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EXAMINATION OF STABILITY AND EXTRACTION OF Cu(II) COMPLEXES OF BENZIMIDAZOLE DERIVATIVES BY MEANS OF COPPER ELECTRODE

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By means of the potentiometric methods based on simultaneous measurements of $[Cu^{2+}]$ and $[H_3O^+]$, respectively, the stability constants β_n and individual partition coefficients P_n of Cu(II) complexes of 2-hydroxymethylbenzimidazole, 2-methyl-4-azabenzimidazole and 7-methyl-4-azabenzimidazole have been determined. The stability differences of the complexes may be explained by the possible formation of five-membered chelate rings with 2-hydroxymethylbenzimidazole while the Cu(II) compounds with methyl derivatives of 4-azabenzimidazole are four-membered. The knowledge of the partition coefficients of particular complexes enables to determine magnitudes characterizing the extraction systems such as extraction coefficient D and percentage of extraction E %. All measurements were run at 25 ±0.1°C at a ionic strength I = 0.1 ($NaClO_4$, KNO_3).

Metodą potencjometryczną opartą na równoczesnych pomiarach $[Cu^{2+}]$ i $[H_3O^+]$ wyznaczono stałe trwałości oraz indywidualne współczynniki podziału kompleksów Cu(II) z 2-hydroksymetylobenzoimidazolem, 2-metylo-4-azabenzoimidazolem oraz 7-metylo-4-azabenzoimidazolem. Różnice w trwałości porównywanych kompleksów można wyjaśnić możliwością tworzenia przez 2-hydroksymetylobenzoimidazol pięcioczłonowych pierścieni chelatowych, podczas gdy połączenia Cu(II) z pochodnymi metylowymi 4-azabenzoimidazolu są czteroczłonowe. Znajomość współczyn-ników podziału poszczególnych kompleksów pozwoliła wyznaczyć wielkości charakteryzujące układy ekstrakcyjne, takie jak współczynnik ekstrakcji D oraz procent ekstrakcji E %. Wszystkie pomiary wykonano w temperaturze 25±0.1°C, przy stałej sile jonowej I = 0.1 ($NaClO_4$, KNO_3).

A transformation of metal cation into its neutral compound is a prerequisite for an efficient extraction of the metal cation from aqueous solution by means of

organic solvent. The larger, more hydrophobic, and more stable is metal complex, the easier will be its passing from aqueous to organic phase.

From our previous works it results that 4-azabenzimidazole and 2-hydroxymethylimidazole derivatives form stable chelate compounds with Cu(II) cations, which have explicit hydrophobic properties [1–4]. This fact enables us to use those ligands for selective extraction and separation of Cu(II) ions from the ions of other metals present in the aqueous solution. The aim of this work was to find how high can be the stability of the Cu(II) complexes of 2-methyl-4-azabenzimidazole (2-Me-4-azaBIm), 7-methyl-4-azabenzimidazole (7-Me-4-azaBIm), and 2-hydroxymethylbenzimidazole (2-MeOHBIm), and to examine the extraction process of those complexes by means of organic solvents. Basing on the results from this work and earlier works [5] we tried to elucidate an influence of the kind and localization of substituent in the ligand on the stability and extraction process of Cu(II) compounds with benzimidazole derivatives.

EXPERIMENTAL

Reagents and apparatus

7-Me-4-azaBIm (m.p. 255°C) was synthesized in the Organic Chemistry Department, Economy Academy, Wrocław [6], the 2-Me-4-azaBIm (m.p. 196–198°C) and 2-MeOHBIm (m.p. 173–175°C) were prepared at Pharmacology Institute, Gdańsk [7, 8].

Standard solutions of perchloric and nitric acids, as well as the solutions of sodium and cupric perchlorates and potassium and cupric nitrates were applied in the experiments.

Benzyl, isobutyl, and isoamyl alcohols were used besides cyclohexanone as the organic solvents in the experiments.

