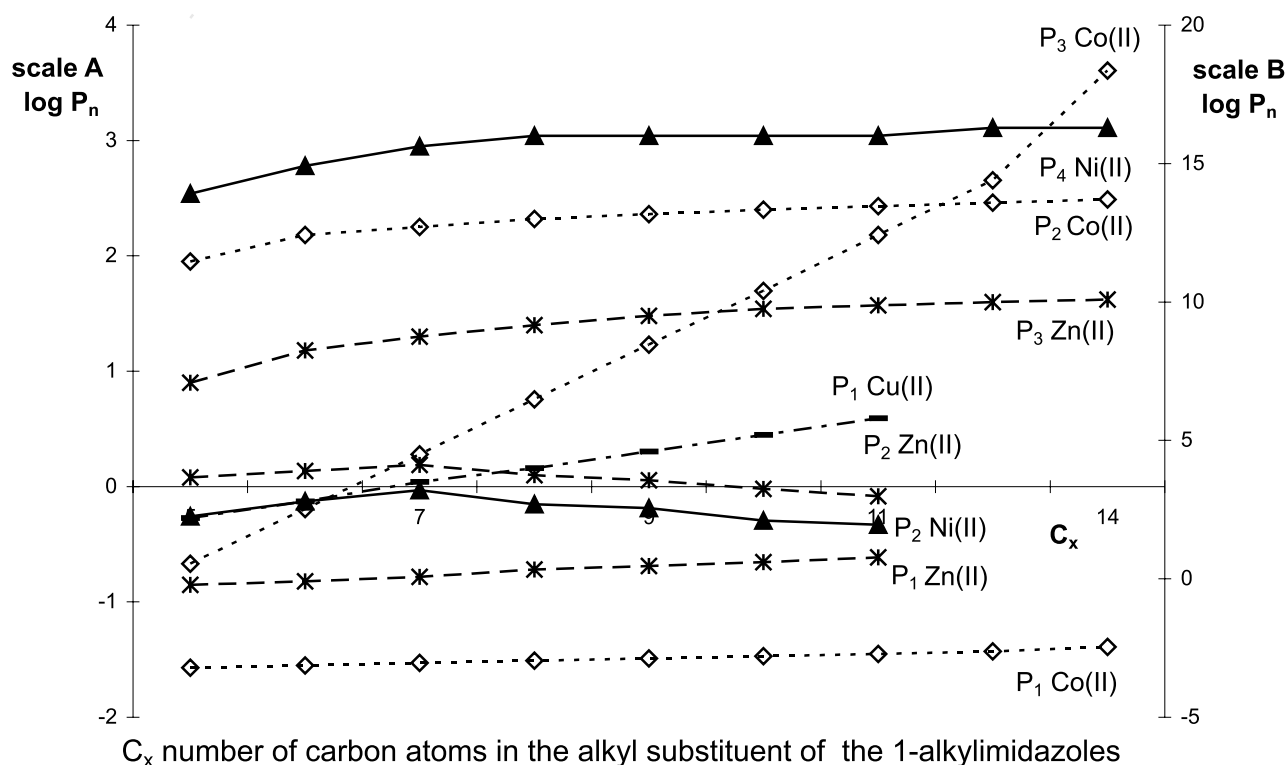


Figure 3. The influence of the alkyl chain length on the partition ratios (P_n) of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 1-alkylimidazoles for methylene chloride [scale B – for $\log P_3$ of Co(II) – 1-alkylimidazole complexes]

