

Search for differences in the complex forming abilities of alkyimidazoles and making use of them

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An imidazole (1,3-diazole) ring is a building unit of compounds occurring in living organisms. The most common ones include histidine, histamine, pilocarpine, adenine, guanine, purine as well as vitamin H (biotin); the one named last was discovered by Utter [1] in 1960. Some derivatives of imidazole, for instance pilocarpine, have been used as medicines [2].

Imidazole (Fig. 1), discovered in the 19th century by the Polish chemist Radziszewski [3], belongs to the family of five-membered heterocyclic bases called azoles. It is an aromatic compound with a planar ring structure. The pyridine nitrogen atom carries a lone electron pair which can bind hydrogen ions and form co-ordination bonds with metal ions.

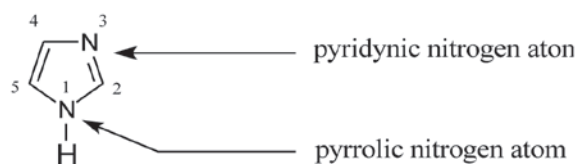


Fig. 1. The imidazole molecule

Owing to the intermolecular hydrogen bonds, imidazole is a solid compound. In an aqueous solution it is a base (pK_a 7.03), stronger than pyridine (pK_a 5.31) but weaker than ammonia (pK_a 9.63). At the same time, it is the strongest base among both the five- and six-membered heterocyclic compounds. In Pearson's classification of soft and hard acids and bases, imidazole occupies an intermediate position, thus being capable of the formation of stable complexes with intermediate and soft Lewis bases. The basicity of the pyridine nitrogen atom can be varied by introducing appropriate substituents to the imidazole ring. All hydrogen atoms in the ring can be substituted, amongst others, by alkyls to give a homologous series of alkyimidazoles. It has been claimed recently [4] that basicity in particular homologous series of compounds increases linearly with an increasing number of carbon atoms in the alkyl substituents. Hence, the magnitude of the constant b in the respective linear relationships can be used for the comparison of basicities of particular series of compounds. Thus,

$$\text{for 1-alkylimidazoles} \quad pK_a = 0.0222n + 7.165 \quad (1)$$

$$\text{for 1,2-dialkyimidazoles} \quad pK_a = 0.0432n + 8.01 \quad (2)$$

$$\text{for 1,2,4-trialkyimidazoles} \quad pK_a = 0.0503n + 8.46 \quad (3)$$

$$\text{for 1,4-dialkyimidazoles} \quad pK_a = 0.0279n + 7.79 \quad (4)$$

$$\text{for 2-alkylimidazoles} \quad pK_a = 0.0349n + 7.87 \quad (5)$$

n is the number of carbon atoms in the alkyl substituent

Trialkylimidazoles are the strongest bases while 1-alkylimidazoles are the weakest ones.

Paper [4] was of crucial importance because determination of the dissociation constants of alkyimidazoles paved a way to the investigation of complexation reactions of sparingly soluble alkyimidazoles with transition metal ions, irrespective of the position of the alkyls in the ring.

Having in hand the basicities of alkyimidazoles, it was possible to initiate extensive studies on the solvent extraction of Co(II) [5, 6], Ni(II) [7], Cu(II) [8–14], Zn(II) [15–17] and Cd(II) [18, 19] with sparingly soluble alkyimidazoles. The purpose of those studies was to determine the influence of steric and hydrophobic effects associated with the structural features of ligands on the extraction characteristics of the

ions. When carrying out the experiments, identical procedures have been used throughout (as reported in detail in [5–17]), wherein an imidazole base was dissolved in an organic solvent, whereas a metal salt was dissolved in water. After equilibration, the concentration of the metal was determined in both phases, the pH of the water phase was measured and the absorption spectra of both phases were recorded over the visible range for colored solutions.

To arrive at a full quantitative description of a complex-forming system consisting of water and organic solvent [20], knowledge of the following quantities is mandatory:

- dissociation constant of the proposed form of the ligand in water
- stability constants of the metal complexes being formed in the aqueous phase
- partition constants of the metal complexes between the two phases.