The pH measurements were carried out by means of the digital PHM 64 pH-meter (Radiometer, Copenhagen) equipped with the glass (G 202 C) and calomel (K 401) electrodes. Buffer solutions (pH = 4.01, and pH = 7.00, respectively) of the same company production were being used for the pH-meter calibration.

The concentration cell used was composed of two ion -selective copper electrodes supplied by the Department of Analytical Chemistry and Instrumental Analysis, UMCS University, Lublin. The e.m.f. values of the cell were measured by means of the PHM 84 digital pH-meter (Radiometer, Copenhagen).

Procedure

All the experiments were carried out at 25±0.1°C and constant ionic strength $I = 0.1$ ($NaClO_4$, KNO_3).

Stability constant values of the Cu(II) complexes were determined for the ligands investigated in aqueous solutions by means of a potentiometric method, in which both pH and e.m.f. values were measured simultaneously in the following concentration cell:

	$Cu(NO_3)_2$			ligand			
		0.1 mol l^{-1}		$Cu(NO_3)_2$	(+)Gl	0.1 mol l^{-1}	
(+)Cu	HNO_3	KNO3	(–)Cu	HNO_3		KNO_3	NEK(–) (1)
	KNO_3			KNO3			

The method used allowed us to determine directly both the free ligand [L] and central ion [Cu^{2+}] concentrations at equilibrium. A series of titrations was being carried out at constant concentrations of cupric ion (0.75–6 mmol l^{-1}) and protonated form of the ligand (5–10 mmol l^{-1}).

For the extraction experiments, two-phase mixtures obtained from two initial aqueous solutions and the organic solvent were prepared. The aqueous solution was composed of nitric acid and cupric nitrate (6 mmol l^{-1}) and potassium nitrate to maintain the constant ionic strength of $I = 0.1$ in the solution. The second phase was a heterocyclic base dissolved in the organic solvent. Both solutions were mixed with the solvent in different ratios in such a way that the volume ratio of the aqueous phase to the organic one was always 1:1. So obtained mixtures were then shaken for 20 min. No changes in the values of phase volumes were observed during the experiments. After establishing of the partition equilibrium the aqueous and organic phases were separated and placed in water hermostat to ensure the constant temperature (25°C) required for the measurements. Then, the pH and e.m.f. values were determined by measurements accomplished in the following concentration cell:

$$(+)\mathrm{Cu} \;\Big|\; \begin{matrix}\mathrm{Cu(NO_3)_2}\\ \mathrm{HNO_3}\\ \mathrm{KNO_3}\end{matrix} \;\Big\|\; \begin{matrix}0.1\ \mathrm{mol\ l^{-1}}\\ \mathrm{KNO_3}\end{matrix} \;\Big\|\; \begin{matrix}\text{aqueous phase}\\ \text{after extraction}\end{matrix} \;\Big|\; \mathrm{Cu}(-) \qquad (2)$$

If the measurements of stability and extraction were carried out for the Cu(II) complexes of 7-Me-4-azaBIm, the perchloric acid and sodium perchlorate had to be used instead nitrates in order to prevent unwanted precipitation.

Calculations

The stability constants values for Cu(II) complexes with the ligands investigated were calculated from the Leden's equation. Leden's function could be used effectively for calculations if the equilibrium values of ligand concentrations, [L], were known. These values were calculated for every pH measurement from the following equation:

$$[\mathrm{L}] = \frac{K_a(c_{\mathrm{HNO_3}} - [\mathrm{H_3O^+}])}{[\mathrm{H_3O^+}]} \qquad (3)$$

to which the determined values of dissociation constants, K_a, had been introduced.

The values of individual partition coefficients, P_n, could be calculated for the extraction of the Cu(II) compounds from the earlier derived [9] formula:

$$F_1 = \frac{\Phi - 1}{[\mathrm{L}]} = (1 + P_1)\beta_1 + (1 + P_2)\beta_2[\mathrm{L}] + \ldots \qquad (4)$$

The overall extraction coefficient, D, was calculated from the expression:

$$D = \sum_{n=1} P_n \alpha_n \qquad (5)$$

where α_1 and α_2 were the molar contributions of the individual complexes.