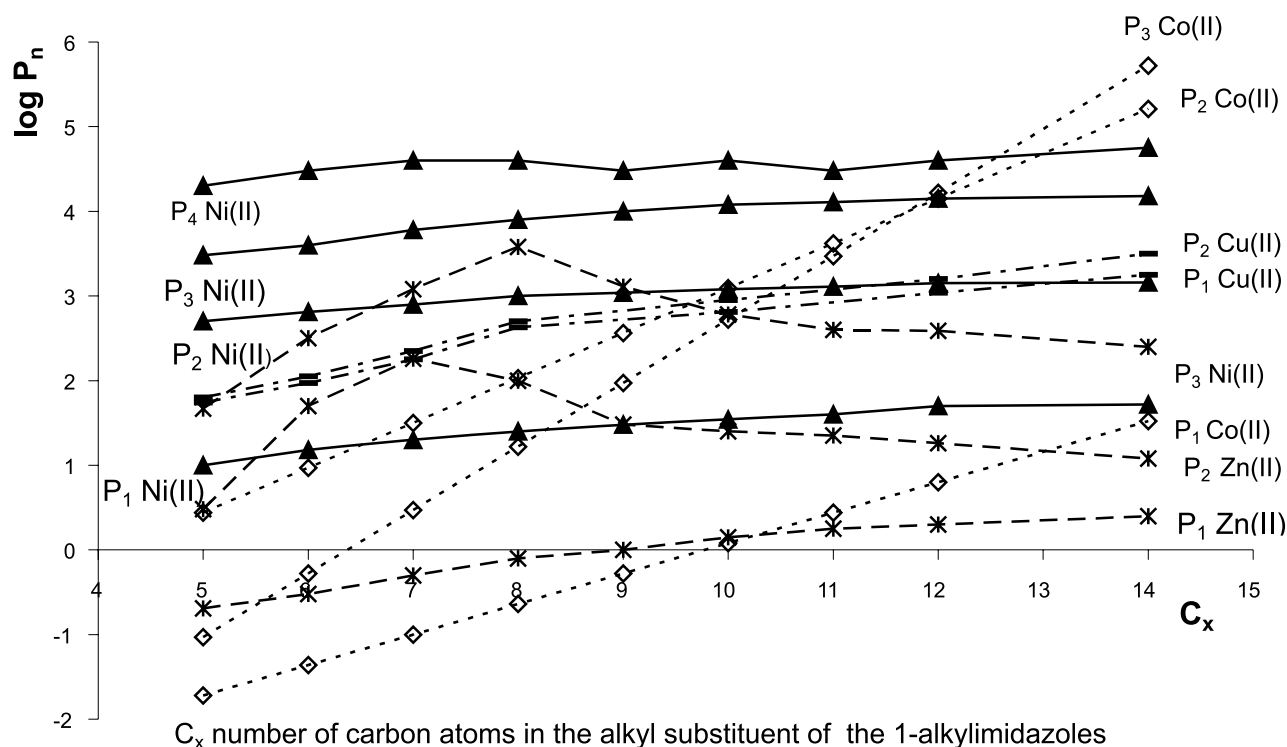
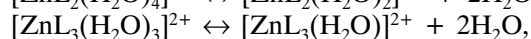
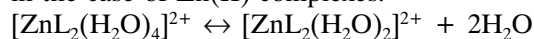


Figure 4. The influence of the alkyl chain length on the partition ratios (P_n) of Co(II), Ni(II), Cu(II), and Zn(II) complexes with 1-alkylimidazoles for 2-ethylhexanol

in the case of Zn(II) complexes:



where L – molecule of 1-alkylimidazoles.

Formation of the tetrahedral complexes enhances the extraction of Co(II) and Zn(II). The magnitudes of P_1 and P_2 suggest that the extraction of Cu(II) from the aqueous phase with 1-alkylimidazoles is controlled mostly by the first (ML) and second (ML₂) species. Again, under comparable conditions, the

extraction of Co(II), Ni(II), and Zn(II) depended on the partition ratios of either three or four complexes.^{10–12}

The aforementioned scrutiny has shown that:

(i) Elongation of the alkyl chain of the 1-alkylimidazole molecule (i.e. strengthening their hydrophobicity) is favourable for the extraction efficiency of the complexes on account of increasing their stability and partition constants.