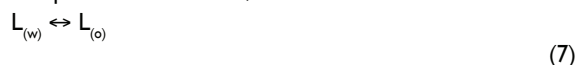
On the basis of experimental data, the ratio of partition of the metal (D_M) was determined as a dependent variable of the free ligand concentration $[L]$ in the aqueous phase, the ratio being expressed by Equation (6):

$$D_M = \frac{C_M^o - C_M}{C_M} \quad (6)$$

where C_M^o and C_M are metal ion concentrations before and after attaining a partition equilibrium, respectively.

D_M is a function of the free ligand concentration $[L]$ in the aqueous phase, which is calculated from Equation (8) on the basis of pH measurement.

In equilibrium conditions, when



(where L is the ligand molecule, w denotes the aqueous phase and o denotes the organic phase):



$$[L]_{(w)} = \frac{K_a \{HL^+\}_{(w)}}{[H_3O^+]} \quad (9)$$

In the mid 1900's, Rydberg developed the following equation, relating the partition constant of the complex (P_n) to the stability constant (β_n) and dissociation constant of the ligand:

$$D_M = \frac{P_1\beta_1[L]^n + P_{n+1}\beta_{n+1}[L]^{n+1} + \dots + P_N\beta_N[L]^N}{\sum_{n=0}^{n=N} \beta_n[L]^n} \quad (10)$$

He demonstrated that the partition constants of the complexes could be determined from Equation (10) on the condition that the composition of the complex being extracted is known.

After rearrangement of Equation (10), a simpler form of the Rydberg's equation is obtained:

$$\frac{[L]^n}{D_M} = \frac{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n}{P_n\beta_n} \quad (11)$$

which can be used for the calculation of both the stability constants and partition constants for any extraction system, as has been demonstrated by Lenarcik *et al.* in a number of his papers [5–19].

In Equations (10) and (11) n denotes the number of the metal complex which is so much hydrophobic that it is extracted first.

The procedure for determination of the equilibrium constants from extraction experiments is a novelty in the literature. It soon became recommendable, especially for sparingly soluble ligands for which the stability constants of their metal complexes could not be determined by the routinely used potentiometric method. The newly developed partition method in a liquid-liquid system applied in the determination of equilibrium constants has been verified through the comparison of stability constants with those previously determined by the potentiometric method.

The stability constants of Co(II), Ni(II), Cu(II) and Zn(II) complexes with 1-alkylimidazoles are summarized in Table 1.

Table 1

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

$\log \beta_n$	Co(II) [5]	Ni(II) [7]	Cu(II) [8]	Zn(II) [15]
$\log \beta_1$	$y=0.302x+1.653$	$y=0.161x+2.631$	4.15	$y=0.229x+1.986$
$\log \beta_2$	$y=0.342x+3.592$	$y=0.164x+5.290$	7.57	$y=0.229x+4.500$
$\log \beta_3$	$y=0.377x+4.881$	$y=0.164x+7.233$		$y=0.229x+6.700$
$\log \beta_4$	$y=0.434x+5.780$	$y=0.166x+8.653$		

x is the number of carbon atoms in an alkyl substituent in position 1 of the imidazole ring

The stability constants of 1-alkylimidazole complexes with transition metal ions are comparable with those of the unsubstituted imidazole. Their stabilities increase in the following order: Co(II), Zn(II), Cd(II), Ni(II) < Cu(II). In the case of the Zn(II) and Cu(II) complexes, configurational octahedron \rightleftharpoons tetrahedron equilibria were observed, manifesting themselves in an increase in the stability constants at 1 through 4 complexation steps, as they make up the sum of partial constants describing the stability of the octahedral and tetrahedral species [5, 15]. The stability constants of the Cu(II) complexes were alike for all the 1-alkylimidazole complexes studied, irrespective of the alkyl chain length and the increasing ligand basicity [8]. This is a surprising phenomenon because, in the previously studied 1-alkylimidazole complexes of Co(II), Ni(II) and Zn(II), the stability constants increased with the elongation of the 1-alkyl substituent [5, 7, 15]. Moreover, the stability constants of the Cu(II) complexes are much higher than those of their Co(II), Ni(II) and Zn(II) counterparts. This can be interpreted in terms of a strong impact of the $\pi_{M \rightarrow L}$ back-bonding on the interaction of the Cu(II) ion with the imidazole ring [8].