The molar extraction percentage, E %, was calculated, for every value of equilibrium concentration of the ligand, from the following expression:

$$E\% = \frac{D}{1+D} 100\% \tag{6}$$

All the calculations and approximations were accomplished numerically.

RESULTS AND DISCUSSION

Complex forming properties of benzimidazole derivatives

The values of exponents for dissociation constants determined for the protonated forms of 2-hydroxymethylbenzimidazole, 2-methyl-4-azabenzimidazole, and 7-methyl-4-azabenzimidazole, are listed in Table 1.

Table 1. The values of stability constants of Cu(II) complexes with benzimidazole derivatives

Ligand	pK_a	logβ_1	logβ_2	logβ_3	logβ_4
4-AzaBIm [1]	4.10	2.48	6.85	7.95	–
7-Me-4-azaBIm	4.54	3.91	7.68	10.44	–
2-Me-4-azaBIm	4.61	3.50	6.57	8.59	–
2-MeOHBIm	5.52	2.85	6.26	10.19	–
2-MeBIm [5]	6.52	2.42	4.69	–	–
2-NH_2BIm [5]	7.45	3.51	6.21	–	–
BIm [5]	5.66	3.26	6.02	8.36	10.21
Im [13]	7.12	4.31	7.84	10.76	12.90
2-MeIm [12]	8.05	3.35	6.38	9.23	–
1-Me-2-MeOHIm [3]	6.98	4.04	7.48	10.08	–

Stability of copper(II) complexes of those ligands was estimated after simultaneous measurements of electromotive force of the appropriate cell and the pH value for the solvent. For every pH and e.m.f. measurement, the equilibrium concentration of free ligand, [L], and the Leden's function values were calculated basing on the measured values and known values of the dissociation constant, K_a. It results from the successive approximations of the $F_n = f([L])$ function that three mononuclear complexes have been formed in every of the systems investigated. In Table 1 there are listed, beside the values for other earlier examined imidazole and benzimidazole derivatives, the actual, numerically calculated values of stability constants for the complexes formed. It results from Table 1 that the condensation of imidazole ring with the benzene or pyridine rings has reduced the basicity of the base nitrogen atom by 1.5 and 3 orders of magnitude, respec-

tively. The incorporation of methyl and amino groups into heterocyclic ring increases basicity of a compound, and incorporation of hydroxymethyl group lowers the K_a value. From the literature data [10, 11] it results that a presence of a substituent in molecule, adjacent to donor nitrogen atom, should lower the stability of the complex due to the appearance of steric effect. This supposition was proved to be valid for the copper(II) compounds with 2-methylbenzimidazole [5] and 2-methylimidazole [12]. The presence of hydroxymethyl group in those compounds have not reduced significantly, however, the stability of the complexes, just so, as if the —CH_2OH group had not played a part of the blocking group in the complex.

These observations are illustrated quantitatively by the values of the replacement constant, $(1/n)\log^*\beta_n$ (Table 2).

Table 2. The values of the replacement constant $(1/n)\log^*\beta_n$ for the complexes of Cu(II) with benzimidazole derivatives

Ligand	$\log^*\beta_1$	$(1/2)\log^*\beta_2$	$(1/3)\log^*\beta_3$	$(1/4)\log^*\beta_4$
4-AzaBIm	–1.62	–0.67	–1.45	–
7-Me-4-azaBIm	–0.63	–0.70	–1.06	–
2-Me-4-azaBIm	–1.11	–1.33	–1.75	–
2-MeOHBIm	–2.67	–2.39	–2.13	–
2-MeBIm	–4.10	–4.17	–	–
2-NH_2BIm	–3.94	–4.34	–	–
BIm	–2.40	–2.65	–2.87	–3.11
Im	–2.82	–3.22	–3.53	–3.90
2-MeIm	–4.70	–4.86	–4.97	–
1-Me-2-MeOHIm	–2.94	–3.24	–3.62	–