(ii) 1-Alkylimidazoles with more than nine carbon atoms in the alkyl chain can be used for the separation of Co(II), Zn(II),

Ligand [literature]	pKa	Me ⁿ⁺	log β ₁	log β ₂	log β ₃	log β ₄	log β ₅
1,2-dimethylimidazole [21]	8.21	Co ²⁺	1.13	2.39	3.81	4.32	
		Ni ²⁺	2.15	3.55	4.24		
		Zn ²⁺	1.92	4.32	7.11	9.00	9.62
		Cu ²⁺	3.70	6.80	9.18	10.8	11.7
1-ethyl-2-methylimidazole [21]	8.21	Co ²⁺	1.40	1.88	3.55		
		Ni ²⁺	1.88	3.43	3.37		
		Zn ²⁺	1.11	4.45	7.11	9.05	
		Cd ²⁺	2.28	3.94	4.62		
		Cu ²⁺	3.52	6.60	8.98	10.3	
1-propyl-2-methylimidazole [21]	8.25	Co ²⁺	1.61	2.00	3.08	5.40	
		Ni ²⁺	2.05	2.41	4.19		
		Zn ²⁺	2.35	4.40	7.45	9.41	
		Cd ²⁺	2.56	4.06	5.57		
		Cu ²⁺	3.67	7.23	9.65	12.0	10.4
1-butyl-2-methylimidazole [21]	8.18	Co ²⁺	1.73	2.08	2.76	5.65	
		Ni ²⁺	2.03	3.49	4.54	5.00	
		Zn ²⁺	1.20	4.96	6.97	9.73	
		Cd ²⁺	2.44	4.02	5.37	6.03	
		Cu ²⁺	3.74	6.98	9.44	11.3	10.6
1-pentyl-2-methylimidazole [22,23]	8.27	Zn ²⁺	3.07				
		Cu ²⁺	3.50	6.59	9.18		
1-hexyl-2-methylimidazole [22,23]	8.32	Zn ²⁺	3.48	5.80	8.30	10.1	
		Cu ²⁺	3.52	6.63	8.98		
1-octyl-2-methylimidazole [22,23]	8.40	Zn ²⁺	4.45	6.80	9.10		
		Cu ²⁺	3.53	6.65	9.65		
1-nonyl-2-methylimidazole [22,23]	8.47	Zn ²⁺	4.75	7.15	9.50		
1-decyl-2-methylimidazole [22,23]	8.49	Zn ²⁺	5.1	7.75	9.90		
		Cu ²⁺	3.54	6.68	9.44		
1-dodecyl-2-methylimidazole [22,23]	8.53	Zn ²⁺	5.40	8.25	10.3	10.9	
		Cu ²⁺	3.58	6.75	9.37		

Table 2. The stability constants of the 1-alkyl-2-methylimidazole complexes with Co(II), Ni(II), Cu(II), Cd(II) and Zn(II) at 298 K, ionic strength 0.5 mol/L (KNO₃)

and Cu(II) from Ni(II) and other six-coordinate cations that do not change their coordination numbers. At the same time, there is an opportunity of predicting an optimum pH for each extractant (1-alkylimidazole) and the selection of the most effective solvent.

COMPOUNDS WITH 1-ALKYL-2-METHYLIMIDAZOLES

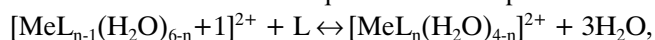
Further, let us consider what changes in the extraction process of the metal complexes can be expected by the substitution of an alkyl in position 2 of the 1-alkylimidazole molecule.

