Bydgoszcz, 16.12.2016 r.

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Central Commission
for Degrees and Titles

APPLICATION OF ALKYL IMIDAZOLE DERIVATIVES FOR SEPARATION AND RECOVERY OF CHOSEN HEAVY METAL IONS FROM MODEL AND REAL ENVIRONMENTAL SOLUTIONS

Załącznik 3. AUTOREFERAT DO WNIOSKU HABILITACYJNEGO
w języku angielskim

Appendix 3. Summary of Professional Accomplishments

Diplomas and academic degrees:

1999 obtaining the degree of **Philosophy Doctor in Chemical Sciences** in the field of chemical technology – Faculty of Chemical Technology, Poznań University of Technology

1987 completion of post-graduate studies in the field of **environmental protection**, Wrocław University of Technology, Faculty of Chemistry

1978 obtaining the diploma of completion of studies for a **Master's degree** in the Faculty of Mathematics, Physics and Chemistry, Lodz University of Technology, area: chemistry

Details of previous employment in research units:

1991–1995 Assistant Lecturer– Department of Chemical Technology of Environmental Protection, Academy of Technology and Agriculture in Bydgoszcz

1996-1999 Assistant Lecturer– Department of Coordination Chemistry, Academy of Technology and Agriculture [ATR] in Bydgoszcz

since 1999 Assistant Professor – Department of Inorganic Chemistry in UTP University of Sciences and Technology (previously ATR) in Bydgoszcz

SCIENTIFIC ACTIVITY:

- author or co-author of **24** research papers, including **20** post-doctoral papers, **20** of which are those listed in the Philadelphia List

- **total Impact Factor** according to Journal Citation Report for post-doctoral papers: IF = **18.616** (referring to year of publishing according to Web of Science), average IF per paper (post-doctoral) = **0.93**

- co-author of **13** chapters in monographs, 5 of which are those published in foreign conference proceedings

- total **number of citations** in papers according to Web of Science: **110** (excluding self-citation: **23**), October 2016

- **Hirsch index** = **7** (according to Web of Science, October 2016)

- **total Impact Factor** of the papers my habilitation dissertation was based on: **11.607** (in accordance with year of publication), average IF per paper = **0.97**, average personal contribution in the paper: **81.82 %**

- **member of Organization Committee of the Foreign Conferences** *International Symposium on Physicochemical Methods of Separations* "Ars Separatoria" in the years 2005-2010

- **Assistant Chief Editor** of the journal „Ars Separatora Acta" in the years 2008 – 2011

- **Chief Editor** of the scientific journal „Ars Separatora Acta" since 2012, now listed in the List of Ministry of Science and Higher Education in Part B item 214, ISSN 1731-6340, score 6

- **assistant promoter** of the doctoral dissertation of Agnieszka Wasilewska, M.A.; promoter: Włodzimierz Urbaniak, D.Sc. (Adam Mickiewicz University); working title of the doctoral dissertation: *The obtaining and the properties of new, type1:2, colored metal-complex compounds containing derivatives of 1,2-diazoxy-4-naphthalenesulfonic acid and derivatives of β-diketones* (defense is scheduled in June 2017)

Application of alkyl imidazole derivatives for separation and recovery of chosen heavy metal ions from model and real environmental solutions

Introduction

Industrial waste have been a burden to the environment for many years. Huge amounts of waste are generated by the metallurgic, chemical, paper making industries, power engineering based on coal and lignite combustion, transportation, municipal services, waste dumping sites, ore mining and by agriculture (fertilizers and plant protection agents). More often than not, such waste in the form of dust, sludge or liquids is introduced – directly or indirectly – into the environment, especially in developing countries. The waste is a serious threat to the environment because it frequently has a content of heavy metals (Cu, Co, Cr, Cd, Fe, Zn, Pb, Sn, Hg, Mn, Ni, Mo). In contrast to organic contaminants heavy metals, such as Hg, Pb, Cd, Tl, Ba, are not biodegradable and they tend to bioaccumulate. Some of the heavy metals (Fe, Zn, Cu, Mn, Co, Cr) are regular, indispensable components of living organisms, other ones are harmful, toxic or cancerogenic, depending on their form (speciation) [1-3]. Their effect on organisms depends on their concentrations. The phenomenon is illustrated by Bertrand curves [4]. Those heavy metals which function as microelements in the body are usually present in trace amounts which are specific to a given species. Both a deficiency and excess of the microelements have a harmful effect on the organisms. On the other hand, metals such as Hg, Cd, Pb, Cr, Ni, Zn, Cu are considered to be toxic and are commonly present pollutants of the ecosystem. The most strongly-toxic properties characterize water-soluble, strongly-dissociating inorganic metal compounds because they easily pass through the cell membranes and get into the organs [5], most often as metal aqua complexes ($[M(H_2O)_6]^{2+}$, $[M(H_2O)_6]^{3+}$).

On the other hand, heavy metals are of high importance in practice, being indispensable in the life and functioning of man. Some of their uses include the production of machine components, sheet metal plates, structures and buildings, batteries, pigments, they are also used as additives to alloys as well as in electroplating and jewelry. Under the circumstances, efforts to recover the metals from solid and liquid waste are encouraged. Therefore, waste with a content of heavy metals becomes a starting material for the production of metals of economic value [6, 7]. The process is beneficial for the environment, enabling reclassification of waste to less hazardous categories after the recovery of heavy metals from it. The best developed countries have amended their national environmental protection laws and implemented more stringent standards, establishing the minimum permissible amounts of pollution relating to the air, water, and soil. Poland is also compelled to carry out new, specific analyses to efficiently use natural resources and recover raw materials from waste [8]. This encourages the development of new research techniques and change of attitude to heavy metals recovery from industrial waste [8, 9]. The recovery of valuable metals from solid and liquid waste saves considerable amounts of natural resources. The demand on metals, especially non-ferrous metals, has been growing regularly, as indicated by their high sale prices. The recent sale prices of selected metals are shown in Table 1.

Table 1. The price of 1 Mg of selected metals in USD as at 31.10.2016 according to [10]

copper	lead	zinc	tin	nickel
4862.50	2052.00	2444.00	20990.00	10445.00

Methods to obtain metals

Favorable conditions for investigating new ways to obtain metals are accounted for by high prices of pure metals [11-14]. There are two categories of methods to obtain methods:

- o pyrometallurgic methods – based on high-temperature processing of metal-bearing starting materials [12, 13],
- o hydrometallurgic methods – based on the use of physicochemical techniques for the separation of metals from aqueous solutions [14-20].

The choice of technology depends on the content of useful metals in the feedstock.

Most of gold, palladium, platinum metals and lanthanides are obtained by means of hydrometallurgic methods. Since recently, copper, zinc, nickel, and cobalt have also belonged in that group.

The largest volume of metals are now obtained directly from metal ores by means of pyrometallurgic methods (iron, copper, lead, zinc, nickel).

In hydrometallurgy, the most important methods for ion separation from aqueous solutions include:
- solvent extraction [13, 14, 17-20, H-1−H-7],
- ion exchange [21-23],
- ion floatation [24, 25],
- transport through various membranes [26, 27, H-8−H-10].

Such methods are an effective supplement to metallurgic processes in the pretreatment of raw materials or in the treatment of production waste. More than that, they are also better for the environment, not being sources of emission of harmful gas and dust. In such processes, the separation of metal ions in aqueous solutions is especially worth attention because it is essential for the purity of the resulting products. It is usually carried out by solvent extraction [13, 14, 17-20, H-1−H-7], ion exchange, and transport across membranes.

My choice of the appropriate technique for the selective separation of metals from aqueous model solutions and waste solutions was the solvent extraction method and the method of transport across liquid polymer membranes.

My work was dedicated mainly to the recovery of valuable though noxious metals from metal-bearing waste, such as slag, dust, sludge and liquid waste.

My studies on the subject were intended to find effective methods and optimum conditions for the separation of metal ions by means of model solutions [H-1−H-7, 28-40]. My experience was employed in metal recovery from liquid waste by deliberately selecting leaching solutions and effectively matching them with the appropriate extractants [41-43, H-11, H-12]. This enabled the recovery of more than 90% of the metal content of dumped metallurgic waste [41, 42, H-11, H-12].

Solvent extraction

In a number of scientific papers, solvent extraction is demonstrated to be a suitable method for the separation or elimination of metal ions from various aqueous solutions, especially from industrial liquid waste or from spent leaching solutions, applied to ores or waste [43, 44, H-11].

The development of extraction methods for the separation of metals results in the need to search for new, specific extractants, characterized by favorable properties such as selectivity, rate of extraction and re-extraction, low solubility in the aqueous phase, and low cost of synthesis. These requirements are satisfied by carboxylic acids, derivatives of phosphoric acid, derivatives of acid amides, trioctylamine, alkylphenylamines, complex oximes, amides, crown ethers, derivatives of ketones, derivatives of pyridine, as well as alkyl derivatives of imidazole [13, 14, 44-57, H-1−H-7]. Extraction is a solvent-based process. The solvent is compulsorily hydrophobic and has an ability to dissolve the specific extractant [44, 58]. Its availability is also very important from the economic point of view, therefore, hydrocarbon-based solvents (such as kerosene, gasoline) are predominant. In the environmental aspect, a solvent must be biodegradable (such as long-chain alkyl alcohols).

For my own studies on the properties of complexes of metal cations with alkylimidazoles, I chose extraction – the method of partition in a liquid-liquid system – since the availability of research techniques applicable to not-readily water soluble compounds is very limited. The partition method, described by Rydberg [59], allows to establish how many complexes are formed in the aqueous solution and to find their corresponding stability constants. Moreover, it allows to establish the number and composition of complexes passing into the organic phase and to find their corresponding partition constants for partition between the aqueous and the organic phases.