The $(1/n)\log^*\beta_n$ determines the complex stability after elimination of ligand basicity influence, and points to the others, different than σ-donor properties, reasons that can affect the complex stability

$$M + nHL^+ + nH_2O \rightleftharpoons ML_n + nH_3O^+$$

$$^*\beta_n = \frac{[ML_n][H_3O^+]^n}{[M][HL^+]^n} \tag{7}$$

$$(1/n)\log^*\beta_n = (1/n)\log\beta_n - pK_a \tag{8}$$

The low $(1/n)\log^*\beta_n$ values obtained for Cu(II) complexes of 2-methylimidazole, 2-methylbenzimidazole, and 2-aminobenzimidazole confirm the occurrence of steric effect in those compounds. The lowering of $(1/n)\log^*\beta_n$ values can also be partially caused by a reduction of π-acceptor properties of the ligands due to inductive effect interaction of —NH_2 and —CH_3 groups. An incorporation of the —CH_2OH group in a close proximity of donor nitrogen atom in imidazole and benzimidazole practically does not change the $(1/n)\log^*\beta_n$ value, and this fact

confirms a supposition that this substituent does not play the part of blocking group indeed. This phenomenon can be explained by a possibility of appearance of additional interaction between the Cu(II) ion and the oxygen atom of —CH_2OH group, and formation, not too stable, five-membered chelate rings. A localization of the donor nitrogen atoms in 4-azabenzimidazole and its methyl derivatives enables, through influence of those atoms, a formation of four-membered chelate rings. The formation of such rings had been observed earlier, for Cu(II) complexes of 4-aza- and 7-methyl-4-azabenzimidazoles [1, 2]. The low values $(1/n)\log^*\beta_n$ parameter for the Cu(II) compounds with 2-methyl-4-azabenzimidazole testify to the formation of chelate complexes for this group of the compounds. The presence of methyl groups in various positions in imidazole and pyridine rings has, therefore, no significant effect on the stability of the respective complexes with Cu(II) cations.

Examination of extraction of Cu(II) complexes with benzimidazole derivatives

Extraction experiments were based on the potentiometric measurements of equilibrium concentrations of Cu(II) cation and ligand in the aqueous phase, after reaching the partition equilibrium. The concentration of Cu(II) cation in equilibrium was determined by measurement of e.m.f. of the cell (2) and the equilibrium concentration of ligand [L] after extraction was calculated from the pH measurements from eq. (3). Individual partition coefficients P_n of the complexes were determined with a least-square method by means of approximation, with the polynoms of $(n-1)$ degree of $F_1 = f([L])$ dependence [eq. (4)]. The numerically calculated P_n values for the Cu(II) complexes of 7-Me-4-azaBIm, 2-Me-4-azaBIm, and 2-MeOHBIm extracted with benzyl, isobutyl, isoamyl alcohols and cyclohexanone, has been listed in Table 3.

Table 3. The values of individual partition coefficients, P_n, for the complexes of Cu(II) with benzimidazole derivatives

Ligand	Solvent	P_1	P_2	P_3
7-Me-4-azaBIm	benzyl alcohol	–	–	2.1
	isoamyl alcohol	–	2.3	–
	cyclohexanone	–	102.0	–
2-Me-4-azaBIm	benzyl alcohol	15.9	–	–
	isobutyl alcohol	31.7	–	–
	cyclohexanone	111.1	43.0	–
2-MeOHBIm	benzyl alcohol	23.2	–	–
	isobutyl alcohol	0.8	6.7	7.8
	cyclohexanone	21.1	29.3	5.3

Individual partition coefficients, P_n, describe a chance of the passage of respective complexes to the organic phase during its contact with aqueous phase. It results from the P_n values obtained, that in case of 7-Me-4-azaBIm only one complex, containing two or three ligand molecules in its co-ordination sphere, has passed, irrespective of the kind of the solvent used, to the organic phase. If the remaining bases were used, the different number of the successive complexes (one, two or three) could undergo extraction. The highest values of the partition coefficients were obtained for cyclohexanone. The extraction abilities of the different alcohols used proved to be close to one another, and to be low in comparison with that obtained when cyclohexanone had been used.