Substitution of the methyl group in position 2 of the imidazole ring increases by an order of magnitude the basicity of the pyridinic nitrogen atom. At the same time the substituent hampers the formation of the 2-methylimidazole complexes with metal ions due to the steric hindrance. Lowering of the stability of the metal complexes due to steric hindrance depends on the nature of the central ion, as well. The largest decrease in the stability has been noticed for 2-methylimidazole complexes of Ni(II), a lightly smaller for octahedral species of Co(II) and Zn(II), and the smallest one for Cu(II).¹⁶⁻²⁰ The substitution of bulky alkyl groups in position 1 results in enhanced hydrophobicity of the imidazoles, thus providing an opportunity for the extraction of metal complexes of these bases with organic solvents.²¹

The stability constants (Table 2) of Co(II), Ni(II), and Zn(II) complexes with 1-alkyl-2-methylimidazole formed in the aqueous phase increased with increasing the chain length of 1-alkyl substituents. The Cu(II) complexes with 1-alkyl-2-methylimidazole are invariant, regardless of the alkyl chain length and pK_a of the imidazole base.^{21,22} The partition ratios of metal ions complexes, P_n , are collected in Table 3.

In aqueous solutions of Co(II), Zn(II), and probably Cd(II), due to the operating steric effect, the complexes with the coordination number 6 are accompanied by those with the coordi-

nation number 4. Consequently, for each of those cations an octahedron ↔ tetrahedron equilibrium is set up:



where: L – molecule of 1-alkyl-2-methylimidazoles, and $1 \leq n \leq 4$, n depends not only on the nature of the ligand but also on the electronic structure of the central ion.

All extractable Cu(II) complexes are hexacoordinate.

In the case of Co(II) complexes with 1-alkyl-2-methylimidazole [CoL_n] in solutions tetrahedral complexes are formed already for the second $n = 2$ and the third $n = 3$ complexation step. It can thus be suggested that the extractable species have the following composition: [CoL_2S_2], and [CoL_3S], where S denotes a solvent molecule. For Zn(II) complexes the greatest concentration of tetrahedral complexes was observed for $n=3$. The Cd(II) ion hardly changed the coordination number from 6 to 4 for $n=3$ and 4.

The Ni(II) ions have a scarcely deformable octahedral coordination sphere. Consequently, the steric effect dramatically reduces the stability constants but only those of the octahedral complexes, e.g. of Ni(II) (Table 2).

The coordination sphere of the Cu(II) ion is extremely prone to deformation in such a way that the linkage of that ion to the pyridinic nitrogen of the imidazole ring is relatively short, and thus notably strong, this being reflected by high stability constant values.

With the Co(II) and Zn(II) ions, the steric effect impedes the formation of the octahedral species, while much less the tetrahedral ones. Again, the formation of the tetrahedral complexes of the metals, [CoL_4] and [ZnL_4], increases the complexation capacity of the metals as manifesting itself in their high stability constants, β_n , being the sum of the stability constants of the octahedral and tetrahedral complexes ($\beta_n = \beta_{n(\text{octahedral})} + \beta_{n(\text{tetrahedral})}$).

Owing to the combined hydrophobic and steric effects, 1-alkyl-2-methylimidazoles paved the way to the separation of the metal ions.

Table 3. The partition ratios P_n ($T = 298\text{ K}$, $I=0.5\text{ mol/L (KNO}_3\text{)}$) of the metal complexes with 1-alkyl-2-methylimidazole