The method to find the equilibrium constants based on extraction studies is a scientific novelty in the literature globally. It is particularly useful for not-readily water soluble ligands. for which the typically used potentiometric method to determine stability constants for their complexes with metals is not applicable. The use of a new partition method in a liquid-liquid system for the establishing of equilibrium constants has been verified many times and the obtained stability constants for the complexes were similar to those found earlier by the potentiometric method, used for water-soluble ligands [29-39, 60-66, H-1−H-7].

The issue of speciation of metals in the solutions of interest was not considered because the methods used in the study did not enable the precise establishing of the speciation forms, even though the forms did have an effect on the extraction process. The problem is complex enough and the explanation of the effect well deserves to be the subject of another habilitation dissertation.

Conventional methods, such as solvent extraction or ion exchange, are not suitable for the treatment of large volumes of water with low heavy metal contents (liquid waste, pickling solutions and products of leaching of metal-bearing materials). Membrane-based techniques are more effective in such cases.

Membrane techniques

The use of membrane techniques in the separation of metal ions from aqueous solutions is becoming more and more popular. Membrane techniques, such as reverse osmosis, nanofiltration, ultrafiltration, electrodialysis are increasingly being used for purification and desalination of water on an industrial scale [67-70]. Liquid membranes, in which extraction and re-extraction take place at the same time, are an interesting group. In comparison with conventional methods for the separation of metal ions from aqueous solutions, ionic transport through liquid membranes has several advantages. A liquid membrane is a separate, organic phase that separates two different aqueous phases. Membrane processes are characterized by a better use of the ion carrier (extractant) in the organic phase (membrane) in comparison with conventional extraction systems [71-73]. Furthermore avoid environmental risks of solubility in water and toxic solvents. This type of membrane used with other studies of selective separation of Zn, Cu, Co and Ni with model solutions.

Polymer inclusion membranes (PIMs) show the highest stability among all types of liquid membranes. In addition, the use of transport through PIMs has the advantage over extraction processes because they do not use non-water miscible, often volatile, toxic solvents (toluene, benzene, halogen derivatives of methane, higher alcohols, ketones, and esters). Inclusion membranes are obtained by casting the solution of a suitable polymer, plasticizer, and ion carrier over a neutral substrate. Selectivity and stability of the performance of liquid membranes largely depend on the physicochemical properties of the plasticizer and the ion carrier [72, 73]. A majority of commercial extractants, which were previously used as non-ferrous metal ion carriers during the transport through liquid membranes do not have the sufficient selectivity to a number of metals. Therefore, it is necessary to find new, selective carriers, enabling the separation of metal ions from aqueous solutions.

The experience I gained in the investigation and analysis of the processes taking place in solvent extraction processes by means of alkyl derivatives of imidazole has enabled me to establish the optimum conditions for conducting the membrane transport process as well as to select a suitable carrier (alkylimidazole) for the selective recovery of the desired metal from mixtures.

A membrane process based on polymer inclusion membranes (PIMs) enables two objectives to be gained: to purify metal cation solutions and to separate their mixtures [74-88, H-8−H-10]. Whether the two objectives are gained depends on the correct choice of the metal ion carrier and on the experimental conditions.

As extractants of solvent extraction and as carriers for membrane processes, I have chosen sparingly soluble in water alkyl derivatives of imidazoles.

The properties of alkyl derivatives of imidazole

For my own studies, I chose a ligand group in the form of alkyl derivatives of imidazole, of which the molecular formula is shown in Fig. 1.
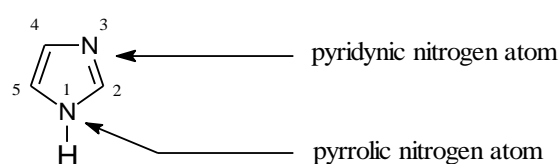

Fig. 1. Chemical formula of imidazole

That group of stable, heterocyclic organic bases for the solvent extraction of cations, such as Cu(II), Hg(II), Co(II), Pb(II) and Zn(II) were recommended in patents [55, 56]. Specifically, the compounds proposed therein were complex imidazole derivatives containing in their substituents in position 1,2 or 1,2,4,5 large alkyl groups having 6 to 40 carbon atoms or cycloalkyl groups composed of 5-12 carbon atoms.

For my model studies, I chose extractants in the form of compounds belonging to the homologous series of 1-alkylimidazoles, 2-alkylimidazoles, 1,2-dialkylimidazoles and 1,4-dialkylimidazoles, with rather small alkyl substituents containing 4 to 16 carbon atoms [28-40, 63,74-81, 84, 85, 87−89, H-1 −H-12]. Starting from alkyl derivatives containing five carbon atoms in their substituent, the compounds are not readily water soluble, which is of practical value, enabling them to be used in the solvent extraction of metals (as extractants) or in other separation methods, for instance as carriers in PIMs.

The basicity of the electron pair of the pyridine nitrogen atom can be modified [28-40, 60-66, 90, H-1 −H-6] by introducing appropriate substituents in the imidazole ring (Table 2).

Table 2. Change in the basicity of alkylimidazoles vs. the position of alkyl groups according to [91], at a temperature of 25°C, ionic strength of aqueous solution I=0.5 mol/dm^3 (KNO$_3$)

	linear equation describing the basicity $pK_a = an+b$
1-alkylimidazole	$pK_a = 0.0222\ n + 7.165$
1,2-dialkylimidazole	$pK_a = 0.0432\ n + 8.01$
1,2,4-trialkylimidazole	$pK_a = 0.0503\ n + 8.46$
1,4-dialkylimidazole	$pK_a = 0.0279\ n + 7.79$
2-alkylimidazole	$pK_a = 0.0349\ n + 7.87$

n-means the sum of carbon atoms in the alkyl substituents

The value of the absolute term (constant "b") in the linear equations in Table 2 ($pK_a = an +b$) may be used for comparing the two series with respect to their basicity. The basicity of imidazole molecule at 25°C is 7.14 [92].

The alkyl group's location in position 1 in the imidazole molecule accounts for its reduced water solubility (hydrophobic effect) and just slightly improves its basicity and complex-forming properties, without affecting the participation of component $\pi_{M \to L}$ in complex combinations with metal cations.

The introduction of even a small alkyl group in positions 2 or 4 of the imidazole ring results in the molecule having a much higher basicity (Table 2). 2-alkylimidazole and 4-alkylimidazole are harder bases in comparison with imidazole and 1-alkylimidazoles. In harder bases, the participation of component $\pi_{M \to L}$ in the formation of complex compounds is reduced. The group in position α with respect to the donor (pyridine) nitrogen atom (positions 2 or 4) in alkylimidazoles is a steric hindrance in the formation of complexes with metal cations, leading eventually to their lower stability constants (so-called "steric effect"). The effect of steric hindrance also depends on the properties of metal ions because it hinders the formation of octahedral or nearly-octahedral complexes. However, the steric effect does not hinder the formation of tetrahedral or nearly-tetrahedral complexes and, which is more, it may even increase the summary stability constants of certain consequent complexes ML$_n$. The phenomenon may be observed for those steps of complexation in which, tetrahedral or nearly-tetrahedral combinations $[M(H_2O)_{4-n}L_n]^{2+}$ are formed in the solution, in addition to octahedral complexes of the type $[M(H_2O)_{6-n}L_n]^{2+}$:

$$[M(H_2O)_6]^{2+} + nL \leftrightarrow [M(H_2O)_{4-n}L_n]^{2+} + (n+2)H_2O \tag{1}$$
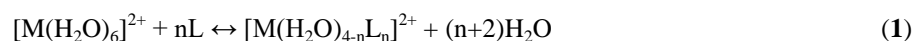
In that case, the summary stability constant β_n is the sum of stability constants of the 6-coordination complex ($\beta_{n(o)}$) and the 4-coordination complex ($\beta_{n(t)}$) ($\beta_n = \beta_n(o) + \beta_{n(t)}$) [61, 63, 65, 66, H-2 −H-6].

Subject of my own studies

My interest as a scientist was:
- metalliferous waste - sludge from the production of zinc and copper. Practical use of an alkyl derivative of imidazole as extractant for recovering zinc from metallurgic waste by solvent extraction. These wastes can be found in heaps at the premises of the producing zinc and copper. The one consists of As, Cd, Pb, Cu, Ni, Zn, Cr.
- aqueous solutions (nitrate, sulfate and chloride) of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} cations. The metals are in the first series of transition metals have different numbers of electrons in the 3d subshell.
- not-readily water soluble alkyl derivatives of imidazole, both those on extraction processes and on transport through membranes, were used as the ligands. Alkylimidazole are heterocyclic aromatic bases of which the complex-forming and extraction properties, as shown above, can be modified by changing the size and location of the substituents in the imidazole ring. Such modification has an effect both on the basic properties (donor properties) and solubility of the molecule but it may as well cause steric hindrance in the complexing process. These effects lead to changes in the stability and structure of the complexes formed by alkylimidazoles with metal cations.

Aim of work

It was the main objective of my studies to search for optimum methods and conditions for the recovery of heavy metals from metal-bearing waste by means of solvent extraction and membrane techniques. To achieve the objective, I searched for differences in formation processes, stabilities, structures and extractive properties of metal cation complexes in the model solutions. I assumed that the differences could be due to the choice of a suitable extractant (alkyl derivative of imidazole) accompanying a correctly matched solvent. The experience I gained in my studies of the model solutions was helpful in selecting the appropriate extractant, providing the effective, selective recovery of the desirable metals from industrial waste.