The stability constants of transition metal complexes with 1,2-dialkylimidazoles are collected in Table 2.

Table 2

Stability constants of transition metal complexes with 1,2-dialkylimidazoles

Ligand [references]	Me^{n+}	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
1,2-dimethylimidazole [22]	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
	Cu ²⁺	3.70	6.80	9.18	10.8

Ligand [references]	Me^{n+}	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$	$\log \beta_4$
1-ethyl-2-methylimidazole [22]	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	10.30
1-propyl-2-methylimidazole [22]	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	12.00
1-butyl-2-methylimidazole [22]	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	11.30
1-pentyl-2-methylimidazole [9, 16]	Zn ²⁺	3.07			
	Cu ²⁺	3.50	6.59	9.18	
1-hexyl-2-methylimidazole [9, 16]	Zn ²⁺	3.48	5.80	8.30	10.10
	Cu ²⁺	3.52	6.63	8.98	
1-octyl-2-methylimidazole [9, 16]	Zn ²⁺	4.45	6.80	9.10	
	Cu ²⁺	3.53	6.65	9.65	
1-nonyl-2-methylimidazole [9, 16]	Zn ²⁺	4.75	7.15	9.50	
1-decyl-2-methylimidazole [9, 16]	Zn ²⁺	5.10	7.75	9.90	
	Cu ²⁺	3.54	6.68	9.44	
1-dodecyl-2-methylimidazole [9, 16]	Zn ²⁺	5.40	8.25	10.30	10.90
	Cu ²⁺	3.58	6.75	9.37	

Alkyl substituents in α -position to the pyridine nitrogen of the 1,3-diazole ring strengthen its basicity, though at the same time they inhibit the formation of metal complexes due to steric hindrance. The steric effect suppresses the stability constants especially of the octahedral species, for instance, those of Ni(II) [22]. It can also affect the structure of the coordination polyhedron. In the case of the Co(II), Zn(II) and Cu(II) complexes, steric hindrance due to a 2-alkyl substituent promotes mostly the formation of tetrahedral species in aqueous solution, which are considerably less sensitive to its influence [16, 22]. This phenomenon is of major importance, because tetrahedral species, being less hydrated than octahedral ones, are more readily extractable. This feature was used, for instance, for the separation of Co(II) and Ni(II).

Elongation of the 1-alkyl substituent contributes, first of all, to the enhancement of the hydrophobic properties of the complex, thus facilitating its extraction [5, 7, 8, 15].

Bearing in mind the hydrophobic effect associated with the length of the 1-alkyl substituent on the one hand and the steric effect due to a small substituent in either position 2- or 4- on the other hand, it is possible to suggest optimum conditions for the separation of Co(II) and Ni(II), Cu(II) and Co(II) as well as Zn(II), Cd(II) and some other cations, depending on the original composition of the solution.

To sum up, it can be stated that the metal complexes with substituted imidazoles are rather poorly represented in the literature even though they have interesting properties, in contrast to those of the complexes with other ligands, e.g., benzimidazole, pyrazole and pyridine. Those unique properties can be utilized for the separation of metals using various separation techniques. In particular, those properties which differentiate the complex-forming capacities of the alkylimidazoles are:

- steric effect, caused by substituents in either position 2- or 4-
- hydrophobic effect, associated with the length of an alkyl substituent.

These features affect both the stability and structure of the coordination sphere of the metals, thus facilitating their separation.

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Translation into English by the Author

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