Ligand [Literature]	Me ⁿ⁺	P ₁	P ₂	P ₃	P ₄	solvent
1,2-dimethylimidazole [21]	Co ²⁺	48.0	22.0			benzyl alcohol
	Cu ²⁺	3.0	9.0			benzyl alcohol
	Ni ²⁺	1.70	5.70			benzyl alcohol
	Zn ²⁺	5.0	291			benzyl alcohol
1-ethyl-2-methylimidazole [21]	Cu ²⁺	2.0	27.0	12.0		benzyl alcohol
	Ni ²⁺		2.08	42.0		benzyl alcohol
	Zn ²⁺	130	303	1870	10.0	benzyl alcohol
	Cd ²⁺	2.90	10.3	582		benzyl alcohol
1-propyl-2-methylimidazole [21]	Co ²⁺	75.0	3500			benzyl alcohol
	Cu ²⁺		4.10	27.0		benzyl alcohol
	Ni ²⁺	1.00	5.10			benzyl alcohol
	Zn ²⁺	0.05	98.5	49.0	80.0	benzyl alcohol
1-butyl-2-methylimidazole [21]	Cd ²⁺	0.50	10.0	30.5		benzyl alcohol
	Co ²⁺			40.0		benzyl alcohol
	Cu ²⁺			3100		benzyl alcohol
	Ni ²⁺			251	931	benzyl alcohol
1-pentyl-2-methylimidazole [22,23]	Zn ²⁺		261	1000		benzyl alcohol
			250	100		benzyl alcohol
			250	100		benzyl alcohol
	Cd ²⁺	8.00	371	2130		benzyl alcohol
1-hexyl-2-methylimidazole [22,23]	Zn ²⁺	0.2	2	14		p-xylene
		0.5	5	8		tetralin
		15	271	16		methylene chloride
	Cu ²⁺	1.2	29	458		chloroform
1-octyl-2-methylimidazole [22,23]		2.5	15			2-ethylhexanol
	Zn ²⁺	0.6	6	75		p-xylene
		1	15	120		tetralin
		26	307	150	330	methylene chloride
1-nonyl-2-methylimidazole [22,23]	Cu ²⁺	2.7	35	590		chloroform
		4.0	26			2-ethylhexanol
	Zn ²⁺	2	50	2000		p-xylene
		10	80	1800		tetralin
1-decyl-2-methylimidazole [22,23]		29	346	3200		methylene chloride
	Cu ²⁺	2.9	42	725		chloroform
		4.8	38			2-ethylhexanol
	Zn ²⁺	4	100	1,8*10 ⁴		p-xylene
1-dodecyl-2-methylimidazole [22,23]		17	180	6500		tetralin
	Zn ²⁺	10	180	9*10 ⁵		p-xylene
		30	300	1,4*10 ⁴		tetralin
	Cu ²⁺	41	395	1,5*10 ⁴		methylene chloride
1-dodecyl-2-methylimidazole [22,23]		3.1	50	840		chloroform
		6	52			2-ethylhexanol
	Zn ²⁺	15	240	9,5*10 ⁵		p-xylene
		50	450	2,5*10 ⁴		tetralin
1-dodecyl-2-methylimidazole [22,23]		48	432	3*10 ⁴		methylene chloride
	Cu ²⁺	3.2	58	980	1,8*10 ⁹	chloroform
		9.2	65			2-ethylhexanol

SUMMARY

– The stability constants of the Co(II), Ni(II), and Zn(II) complexes formed in the aqueous phase increased with an increase of the 1-alkyl chain length of the 1,3-diazoles. The stability constants of all the 1-alkyl- and 1-alkyl-2-methylimidazole complexes with Cu(II) are constant and independent of the alkyl length and pK_a of the base. An increase in hydrophobicity of the ligands resulted in the increase in partition ratios of the complexes.

The extraction curves were shifted towards lower pH values with an increase of the 1-alkyl chain length. The lowest $pH_{1/2}$ values were obtained for the metal ions complexes with 1-tetradecylimidazole and 1-dodecyl-2-methylimidazole.

– The steric effect, due to the methyl group in position 2 of the imidazole ring, enables the formation of tetracoordinate Co(II), Zn(II), and Cd(II) complexes, thus facilitating the extraction of these cations.

– Owing to the combined hydrophobic and steric effects, 1-alkyl-2-methylimidazoles paved the way to the separation of the

Co(II), Zn(II), and Cu(II) from other ions of metals. By the substitution of alkyl groups in position 1 or 2 of the imidazole ring it is possible to program the extraction properties of extractants and to control the selectivity of extraction.

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