The research objectives were achieved by:

1. performing extraction studies in an aqueous phase-organic phase system; in order to obtain information on optimal conditions relevant for the recovery of metals
2. recording visible-range absorption spectra of the aqueous-organic phases in order to obtain information on the amount and structure of forming complexes;
3. examine the possibility of separation and recovery of palladium from a mixture of Cu^{2+}-Pd^{2+}-Co^{2+}-Ni^{2+} using alkyl imidazole derivatives as extractants
4. investigating the possibilities of separation and recovery zinc and copper of Cu^{2+}-Zn^{2+}-Cd^{2+}-Co^{2+}-Ni^{2+} mixtures by means of alkyl derivatives of imidazole as metal carriers in polymer inclusion membranes to recover copper or zinc;
5. practical use of an alkyl derivative of imidazole as extractant for recovering zinc from metallurgic waste by solvent extraction.

Results and discussion of my own studies

My habilitation dissertation is based on 12 papers [H-1–H-12], most of which have been published in the journal Separation Science and Technology and four patent applications [92-95]. Six of them relate to studies on the composition, stability, structure and extraction properties of Cu(II) complexes [H-1 –H-5] and Co(II) complexes (H-6) with various alkylimidazoles. All my extraction studies were carried out at a temperature of $25^{o}C$ at a constant aqueous-solution ionic strength I = 0.5 M, maintained by addition of nitric(V) acid and potassium nitrate(V). The problem of speciation of the metals in the solutions was not considered because of its vastness and complexity. It can be tackled later on in my continued studies on the subject, e.g., using X-radiation in solution. In [H-7], I discussed the separation of palladium from a mixture of Co^{2+}-Ni^{2+}-Cu^{2+}-Pd^{2+} ions by means of solvent

extraction, using 1-hexyl-2-methylimidazole as the extractant. My experience in the extraction studies enabled me to identify environmentally optimum conditions for membrane separation processes.

Papers which followed were dedicated to the recovery of zinc from spent metallurgical sludge arising in the production of zinc [H-11] and copper [H-12] using solvent extraction, which is essential in the aspect of environmental protection. Having examined the qualitative composition of waste, owing to my experience in the subject of model solutions, I was able to correctly match the extractants with the pH of the spent leaching solution. The processes were conducted at ambient temperature, which also is environmentally friendly. Patents were applied for in the Polish Patent Office and the European Patent Office for the methods of selective separation of metals from waste, as discussed in [H-11, H-12, 93-96].

Studies on extraction

• **1-alkylimidazoles as extractants of Cu(II) ions**

In paper [H-1], I focused on the complexation of 1–alkylimidazoles with Cu(II). The selected group of 1-alkylimidazoles comprised 10 compounds of which the formulas are shown in Fig. 2.

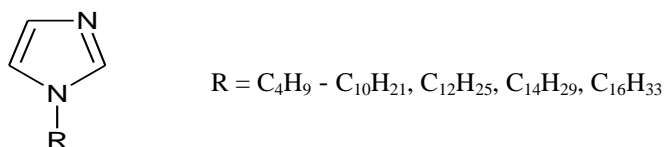$$R = C_4H_9 - C_{10}H_{21}, C_{12}H_{25}, C_{14}H_{29}, C_{16}H_{33}$$

Fig. 2. The 1-alkylimidazoles used in the studies in work [H-1]

The length of the carbon chain in the alkyl substituent varied from n-butyl to n-hexadecyl. The tests were carried out by the trial-and-error, using 8 effective, non-water miscible solvents: benzene, toluene, p-xylene, tetrahydronaphthalene, methylene chloride, chloroform, 2-ethylhexanol and cyclohexanol. The 54 extraction systems tested were composed of an aqueous phase (solution of Cu^{2+} ions) and an organic phase, comprising the extractant (1-alkylimidazole), dissolved in the organic solvent.

According to Bjerrum [97], metal ions (M^{z+}) with complex forming properties gradually fix anions or neutral molecules (L) which may form a coordination bond with the metal ions (Equation (2)):

$$[M (H_2O)_{N-n+1}L_{n-1}]^{z+} + L \leftrightarrow [M(H_2O)_{N-n}L_n]^{z+} + H_2O \tag{2}$$

in which N−is the ion's maximum coordination number.

This leads to established equilibria of the gradual formation of single-core complexes (ML, $ML_2...ML_N$).

The process of Cu^{2+} complex formation in both phases was investigated by measuring the pH of the aqueous phase and the concentration of the metal residue in it. The results are reported in the form of graphs illustrating the relationship $logD_M=f(pH)$ (extraction curves) individually for each solvent used in the tests. Representative graphs of this type for toluene and methylene chloride are shown in Figures 1 and 2 in the paper [H-1]. In my own studies, it was shown that, for all the solvents tested, the extraction curves tend to shift toward lower pH values as the length of the alkyl group in position 1 of the ligand molecule increases. This means that intensified hydrophobic properties of the extractant molecule lead to an intensified extraction of Cu^{2+}. In other words, increasing the length of the alkyl group results in that the passage of copper into the organic phase takes place at lower pH values; this means that the process requires lower concentrations of the extractant (ligand) in both phases. It is very useful from the practical point of view.

The extraction process runs at pH < 7 for the aqueous phase. For the toluene solvent, the pH is between 4.25 and 5.5; for methylene chloride the extraction curves cover a very wide range of pH – from 1.9 to 6.45. For Cu^{2+} complexes [with] 1-butylimidazole and 1-hexadecylimidazole, differences in the values of parameter $pH_{1/2}$, denoting a 50% metal extraction from the solution, are around 1 pH unit for toluene and around 2 pH units for methylene chloride; this can be made use of in practice.

Moreover, it was shown that the cation $[Cu(H_2O)_6]^{2+}$ forms only two complexes (ML and ML_2), having the following compositions $[Cu(H_2O)_5L]^{2+}$ and $[Cu(H_2O)_4L_2]^{2+}$, with the 1-alkylimidazoles of

interest. Both complexes have a chance to pass into the organic phase, as indicated by their high partition constants (Table 1 in the paper H-1). Their stability constants, as found by the method of partition in the liquid-liquid system, do not depend on the length of the alkyl group. This is rather surprising because stability constants for the complexes Co^{2+} [60], Ni^{2+} [62] and Zn^{2+} [64] with the ligands increase linearly with the length of the alkyl group, as indicated by the data in Table 3. This is in contradiction to the known theory that increasing ligand basicities lead to improved stabilities of complexes [98].

Table 3. Stability constants of transition metal complexes with 1-alkylimidazoles in aqueous solutions, at a temperature of 25°C, ionic strength of solution I= 0.5 M (KNO$_3$)

$\log \beta_n$	Co^{2+} [60]	Ni^{2+} [62]	Cu^{2+} [H-1]	Zn^{2+} [64]
$\log \beta_1$	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 - number of carbon atoms in alkyl substituent

Cu^{2+} complexes with 1-alkylimidazoles fix each two nitrate anions; this enables them to pass into the organic phase as electrically neutral combinations $[M(H_2O)_3L(NO_3)_2]$ and $[M(H_2O)_2L_2(NO_3)_2]$ because – as shown in paper [99] – nitrate ions are able to form coordination bonds. Possibly, water molecules are replaced by the organic solvent molecules when passing into the organic phase. Chances of passage into the organic phase are illustrated by the partition constants P_1 and P_2, found for the Cu^{2+} complexes being formed. Their values are high and increasing with the length of the alkyl group in position 1 of the extractant (ligand) (Figures 3 and 4 in H-1) and they depend on the organic solvent type. The lowest partition constants were obtained for p-xylene ($\log P_1 \approx 2$, $\log P_2 \approx 2 - 3$). The findings are a significant contribution to studies on Cu^{2+} complexes being formed in aqueous and organic solutions.

- **1-alkyl-2-methylimidazoles as extractants of Cu(II) ions**

Paper [H-2] describes findings of studies on the complexation of 1-alkyl-2-methylimidazoles (Fig. 3) with Cu^{2+} cations.
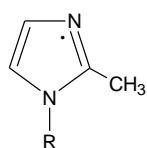
R = -C$_4$H$_9$, iso-C$_4$H$_9$, -C$_5$H$_{11}$, iso-C$_5$H$_{11}$, -C$_6$H$_{13}$, -C$_8$H$_{17}$, -C$_{10}$H$_{21}$, -C$_{12}$H$_{25}$

Fig. 3. The 1-alkyl-2-methylimidazoles used in the studies in work [H-2]

Their objective was to establish the effect of the length of alkyl group in position 1 (that is, the increase in the ligand hydrophobicity) and the steric effect (resulting from the presence of a substituent in position 2) on the stability and structure of the Cu^{2+} complexes being formed as well as their passage into the organic phase.

The solvents, selected for use in the tests, included: 2-ethylhexanol, methylene chloride, chloroform and toluene (only for 1-dodecyl-2-methylimidazole). The results of partition of the Cu(II) complexes with the ligands are shown in the form of extraction curves ($\log D_M = f(pH)$). It was shown that the curves tend to shift toward lower pH values with increasing ligand hydrophobicity. A similar phenomenon was observed in the previous work [H-1]. However, for the most hydrophobic ligands in the 1-alkyl-2-methylimidazoles series, the extraction curves are very close, some of them overlap each other (Fig. 1-3 in work H-2). The Cu^{2+} complexes with 1-*iso*butyl- and 1-*iso*pentyl-2-methylimidazole are worst extracted. Their corresponding extraction curves are located at the highest pH values for all

of the solvents tested. The lowest values of partition ratio of the metal (D_M) between the aqueous and organic phases were obtained for them. The highest values $\log D_M$ (approx. 1.5) for such combinations were obtained for extraction with methylene chloride (Fig. 2 in work H-2). For chloroform and 2-ethylhexanol, the values of $\log D_M$ are approx. 0.1 and 0.4, respectively (Fig. 1 and 3 in work H-2).