The P_n values obtained were helpful for calculation of other parameters characterizing metal extraction process, such as the extraction coefficient D [eq. (5)] and molar extraction percentage E % [eq.(6)] of the metal ions. The obtained results have been shown in form of extraction curves log $D = f$(pH) (Fig. 1) and E % = f(pH) (Fig. 2). The diagrams confirm the fact that cyclohexanone is the best solvent among those used in the systems under investigation. Using the solvents discussed, one can obtain the 50% of extraction (D = 1) of Cu(II) ions at pH values ranging between 3.2 and 3.5 units.

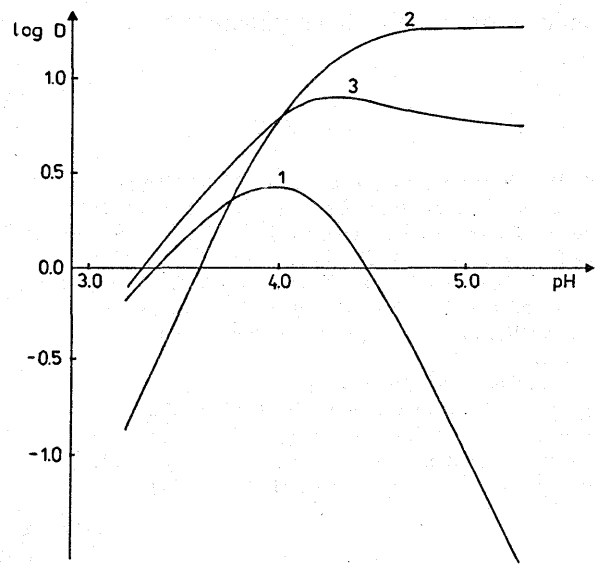

Fig. 1. Dependence of log$D$ on pH for the extraction of Cu(II) complexes with 2-hydroxymethylbenzimidazole: 1 – benzyl alcohol; 2 – isobutyl alcohol; 3 – cyclohexanone

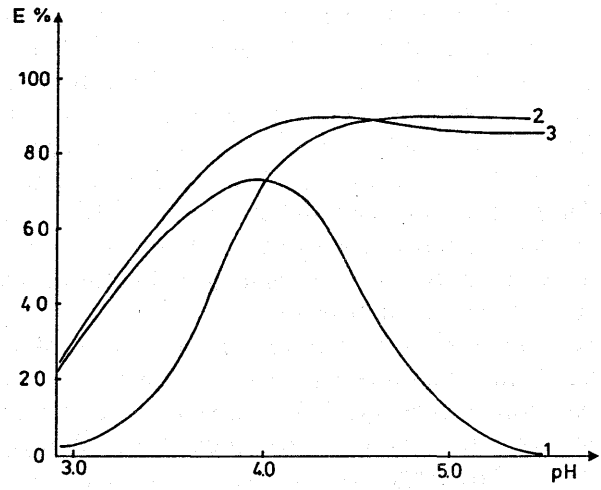

Fig. 2. The extraction efficiency (E %) of complexes of Cu(II) with 2-hydroxymethylbenzimidazole as a function of the pH solution : 1 – benzyl alcohol; 2 – isobutyl alcohol; 3 – cyclohexanone

The results obtained confirm the high extraction abilities of the ligands investigated in relation to the Cu(II) ions due to a possibility of formation with this metal the stable, hydrophobic chelate compounds.

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