Moreover, it was shown that, owing to the steric effect (methyl group in position 2) the stability of complexes of 1-alkyl-2-methylimidazoles with Cu^{2+} was lower by, roughly, one order of magnitude in comparison with 1-alkylimidazoles [H-1], although the former ligands are stronger bases. The values of stability constants (β_n) of the complexes of interest do not depend on the length of the alkyl group in position 1, like for the 1-alkylimidazoles series. This proves that the participation of the $\pi_{M \to L}$ bond for complexes of 1-alkyl-2-methylimidazoles with Cu^{2+} continues to be quite remarkable. 1-Alkyl-2-methylimidazoles with Cu^{2+} ions form three consequent complexes ML, ML_2 and ML_3, of which the partition constants for partition between the aqueous and organic phase (P_n) increase in the order $P1 < P_2 < P_3$ and they depend on hydrophobicity and the specific solvent (Fig. 4 in work H-2). The highest values of partition constants P_1, P_2 and P_3 were obtained for the system Cu^{2+}–1-dodecyl-2-methylimidazole – methylene chloride and they are: 48, 432 and 980, respectively.

In order to verify the values of stability constants and partition constants for the system Cu^{2+}-1-hexyl-2-methylimidazole-toluene, the values of partition coefficients for copper (D_M), as found from experimental data, were compared with theoretical ones, calculated from Formula (5) (Fig. 5 in work H-2). They were found to be in good agreement.

The d-d absorption spectra (Fig. 6-8 in work H-2), recorded for all the test solvents have, in the visible range, one absorption maximum (λ_{max} ab. 600 nm) which shifts slightly toward the shorter wavelengths with increasing pH values for the aqueous phase. The spectra indicate that, in the complexation process, the shape of the Cu^{2+} ion coordination polyhedron does not change. It is safe to assume that complexes with the following composition: $[CuL(NO_3)_2S_3]$, $[CuL_2(NO_3)_2S_2]$, $[CuL_3(NO_3)_2S]$, where S denotes a solvent molecule, pass into the organic phase.

The objective of the studies was achieved by finding stability constants for the Cu^{2+} complexes being formed in the aqueous solution and defining their structure.

- **1-alkyl-2-ethylimidazoles as extractants of Cu(II) ions**

The objective of the third work (H-3) was to investigate the effect of the effect of the alkyl group in position 1 of the extractant and the effect of the solvent type on the extraction of Cu(II) complexes with 1-alkyl-2-ethylimidazoles (Fig. 4).
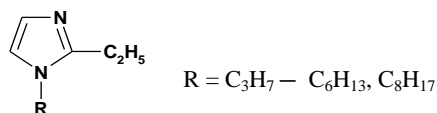

$$R = C_3H_7 - C_6H_{13}, C_8H_{17}$$

Fig. 4. The 1-alkyl-2-ethylimidazoles used in the studies in work [H-3]

Five bases representing the above homologue series were used in the tests. They are stronger bases, compared with 1-alkyl- and 1-alkyl-2-methylimidazoles, moreover, the presence of the ethyl group in position 2 creates a stronger steric hindrance in the complexation process, in comparison with the methyl group in 1-alkyl-2-methylimidazoles. 2-Butanol, isoamyl alcohol, 2-ethylhexanol, methylene chloride, chloroform and toluene were used as non-water miscible solvents.

In comparison with the previous works, more attention was paid to analyses of the electron spectra of the complexes being formed in both phases. Moreover, the effect of the solvent on the course of both the complexation process and the extraction of the complexes being formed was defined, considering Gutmann donor numbers (DN) [44, 100] for the solvents used in the tests. The complex formation and partition processes were characterized quantitatively, and $\log D_M = f(pH)$ curves were plotted for each extractant (Fig. 2-6 in work H-3) and for each solvent (Fig. 7-11 in work H-3). The extraction curves indicate that the extraction process depends on the solvent. This is illustrated by the graph (Fig. 12 in work H-3) showing the dependence of the parameter $pH_{1/2}$ for each extractant vs. the donor numbers for the solvents $pH_{1/2}=f(DN)$. The graph shows that the values of $pH_{1/2}$ decrease with increasing values of the donor numbers for the solvent. This is of practical importance because the solvent can be

selected to match the pH values of the solutions from which the Cu^{2+} ions are to be removed, for instance, a 50% recovery of copper from solution by extraction by means of 1-octylimidazole can be achieved at a pH= 4.75 using 2-ethylhexanol (DN=48 [100]) or at a pH=6.4 using toluene (DN=0.1 [100]) as solvent.

The extraction data were used for determination of stability constants for the Cu^{2+} complexes being formed in the aqueous solution, the number of complexes passing into the organic phase and their corresponding partition constants. It was demonstrated that the presence of the ethyl group in position 2 of the imidazole ring reduces the stability of the Cu^{2+} complexes being formed in comparison with 1-alkylimidazoles, by analogy with 1-alkyl-2-methylimidazoles [H-2]. The stability of Cu^{2+} complexes with 1-alkyl-2-ethylimidazoles increases slightly with an increasing length of the alkyl group in position 1. The increasing length of the alkyl group does not only improve the stability of the complexes but also their chance of passing into the organic phase in the extraction process, as shown by the fact that the extraction curves tend to shift toward lower pH values (Fig. 2-6 in work H-3). A similar effect on the location of the curves is exerted by an increase in the value of the donor number for the solvent (Fig. 7-11 in work H-3). The solvent's strong steric effect and donor properties lead to the coordination number for Cu^{2+} being changed from 6 to 4, as indicated by the electron spectra recorded for the organic phase (Fig. 16-19 in work H-3). The structure of the Cu^{2+} coordination polyhedron changes mainly for the second and third degree of complexation (for ML_2 and ML_3), but also the solvent contributes to the change, for instance in 2-butanol, spectra for 4-coordination bonds of Cu^{2+} are observed as early as in the first stage of complexation (ML). 4-Coordination complexes of Cu^{2+} are most probably in the form of a strongly distorted tetrahedron. Reduction of the coordination number for copper and its accompanying change of the coordination polyhedron is desirable for practical reasons because it improves the extraction properties of the complexes. The 4-coordination complexes are less hydrogenated so they pass into the organic phase more readily than do the 6-coordination ones. The process takes place at lower extractant (ligand) concentration and accounts for better copper recovery, which is in agreement with data reported in the literature [14, 18, 19, 44].

- **1,2-dialkylimidazoles as extractants of Cu(II) ions**

I was encouraged by my observations from [H-3] to investigate the formation and extraction of Cu(II) complexes with extractants showing an even stronger steric effect. Therefore, in my next work (H-4) I tested 1,2-dialkylimidazoles, of which the general formula is shown in Figure 5. In position 2, the compounds have increasingly larger substituents, which are an increasingly stronger obstacle to the formation of combinations with the Cu^{2+} ions.

$R_1=C_2H_5, C_4H_9, C_6H_{13}$
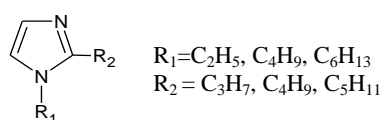$R_2 = C_3H_7, C_4H_9, C_5H_{11}$

Fig. 5. The 1,2-dialkylimidazoles used in the studies in work [H-4]

A total of 9 chemical compounds in the 1,2-dialkylimidazoles homologue series (Fig. 5) were investigated in [H-4]. The solvents were 2-ethylhexanol and chloroform, which have definitely different donor numbers (DN): 4 and 48, respectively [100]. The extraction process is affected by the length of the alkyl groups both in position 1 and in position 2 of the extractants. The extraction curves ($logD_M =f(pH)$) shift toward lower pH values with an increasing length of the substituent both in position 1 and in position 2 (Fig. 1-6 in work H-4). Stability constants for the Cu^{2+} complexes increase with the length of the substituent in position 1. Their values are comparable with those obtained for the Cu^{2+} complexes with 1-alkyl-2-ethylimidazoles [H-3] but lower than stability constants for Cu^{2+} complexes with 1-alkylimidazoles [H-1]. The length of the substituent in position 2 changes partition constants for the complexes and affects the values of $pH_{1/2}$. The values of the partition constants P_1 (Table 1 in work H-4) for all of the tested combinations are low and they practically do not depend on the increase in molecule's hydrophobicity due to an increased length of the alkyl substituent in position 1, moreover, they are slightly higher for chloroform, compared with the alcohol solvent. The

partition constants P_2 and P_3 are high (Table 1 in work H-4) – higher than in the extraction with 2-ethylhexanol using chloroform. Moreover, the values of the partition constants P_2 and P_3 clearly increase with the increasing length of the alkyl group in position 1. In absorption spectra for the system Cu^{2+}-1,2-dibutylimidazol-2-ethylhexanol, the absorption maximum is at the wave length of ab. 620 nm and then, as the extractant's concentration in the aqueous and organic phases increases, there is a second absorption maximum at $\lambda = 540$ nm (Fig. 14 in work H-4).

The higher values of the partition constants P_2 and P_3 and the electron absorption spectra indicate that, starting from the second step of complexation of Cu^{2+} with the 1,2-dialkylimidazoles of interest, the central-ion coordination number decreases, probably from 6 to 4. The phenomenon is clearly favored by the presence of strongly-donor molecules of 2-ethylhexanol. The reactions can be described by the following equations:

$$[Cu(NO_3)_2(H_2O)_2L_2] + S \leftrightarrow [Cu(NO_3)L_2S]NO_3 + 2\ H_2O \tag{3}$$

$$[Cu(NO_3)(H_2O)_2L_3]NO_3 + S \leftrightarrow [CuL_3S](NO_3)_2 + 2\ H_2O \tag{4}$$

wherein S denotes the solvent molecule.

This structural change in the coordination polyhedron leads to complexes which do not contain any water molecules in the Cu^{2+} coordination sphere; this facilitates their passage into the organic phase. The phenomenon may be of practical importance in the separation of Cu^{2+} from solutions which contain a mixture of cations such as Zn^{2+}, Co^{2+}, Ni^{2+} or Cd^{2+}. These metals are often found in solid and liquid industrial waste [6, 7].

In [H-4] it was demonstrated that the process of solvent extraction of Cu^{2+} by means of 1,2-dialkylimidazoles is considerably influenced by two phenomena: hydrophobic effect (depending on the length of the alkyl group (R_1) connected with the nitrogen atom) and steric effect (caused by the presence of the alkyl substituent (R_2) in position 2 of the imidazole ring. Moreover, it was demonstrated that the two effects can be intensified by selecting a solvent with a sufficiently high Gutmann donor number (DN) [H-4].

The three effects may act additively, thus increasing the chances of passage of Cu^{2+} from the aqueous into the organic phase [H-4]. This is shown, first of all, by the decrease in the value of parameter $pH_{1/2}$, which is of considerable practical importance, improving the percentage of metal extraction at lower extractant concentrations in both phases [H-4]. Moreover, the effect is indispensable in various environmental protection projects.

- **1-alkyl-4-methylimidazoles as extractants of Cu(II) ions**

The objective of the next work [H-5] is well described by its title. My intention was to fully describe the process of formation and extraction of complexes by means of parameters which determine the phenomena. In these tests, extractants from another homologue series of alkyl derivatives of imidazoles: 1-alkyl-4-methylimidazoles (Fig. 6) were tested. The methyl substituent in position 4 causes a clear steric effect in the formation of complexes with metal ions, so does the substituent in position 2 [H-2–H-5]. The phenomenon affects the values of stability constants (β_n).
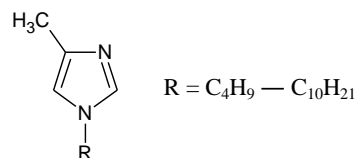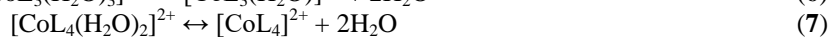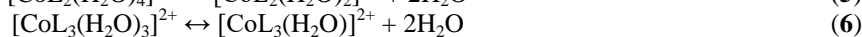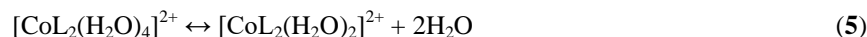

$$R = C_4H_9 - C_{10}H_{21}$$

Fig. 6. The 1-alkyl-4-methylimidazoles used in the studies in work [H-5]

The values for the Cu^{2+} complexes with 1-alkyl-4-methylimidazoles [H-5], are comparable with those obtained for 1-alkyl-2-methylimidazoles [H-3]. Owing to the hydrophobic effect resulting from the extension of the alkyl chain of the substituent in position 1, the steric effect of the substituent in position 4 as well as the solvent's donor properties cause the Cu^{2+} complexes having the coordination number 4 and the shape of a distorted tetrahedron to pass into the organic phase in the extraction process. The phenomenon takes place especially in the complexation stages 2 and 3 for the complexes ML_2 and ML_3. The complexes are more readily extracted, as indicated by their high partition constants

P$_2$ and P$_3$, in comparison with ML complexes, especially for longer alkyl groups in position 1 (the compound is more hydrophobic) and the solvent has a high donor number. For instance, in the case of *p*-xylene and 2-ethylhexanol having donor numbers of 1 and 48, respectively [100], for Cu^{2+} complexes with 1-decyl-4-methylimidazole, the partition constants P$_2$ are 160 and 700, respectively, whereas P$_3$ is 430 and 1300, respectively. All the three phenomena described above facilitate the extraction of Cu^{2+} and lead to lower values of pH$_{1/2}$. This is of practical importance: the process is feasible at low concentrations of this new extractant (ligand) both in the organic and in the aqueous phase, which is desirable for the separation of Cu^{2+} from mixtures with other cations.

- **1-alkyl-2-methylimidazoles as extractants of Co(II) ions**

The testing methods and interpretation of the test results, mastered in the testing of Cu^{2+}complexes with alkyl derivatives of imidazole, were used for testing Co^{2+} complexes with 1-alkyl-2-methylimidazoles [H-7]; the formula of that type of molecules is shown in Fig. 3. The extractants used in this work [H-7] were compounds which, in position 1, had the following alkyl groups: n-C$_4$H$_9$, n-C$_5$H$_{11}$, n-C$_6$H$_{13}$, n-C$_7$H$_{15}$, n-C$_8$H$_{17}$, n-C$_9$H$_{19}$, n-C$_{10}$H$_{21}$, and n-C$_{12}$H$_{25}$. The organic solvents were: methylene chloride, chloroform and 2-ethylhexanol. The testing conditions were the same as in the previous works. The extraction curves for Co^{2+} complexes tended to shift very strongly toward lower pH values with the increase in the hydrophobicity of the extractant molecules (Fig. 1-3, in work H-7). The electron absorption spectra of the Co^{2+} complexes with 1-decylo-2-methylimidazole for both phases show that the absorption bands tended to shift toward higher wave lengths with the increase in pH of the aqueous phase (Fig. 7 and Fig. 8 in work H-7). There are two definite absorption maxima – for the wave lengths 520 and 570 nm – corresponding to the formation of 6- and 4-coordination complexes, respectively. The complexes have different colorations. The phenomenon is attributed to the steric effect of the methyl group in position 2 of the imidazole ring and takes place mainly in the complexation stages 2, 3 and 4. An increase in the summary stability constants is observed (Fig. 5 in work H-7) for their corresponding complexes of the type ML$_2$, ML$_3$, ML$_4$ being formed in accordance with the equations below (6-8):

$$[CoL_2(H_2O)_4]^{2+} \leftrightarrow [CoL_2(H_2O)_2]^{2+} + 2H_2O \qquad (5)$$
$$[CoL_3(H_2O)_3]^{2+} \leftrightarrow [CoL_3(H_2O)]^{2+} + 2H_2O \qquad (6)$$
$$[CoL_4(H_2O)_2]^{2+} \leftrightarrow [CoL_4]^{2+} + 2H_2O \qquad (7)$$

Reaction equilibria for (6), (7) and (8) are definitely shifted to the right for higher ligand concentrations. Stability constants for the complexes being formed increase in the order: β$_1$ < β$_2$ < β$_3$ < β$_4$, and each calculated stability constant tends to increase slightly with an increase in the hydrophobicity of the ligand molecules. The extraction of Co^{2+} is favored by the formation of tetrahedron ↔ octahedron configuration equilibria, as suggested by high partition constants for the complexes, particularly P$_3$ and P$_4$ (Tab. 2 in work H-7). This provides favorable conditions for the extraction of Co^{2+}, especially for its selective separation from cation mixture, for instance, from solutions with a content of Ni^{2+}. This work provides substantial new information to descriptions of the process of formation of new complexes under excess ligand conditions and indicates the possibility of its application for the selective separation of the cobalt [89], in particular from nickel.

- **separation of Co^{2+}, Ni^{2+}, Cu^{2+} and Pd^{2+} ions by extraction**

Solvent extraction was shown in [H-7] to be an efficient method for the separation of Co^{2+}, Ni^{2+}, Cu^{2+} and Pd^{2+} ions from chloride solutions. My experience, which I gained in studies on the extraction of Cu^{2+} and Cu^{2+} ions, enabled me to correctly choose the extractant (1-hexyl-2-methylimidazole), organic solvent (chloroform) and process conditions (temperature 25°C, ionic strength of the aqueous solution I = 0.5 mol/dm^3, maintained with potassium chloride). The molecular structure and complex-forming properties of 1-hexyl-2-methylimidazole enabled the selective separation of Pd^{2+} ions. In aqueous solution, the metal ions concerned are present in the form of octahedral aqua complexes [M(H$_2$O)$_6$]$^{2+}$ [97]. However, after addition of chloride ions according to Equation (2), some of the ions changed the structure of the coordination zone so that the resulting zone was either flat or tetrahedral,

depending on the structure of their 3d electronic subshell [97]. The effect was additionally intensified by the deliberately selected extractant (1-hexyl-2-methylimidazole) of which the structure, as described above, hindered the formation of octahedral complexes. The molecular-symmetry changes lead to higher total stability constants for the complexes (Tab. 1 in paper H-7). In practice, higher susceptibility to extraction is observed in the liquid-liquid system of complexes with a coordination number of 4 because, being less hydrated, they are more likely to pass into the organic phase; this is indicated by the partition constants of the complexes concerned, as shown in Table 2 in paper H-7. The highest partition constants are observed for the square planar complexes of Pd^{2+} with 1-hexyl-2-methylimidazole (L) having the formula $[PdL_2S_2]$ (S-solvent molecule), which I expected to occur when working on my study plan. The formation of this type of complexes during extraction was described by Ma and Dreiser in [101].

The percentage of metal extraction depends on the pH of the aqueous phase. The highest extraction percentages were obtained for pH=7.3 (Fig. 3 in H-7); the value poses no hazard to surface waters. The extraction percentage is 70% for Pd^{2+} and 40% for Cu^{2+}. Only a small percentage of the Co^{2+} and Ni^{2+} ions tend to pass into the organic phase (not more than 10% and 5%, respectively). The highest separation coefficients (Table 3 in H-7] were obtained for the systems: Pd/Ni, Pd/Co, Cu/Ni, Cu/Co; they are 13.3 (for pH 5.4), 7.65 (for pH 5.4), 5.63 (for pH 7.0), 3.2 (for pH 7.33), respectively.

The method of selective separation of palladium from the above mixtures was developed using model solutions in order to verify the feasibility of its recovery from waste arising in the processing of copper ore.

Studies on transport across membranes doped with imidazole derivatives

The above-mentioned extraction tests enabled me to optimum selection of carriers metals (alkyl imidazole derivatives) and conditions of the transport process using the methodology of the membrane. In his work imidazole derivatives I have applied to a selective isolation of ions of Cu^{2+} and Zn^{2+} with a mixture of Cu-Zn-Co-Ni [84−88,H-8−H-10] with a solution of chloride and nitrate in the transport through the membrane. On the imidazole derivatives as carriers also stressed by other authors [87]. They used 1-vinylimidazole for separating ions of Cu^{2+} and Fe^{3+} in the membrane transport of polyvinyl acetate [86].

In diluted aqueous solutions Zn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} ions form of stable aquacomplexes $[M(H_2O)_6]^{2+}$, have either octahedral (Zn^{2+}, Co^{2+}, Ni^{2+}) or pseudooctahedral structure (Cu^{2+}) [97]. Their ionic radii and hydration energy are very similar (for Zn^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+}, the ionic radiuses are 74, 73, 74.4, 69 pm [102], and hydration energy is 2940, 3000, 2920, 3000 kJ/mol [102]), respectively, so the separation and extraction of these cations from aqueous solutions is difficult. However, by rendering the metal ions in the form of complexes with ligands, other than water, it is possible to diversify their properties for use in their separation.

• **1-alkylimidazoles as carriers in polymer inclusion membranes**

The possibility of using 1-alkylimidazoles (with the alkyl ranging from hexyl to decyl) as ion carrier for Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+} ions in the process of transport through polymer inclusion membranes (PIM) was investigated in [H-8]. The carrier's general formula is shown in Fig. 2 [H-8]. The effect of carrier's concentration in the membrane on the values of separation coefficients for the metal ions of interest was defined. The tests were intended to define the kinetic parameters and separation properties of 1-alkylimidazoles in the process of transport of non-ferrous metal ions. It was found that the Cu^{2+} ions were best transported whereas nickel and cobalt ions were transported to a minor extent. At a temperature of $20^{\circ}C$ and a pH of 6.0 for the donor phase, regardless of the alkyl chain length in the R carrier molecule, the ions were transported from nitrate solutions in the order: $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. The highest values of the initial flux in the transport of Cu^{2+} were observed for 1-decylimidazole (7.03 $\mu mol/m^2 \cdot s$). After a 24-hour transport process, that carrier also provided the highest metal recovery factors (RF) which, for the carrier's concentration in the membrane of 1 mol/dm^3, were as follows: 99.4% for Cu, 62.4% for Zn, 13.8% for Co and 10.7% for Ni, and for the carrier's concentration in the membrane of 1.5 mol/dm^3 they were: 99.8% for Cu, 93.1% for Zn, 56.4%, for Co and 50.0% for Ni. The higher the carrier's concentration, the lower the selectivity of transport,

therefore, its optimum concentration in the membrane was assumed to be 1 mol/dm^3. The selectivity of transport of Cu^{2+} ions, as compared with the other metals decreases with an increase in the length of the alkyl substituent in akylimidazoles because the rate of ion transport for Zn^{2+}, Co^{2+} and Ni^{2+} increases. The highest values of selectivity coefficients for Cu^{2+}/Zn^{2+}, Cu^{2+}/Co^{2+} and Cu^{2+}/Ni^{2+} were obtained in the case of 1-hexylimidazole as carrier (for its 1 mol/dm^3 concentration in the membrane): they are 4.3, 39.7 and 46.9, respectively (H-8). Ion selectivity coefficients are higher in the case of the nitrate than the chloride solutions [84], for which they are 3.7, 17.8 and 35.7, respectively, for a same carrier. The values of permeability coefficient (P) increase linearly with an increase in the carrier's basicity. A similar linear correlation for 1-alkylimidazoles was obtained in the case of the chloride solutions [84]; this is in agreement with literature reports.

• **1-hexyl-2-methylimidazole as carrier in polymer inclusion membranes**

In the previous work, 1-hexylimidazole was shown to be the best carrier, therefore, in my next work (H-9) I chose to investigate the steric effect, caused by the introduction of a methyl group in position 2 of the carrier's molecule (1-hexyl-2-methylimidazole), on the transport of Zn^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+} ions by polymer inclusion membranes (PIM) and by supported liquid membranes (SLM). The transport of binary mixtures (Cu^{2+}-Zn^{2+}, Cu^{2+}-Co^{2+} and Cu^{2+}-Ni^{2+}) and of a quaternary mixture Zn^{2+}-Cu^{2+}-Co^{2+}-Ni^{2+} in nitrate solutions was tested at a temperature of 20°C, at a pH = 6.0 of the donor phase. The transport of the investigated ions through SLM decreases in the order: Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}, whereas that through PIM does in the order Cu^{2+} > Zn^{2+} > Co^{2+},Ni^{2+}. The Cu^{2+} ions are best transported through both membrane types.

The transport process consists in carrying a neutral ion pair resulting from the reaction of carrier (L) with the metal ion (M^{2+}):

$$[M(H_2O)_6]^{2+} + L + 2\ NO_3^- \leftrightarrow [M(H_2O)_{6-n}L_n](NO_3)_2 \qquad (8)$$
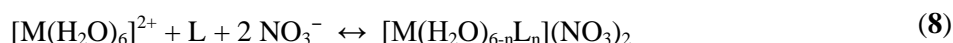
This provides a hydrophobic complex which diffuses through the membrane. The metal ion is released into the acceptor phase and the carrier diffuses further through the membrane into the donor phase. The transfer mechanism is in agreement with the mechanism reported in the literature [56-58]. The values of selectivity coefficients for Cu^{2+}/Zn^{2+}, Cu^{2+}/Co^{2+} and Cu^{2+}/Ni^{2+} in binary mixtures are 1.9, 6.6 and 8.7, respectively, for SLM and 3.0, 12.9 and 13.6, respectively, for PIM. For the quaternary mixture Zn^{2+}-Cu^{2+}-Co^{2+}-Ni^{2+}, the initial fluxes of the Ni^{2+} and Co^{2+} ions in the transport through PIM are small and equal to each other. The phenomenon is caused by the carrier's properties. The steric effect of the methyl group hinders the formation of Co^{2+} and Ni^{2+} complexes and shifts the reaction equilibrium for (8) to the left. Selectivity coefficients for Cu^{2+}/Zn^{2+}, Cu^{2+}/Co^{2+},Ni^{2+} are 3.1 and 15.1, respectively, in the case of PIM and those for Cu^{2+}/Zn^{2+}, Cu^{2+}/Co^{2+} and Cu^{2+}/Ni^{2+} in the case of SLM are lower: 1.7, 9.6 and 10.4, respectively.

The recovery factor (RF) in the case of copper after a 24-hour transport through PIM is 95.1%, and its value for SLM is 78%. For zinc, RF is ab. 53% – comparable for both membrane types. Cobalt and nickel ions practically stay in the donor phase. This is not undesirable: after separating copper and nickel, their solution can be subjected to separation by means of membrane transport using 1-hexylimidazole as carrier.

• **1-decyl-4-methylimidazole as carrier in polymer inclusion membranes**

In [H-10], the transport of Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+} through polymer inclusion membranes (PIM) and supported liquid membranes (SLM) with 1-decyl-4-methylimidazole as carrier [H-10] was investigated. The transport of binary mixtures (Zn^{2+}-Co^{2+}, Zn^{2+}-Cd^{2+} and Zn^{2+}-Ni^{2+}) and the quaternary mixture Zn^{2+}-Cd^{2+}-Co^{2+}-Ni^{2+} in chloride solutions was investigated at a temperature of 20°C, at a pH=6.0 for the donor phase. The ions transport through SLM decreases in the order: Zn^{2+}>Cd^{2+}>Co^{2+},Ni^{2+}; for PIM the order is slightly different: Zn^{2+}>Cd^{2+}>Ni^{2+}>Co^{2+}. The calculated selectivity coefficients for Zn^{2+}/Co^{2+}, Zn^{2+}/Cd^{2+} and Zn^{2+}/Ni^{2+} for the transport through PIM are higher than those through SLM under same conditions: 27.3, 7.9 and 22.4, respectively.

For the quaternary mixture, the recovery factor (RF) for zinc after a 24-hour transport process was 96.9% whereas from the binary mixtures, zinc was recovered with a nearly 99% efficiency. So high a

recovery of zinc results from the structure of the carrier molecule (1-decyl-4-methylimidazole). Zinc readily forms 4-coordination complexes with carriers having a steric hindrance in their molecules according to the equation:

$$[Zn(H_2O)_6]^{2+} + nL \leftrightarrow [Zn(H_2O)_{4-n}L_n]^{2+} + (2+n)H_2O \qquad (9)$$
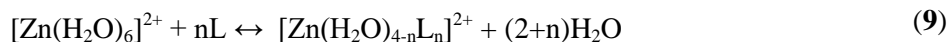
in which L denotes a 1-decyl-4-methylimidazole molecule.

In addition to the 6-coordination complexes, Co^{2+} and Cd^{2+} ions form also 4-coordination ones. The latter are formed at higher (third and fourth) complexation stages [62], therefore, higher carrier's concentrations are required for their formation.

The Ni^{2+} have a rigid coordination sphere, they form 6-coordination complexes and are virtually not carried through this type of membranes at all. This is advantageous in the aspect of separation of metals because the ions practically stay in the donor phase.

This work is a development and novelty in studies on the separation of metals in the process of transport through membranes.

Recovery of zinc from waste: practical aspects in environmental protection

The zinc-and-lead industry in Poland has for centuries had a history of one based on mining and metallurgy. However, the imminent depletion of the mining resources indicates that the future of the industry belongs either to the import of ores or to the recovery of zinc from zinc-bearing materials. The demand on metals has been growing irregularly since 2004, occasionally being higher than the supply, causing price increases on markets (the current prices of metals are shown in Table 1). The use of zinc in various industries has also been increasing, including those in the manufacture of alloy-based, anti-corrosive protective coatings for use in the motor industry [103,104]. At present, zinc metallurgy is based on the recirculation of materials with a high content of zinc, including waste materials arising in copper metallurgy. However, the zinc industry needs materials with a Zn content of 20% or higher [7, 105], therefore, the valuable metal must be recovered from materials having a lower Zn content.

• **recovery of zinc from industrial waste**

In [H-11], the possibility of the recovery of zinc from metallurgical waste arising in zinc production, which is disposed of by landfilling. The content of zinc in the sludge was 10-13%. Given the quantity of such waste and the market prices of pure metals, zinc recovery is cost-effective and desirable from the point of view of environmental protection.

The method of leaching by means of acids and basic solutions was tested [105,107,H-11,H-12]. Considering their effectiveness, the leaching solutions are ranked as follows: concentrated $NH_{3(aq)}$ solution (10.5% Zn), 2 mol/dm³ HNO_3 solution (10% Zn), 30% NaOH solution (10% Zn), 2 mol/dm³ H_2SO_4 solution (9,5%), 2 mol/dm³ HCl solution (9%) and 80% lactic acid solution (8%). However, the selectivity of the process of leaching by means of strong acids (HCl, HNO_3, H_2SO_4), was not high enough because the acids leached out Cd, As, Cr, Cu, Fe, Ni and Pb in addition to zinc. Thus, the best leaching agents were: concentrated ammonia solution, 30% NaOH solution, and 80% lactic acid solution.

Treating the sludge with ammonia is described by the following reaction:

$$[M(H_2O)_6]^{2+} + 4NH_{3(aq)} \leftrightarrow [M(NH_3)_4]^{2+} + 6 H_2O \qquad (10)$$
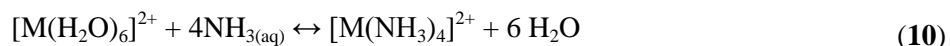
which results in metal ammine complexes passing into the aqueous solution. In addition to zinc (10.5%), about 1% copper is leached out of the sludge.

Leaching by means of soda lye solution is described by the equation below:

$$ZnO + H_2O + 2OH^- \leftrightarrow [Zn(OH)_4]^{2-} \qquad (11)$$
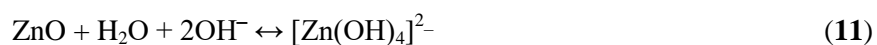
Small amounts of As, Cu, Cr and Pb are leached out as well.

Zinc was separated electrolytically from spent leaching solutions (92-99% of the metal was deposited on the cathode) and by solvent extraction in a liquid-liquid system, using tributylphosphate (TBP) for

acidic solutions and 1-decyl-2-methylimidazole for basic solutions. The two extractants were each dissolved in toluene.

In the extraction process, zinc is carried into the toluene solution by means of the extractant (RH). The process is described by the equation below:

$$4(L)_{org} + [Zn(H_2O)_6]^{2+} + 2A^- \leftrightarrow (ZnL_4A_2)_{org} + 6 H_2O \qquad (12)$$
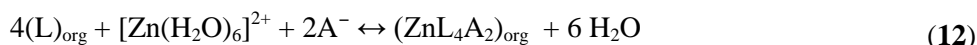
The extractant can be recovered from the organic phase during re-extraction or extraction by means of sulfuric acid (equation (14)) or ammonia whereas the zinc ions stay in the aqueous phase.

$$(ZnL_4A_2)_{org} + 2H^+ \leftrightarrow 4L + 2(HA)_{org} + Zn^{2+} \qquad (13)$$
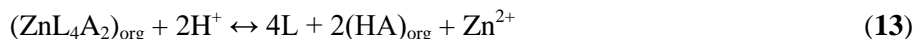
When TBP was used as the extractant at a pH of ab. 2.7, zinc recovery was 99%, while using 1-decyl-2-methylimidazole at a pH in the range 7.5-8.0 resulted in zinc recoveries in the range 96-99%.

The very high recovery of zinc indicates that the above studies are prospective and potentially highly successful in the practice of metal recovery.

- **zinc recovery from copper production waste**

[H-12] is a report on the possibility of zinc recovery from spent neutralization sludge from a waste treatment plant at a copper production facility (80 Mg/day). The material was found to have had a considerable content of zinc (11-13%), iron (ab. 6%) and a low content of non-ferrous metals (ab. 22% Ca, ab. 1.5% Cu, ab.1.3% As, ab. 1% Pb, ab. 0.5% Cd and Cr, as well as ab. 0.1% Al, Co and Ni). The sludge has been kept in several waste storage tanks for several years. At the end of the year 2007, its amount was 8881.1 tons [108]. Interest in recovering the metals which accompany copper ores is mainly due to the necessity to minimize production waste.

The method used was similar to that reported in [H-11]: leaching by means of acids (HCl, HNO3), alkaline solutions (NaOH, $NH_{3(aq)}$) and salt solutions (NH_4Cl, NH_4SCN, KI) [105,106, H-11,H-12]. The leaching agents are classified by efficiency in zinc recovery as follows: 2 mol/dm^3 HCl solution (12.71% Zn), 2 mol/dm^3 HNO_3 solution (12.54% Zn), ammonium buffer (9.74% Zn), 30% NaOH solution (9.38% Zn), concentrated $NH3_{(aq)}$ solution (5.49% Zn). On the other hand, leaching by means of strong acids (HCl, HNO_3), was not sufficiently selective, therefore, the optimum leaching agents appeared to be: ammonium buffer, 30% NaOH solution, and concentrated ammonia solution. However, in addition to zinc, they resulted in the leaching out of ab. 1% calcium which has to be separated from the solution by precipitation, for instance, by means of calcium sulfate which, being characterized by low solubility, will pass into waste almost entirely. The efficiency of NH_4Cl, NH_4SCN solutions is very low: they leach out ab. 1.5% zinc, whereas that of KI solution is negligent.

Zinc can be recovered electrolytically from the solutions, except that the following is removed beforehand:

    a) Fe(III) ions, for instance, by precipitation in the form of jarosite:

$$3Fe_2(SO_4)_3 + Na_2SO_4 + 12H_2O \leftrightarrow 2NaFe_3(SO_4)_2(OH)_6 + 6H_2SO_4 \qquad (14)$$

    b) ions of more-eletropositive cations (Me= Cu, Pb, Ni, Cd....), for instance, in cementation by means of zinc dust:

$$M^{n+} + n/2 Zn^0 \leftrightarrow M^0 + n/2 Zn^{2+} \qquad (15)$$

The rate of chemical dilution of zinc is so low that it does not compete with the cementation process. Moreover, zinc can be recovered by selective extraction by means of an industrial extractant, such as diethylhexaphosphoric acid (D2EHPA) [109] after dissolving it in kerosene:

$$2(RH)_{kerosene} + Zn^{2+} \leftrightarrow (R_2Zn)_{kerosene} + 2H^+ \qquad (16)$$
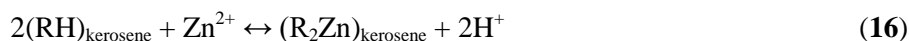
or by means of alkyl derivatives of imidazole [H-11]. The extraction process takes place in accordance with the equation (12).

Summary and conclusions

Summing up, metal complexes with imidazole derivatives have extremely interesting properties whereby they are distinguished from complexes with other ligands (for instance, with pyridine and its derivatives). It was shown that the complex-forming properties of alkyl imidazoles can easily be diversified. Differences with respect to the formation process, structure, and stability of their complexes with metal cations can be used for their effective separation. An innovative aspect of the studies was to use those properties for the selective separation of Cu, Zn and Co from other metals by solvent extraction and membrane techniques, using a variety of separation methods.

It was shown that the complex-forming properties of alkyl derivatives of imidazole are diversified by the following effects:

o   steric effect (substituents in position 2 or 4),
o   hydrophobic effect caused by the length of the substituent in position 1,
o   the presence or absence of the $\pi_{M \to L}$ component in the coordination bond.

Moreover, it was shown that the phenomena are able to affect the stability and structure of the coordination sphere of certain d-electron metals, thus facilitating their separation, both by means of solvent extraction and membrane techniques. It was also demonstrated that the organic solvent having a high donor number is able to participate in the establishing of configurational equilibria, thereby improving the extraction efficiency. The complex-forming properties of alkyl imidazoles particularly facilitate the separation of copper from other transition metals, both by solvent extraction and with the use of membrane techniques. Moreover, I demonstrated that selectivity of transport across polymer inclusion membranes does not only depend on the composition of the donor phase (pH, concentration of metals) and composition of the acceptor phase (distilled water or acid solution), but also on the membrane composition and morphology.

In particular, my studies relate to the possibility of separation of non-ferrous metals from model solutions and from waste solutions having a low metal content, such as those arising in waste treatment processes, regeneration of pickling solutions and spent electrolysis solutions, and by leaching the starting materials with a low metal content (such as metallurgic and industrial waste), which is essential for the removal of toxic contaminants in environmental protection.

Using the steric effect of the extractant (carrier) and donor properties of the solvent, it is possible, specifically, to provide conditions for the selective separation of cations of those metals which change the structure of the coordination polyhedron from octahedral to tetrahedral. The group comprises cobalt, zinc and cadmium, in addition to copper and palladium. In particular, cadmium is highly undesirable in the solutions and has to be removed because of the environmental hazard it poses.

Therefore, my studies, which are described in my habilitation dissertation and which concern both the extraction systems based on alkyl imidazole extractants and the process of transport through polymer inclusion membranes containing alkyl derivatives of imidazole as carriers, are in agreement with the predominant global trends of searching for effective and selective methods for the separation of mixtures containing heavy metal compounds. Patent applications have been applied for in the Polish Patent Office and the European Patent Office for my innovative studies [93-95].

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95. Eitner K., Urbaniak W., Radzymińska-Lenarcik E., Witt K.: Urząd Patentowy Rzeczpospolitej Polskiej

P. 411843 - zgłoszenie w sprawie uzyskania patentu na wynalazek pt. „Sposób usuwania metali ciężkich z roztworów amoniakalnych" z dnia 31 marca 2015 roku

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108. Raport o stanie woj. dolnośląskiego w 2007 r., Dane GUS

109. Pereira D.D., Rocha S.D.F., Mansur M.B.: Recovery of zinc sulphate from industrial effluents by liquid–liquid extraction using D2EHPA (di-2-ethylhexyl phosphoric acid). Separation and Purification Technology, 2007, 53, 89-96

List of published scientific papers being a cycle of paper related to one subject matter, in English

(H-1) **Radzyminska-Lenarcik E.**
Influence of the alkyl chain length on extraction equilibrium of Cu(II) complexes with 1-alkylimidazoles in aqueous solution/organic solvent systems. *Solvent Extraction and Ion Exchange* **2007**, <u>25</u>, 53-64

IF = 1.17
my contribution
100%

My contribution: development of application concept for 1-alkylimidazoles (a total of 10 alkyl derivatives) as extractants for removal of copper(II) ions from aqueous solutions; application of eight water-immiscible organic solvents; planning and carrying out of extraction studies; analysis of the effect of the alkyl chain length in 1-alkylimidazole molecule on copper extraction coefficient; analysis of extraction curves; calculation of stability constants for the Cu(II) complexes being formed and their partition constants; development and discussion of findings; formulation of conclusions; and editorial preparation of the paper for publishing.

(H-2) **Radzymińska-Lenarcik E.**
Effect of alkyl chain length on the extraction of copper(II) complexes with 1-alkyl-2-methylimidazoles.
Separation Science and Technology **2007**, <u>42</u>, 2661-2675

IF = 1.048
my contribution
100%

My contribution: development of application concept for 1-alkyl-2-methylimidazoles (a total of eight alkyl derivatives) as extractants for removal of copper(II) ions from aqueous solutions; planning and carrying out of extraction studies using three water-immiscible solvents (methylene chloride, chloroform, 2-ethylhexanol); analysis of extraction curves; carrying out of visible-range spectrophotometric analyses of aqueous and organic phases; calculation of stability constants for the Cu(II) complexes being formed and their partition constants; analysis of the effect of the alkyl chain length in position 1 and the substituent steric effect in position 2 on the values of the constants; discussion of findings; formulation of conclusions; and editorial preparation of the paper for publishing.

(H-3) **Radzyminska-Lenarcik E.**
Influence of the steric hindrance, ligand hydrophobicity and DN of solvents on structure and extraction of Cu(II) complexes of 1-alkyl-2-ethylimidazoles.
Separation Science and Technology **2008**, <u>43</u>, 794-814

IF = 1.139
my contribution
100%

My contribution: development of application concept for 1-alkyl-2-ethylimidazoles (a total of five alkyl derivatives) as extractants for removal of copper(II) ions from aqueous solutions; planning and carrying out of extraction studies in six water-immiscible solvents; analysis of the effect of the alkyl chain length in 1-alkylimidazole molecule; the substituent steric effect in position 2 (more pronounced than that for 1-alkyl-2-methyloimidazoles) and solvent type on stability constants of the complexes being formed in aqueous solution and their partition constants between aqueous phase and organic phase; analysis of extraction curves; carrying out of visible-range spectrophotometric analyses of aqueous and organic phases; development and discussion of findings, formulation of conclusions; and editorial preparation of the paper for publishing.

(H-4) **Radzyminska-Lenarcik E.**
The influence of alkyl chain length in 1,2-dialkylimidazoles on the extraction capacity and structure of their copper(II) complexes.
Separation Science and Technology **2009**, <u>44</u>, 954-970

IF = 1.028
my contribution
100%

My contribution: development of application concept for 1,2-dialkyl substituted imidazoles (a total of

nine compounds were examined) as extractants for removal of copper(II) ions from aqueous solutions; planning and carrying out of extraction studies in two water-immiscible solvents (chloroform, 2-ethylhexanol) and spectrophotometric studies of aqueous phase and organic phase; analysis of extraction curves; analysis of the effect of alkyl chain length in position 1 and the substituent steric effect in position 2 (more pronounced because of longer carbon chain lengths – in propyl, butyl, pentyl) as well as solvent type on the stability constants of the complexes being formed in aqueous solution and their partition constants between aqueous phase and organic phase; development and discussion of findings; formulation of conclusions; and editorial preparation of the paper for publishing.

(H-5) **Radzyminska-Lenarcik E**.
The influence of steric effect, alkyl chain length and donor number of solvents on the extraction of copper(II) complexes with 1-alkyl-4-methylimidazoles.
Solvent Extraction and Ion Exchange **2010**, <u>28</u>, 636-652

IF = 1.821
my contribution
100%

My contribution: development of application concept for 1-alkyl-4-methylimidazoles (a total of seven compounds were examined) as extractants for removal of copper(II) ions from aqueous solutions; planning and carrying out of extraction studies in five water-immiscible solvents (toluene, *p*-xylene, chloroform, methylene chloride, 2-ethylhexanol), carrying out of spectrophotometric analyses of aqueous phase and organic phase; analysis of extraction curves; analysis of the effect of alkyl chain length in position 1 of the extractant and the substituent steric effect in position 4 and the solvent type effect on stability constants of the complexes being formed in aqueous solution and their partition constants between aqueous phase and organic phase; development and discussion of findings, formulation of conclusions; and editorial preparation of the paper for publishing.

(H-6) **Radzyminska-Lenarcik E**., Witt K.
The influence of alkyl chain length and steric effect on the stability constants and extractability of Co(II) complexes with 1-alkyl-2-methylimidazoles.
Separation Science and Technology **2015**, <u>50</u>, 676-682

IF = 1.083
my contribution
80%

My contribution: development of application concept for 1-alkyl-2-methylimidazoles (a total of eight alkyl derivatives) as extractants for removal of Co(II) ions from aqueous solutions; planning and administration of extraction studies in three water-immiscible solvents (methylene chloride, chloroform, 2-ethylhexanol); analysis of extraction curves; analysis of the effect of alkyl chain length in 1-alkylimidazole molecule; substituent steric effect in position 2 and solvent type effect on stability constants for the complexes being formed in aqueous solution and their partition constants between aqueous phase and organic phase; analysis of van Pantaleon van Eck, relationship; discussion of findings; formulation of conclusions; and editorial preparation of the paper for publishing.

(H-7) **Radzyminska-Lenarcik E**., Urbaniak W.
Separation of Co(II), Ni(II), Cu(II), and Pd(II) ions by solvent extraction.
Rekultywacja i rewitalizacja terenów zdegradowanych. Red. prof. Grzegorz Malina, Wyd. Polskie Zrzeszenie Inżynierów i Techników Sanitarnych, oddział wielkopolski, Poznań **2013**, str. 105-117

my contribution
80%

My contribution: development of the concept for the monograph; carrying out of extraction studies; development and discussion of findings; formulation of conclusions; and editorial preparation of the monograph for publishing.

(H-8) **Radzyminska-Lenarcik E.**, Ulewicz M.
Selective transport of Cu(II) across a polymer inclusion membrane with
1-alkylimidazole from nitrate solutions.
Separation Science and Technology **2012**, 47, 1113-1118

IF = 1.164
my contribution
50%

My contribution: development of the concept for the paper; selecting carriers for use in membranes;
development and discussion of findings; formulation of conclusions; and editorial preparation of the
paper for publishing.

(H-9) Ulewicz M., **Radzyminska-Lenarcik E.**
Supported liquid (SLM) and polymer inclusion (PIM) membranes
pertraction of copper(II) from aqueous nitrate solutions by 1-hexyl-2-
methylimidazole.
Separation Science and Technology **2012**, 47, 1383-1389

IF = 1.164
my contribution
50%

My contribution: development of the concept for the paper; selecting carriers for use in membranes;
development and discussion of findings; formulation of conclusions; and editorial preparation of the
paper for publishing.

(H-10) Ulewicz M., **Radzyminska-Lenarcik E.**
Application of polymer and supported membranes with 1-decyl-4-me-
thylimidazole for pertraction of transition metal ions.
Separation Science and Technology **2014**, 49, 1713-1721

IF = 1.2
my contribution
50%

My contribution: development of the concept for the paper; selecting carriers for use in membranes;
development and discussion of findings; formulation of conclusions; and editorial preparation of the
paper for publishing.

(H-11) **Radzyminska-Lenarcik E.**, Sulewski M., Urbaniak W.
Recovery of zinc from metallurgic waste sludges.
Polish Journal of Environmental Studies **2015**, 24, 1277-1282

IF = 0.79
my contribution
70%

My contribution: development of the concept for the paper; planning and administration of studies;
selecting of agents for zinc leaching from waste (a total of 6 compounds); selecting extractants which
are useful in removal of zinc from acidic and alkaline spent leaching solutions; development and
discussion of findings; formulation of conclusions; and editorial preparation of the paper for
publishing.

(H-12) **Radzyminska-Lenarcik E.**, Urbaniak W.
The study of the leaching process sludge from the production of copper
for recovery of zinc contained in them.
Gospodarka Odpadami Komunalnymi, Monografia Komitetu Chemii
Analitycznej PAN pod red. K. Szymańskiego, **2013**, 249, 33-44

my contribution
80%

My contribution: development of the concept for the monograph; carrying out of studies; development
and discussion of findings; and formulation of conclusions and editorial preparation of the monograph
for publishing.

TOTAL IMPACT FACTOR OF THE PAPERS MY HABILITATION DISSERTATION:

IF = 11.607