Copper recovery from model chloride solution using polymer inclusion membranes with 1-decyl-2,4-dimethylimidazle

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Abstract. The recovery of Cu(II) ions from chloride solutions by the transport of a binary Cu(II)-Zn(II) and Cu(II)-Cd(II), and a ternary Cu(II)-Zn(II)-Cd(II) mixture ions through inclusion membranes doped with 1-decyl-2,4-dimethylimidazole (DDMI) was studied (c_{M(II)} = 0.001 M; pH 5.5). The efficiency of metal ions separation by DDMI increased as: Cu(II) > Zn(II) > Cd(II). Selectivity coefficients Cu(II)/Zn(II) and Cu(II)/Cd(II) were equal 1.5 and 13.5, respectively for binary solutions and 1.6 and 27.7 for ternary solution. The step limiting the rate of transport of metal ions by PIM doped with DDMI may be membrane diffusion coefficients of cation complexes with DDMI. The recovery factor of Cu(II), Zn(II), and Cd(II) ions during transport across PIMs from an equimolar mixture of cations after 24 hrs was above 96%, 60% and 3.5% for Cu(II), Zn(II) and Cd(II), respectively. PIM containing DDMI are stable for 120 hrs.

1. Introduction
Due to their wide application, copper, zinc and cadmium are classified as strategic metals [1]. Such a wide industrial use of these metals causes the generation of metal-bearing wastes in the form of sewage, dust, sludge, waste heap, etc. Due to its threat to the environment and human health, all waste should be managed or cleaned of toxic metals [2]. An increasing demand for metal production has led to researching more efficient and economical methods for purification required by the industry.

Membrane technology has become an important alternative to normal processes employed for wastewater treatments, separation and recovery of target metals.

Polymer inclusion membranes (PIMs) represent an attractive liquid-to-liquid extraction for the selective removal and concentration of nonferrous metal ions (Zn(II), Co(II), Ni(II), Cd(II), Cu(II) and Pb(II)) from aqueous solutions. The transport of such metal ions across PIMs can be described as the simultaneous extraction and back-extraction operations combined in a single stage [3,4]. The cations transport and the possibility of their selective separation are determined by the way the cations react with the carriers and by the structure and stability of the complexes being formed [3-6].
Table 1. Example of nonferrous metal ions transport across PIMs doped imidazole derivatives from chloride or nitrate aqueous solutions reported in the literature.

| Carriers                      | Target solutions                              | Solution | J_0, mol/m^2·s | RF, % | Ref.       |
|-------------------------------|-----------------------------------------------|----------|----------------|-------|------------|
| imidazole azocrown ethers     | Zn(II), Cu(II), Pb(II)                       | NO_3^-   | 1.03-0.29·10^{-7} | <20.0_{Zn(II)} | [12,13]   |
| imidazole azothiacrown ethers | Zn(II), Pb(II), Ni(II), Co(II), Cd(II), Cu(II) | NO_3^-   | 0.27-1.13·10^{-7} | <30.0_{Zn(II)} | [14]      |
| 1-alkylimidazole              | Cu(II), Zn(II), Co(II), Ni(II)               | NO_3^-   | 1.19-2.02·10^{-6} | -     | [15]       |
| 1-alkylimidazole              | Cu(II), Zn(II), Co(II), Ni(II)               | Cl^-     | 1.7-2.15·10^{-6}  | -     | [16]       |
| 1-alkyl-2-methylimidazole     | Cu(II), Zn(II), Co(II), Ni(II)               | NO_3^-   | 2.42-0.2·10^{-6}  | -     | [17]       |
| 1-hexyl-2-methylimidazole     | Cu(II), Zn(II), Co(II), Ni(II)               | NO_3^-   | 0.72·10^{-6}      | 53.5_{Cu(II)}  | [18]       |
| 1-hexyl-4-methylimidazole     | Zn(II), Cd(II), Ni(II), Co(II)               | Cl^-     | 3.64-0.16·10^{-6} | 96.0_{Zn(II)}  | [19]       |
| 1-heptyl-2-methylimidazole    | Cu(II), Zn(II), Co(II), Ni(II)               | NO_3^-   | 3.86-0.21·10^{-6} | 85.0_{Cu(II)}  | [20]       |
| 1-decyl-2-methylimidazole     | Cu(II), Zn(II), Co(II), Ni(II)               | NO_3^-   | 1.23-0.14·10^{-6} | <92.0_{Cu(II)} | [21]       |
| 1-decyl-4-methylimidazole     | Zn(II), Cd(II), Ni(II), Co(II)               | Cl^-     | 3.72-0.15·10^{-6} | <95.0_{Zn(II)} | [22]       |

In a majority of studies, commercial extractants which exhibit low selectivity separation are used as ion carriers in transport through the liquid membranes [7-11]. Also imidazole and its derivatives, have been used for the membrane separation of metals such as Co(II), Ni(II), Cu(II), Zn(II), Fe(III), and Cd(II). Several works on their application in transport of nonferrous metal ions across PIMs have been collected in table 1.

The data compiled in table 1 show that alkyl imidazole derivatives more efficiently separate metal ions compared to crown ethers, as well as that the alkyl substituent placed in the 2 or 4 position in alkylimidazole molecules increases the possibility of effective separation of metal ions.

In this work, the authors present the results of investigation of the competitive transport of nonferrous metal ions as copper(II), zinc(II), and cadmium(II) across polymer inclusion membranes doped with 1-decyl-2,4-dimethylimidazole (DDMI) from dilute chloride solutions. The results were compared with the previously published results of liquid-liquid extraction of a mixture of Cu(II), Zn(II), and Cd(II) ions [23].

2. Experimental

2.1. Reagents

Analytical grade chemical reagents: copper (II), zinc(II) and cadmium(II) chlorides, hydrochloric acid, tetramethylammonium hydroxide were purchased from POCh (Gliwice, Poland). All aqueous solutions were prepared using analytical reagent grade chemicals and deionized water (conductivity –
0.10 μS/cm). Solutions of Cu(II), Zn(II) and Cd(II) were prepared by dissolving appropriate amounts of metal chlorides in water.

Analytical grade organic reagents, i.e. cellulose triacetate (CTA), o-nitrophenyl pentyl ether (o-NPPE) and dichloromethane (all from Fluka) were used without further purification. 1-Decyl-2,4-dimethylimidazole (DDMI) (figure 1) was synthesized by the alkylation of 2,4-dimethylimidazole (Sigma-Aldrich Company, Poland) in yields amounting to 63% according to the procedure described in paper [24].

![Structure of 1-decyl-2,4-dimethylimidazole (DDMI)](image)

Figure 1. Structure of the carrier 1-decyl-2,4-dimethylimidazole (DDMI), and its boiling point and acid dissociation constant (pKₐ)

2.2. The preparation of PIMs

The polymer membranes were prepared according to the procedure reported in the previous paper [15-22]. Organic solutions consisting of support (CTA), carrier (DDMI) and plasticizer (NPPE) in dichloromethane were prepared. A portion of this solution was poured into a membrane mould comprised of a 6.0 cm glass ring attached to a glass plate with CTA – dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resulting membrane was separated from the glass plate by immersion in cold water. The thickness of the PIM samples was measured using a digital micrometer (Panametrics® Magna-Mike® 8500 (San Diego, CA, USA)) with an accuracy of 0.0001 mm.

The thickness of a membrane was measured 10 times for each case and shown as the average value of these measurements, with the standard deviation below 1%. The thickness of the membrane before and after transport was the same. The average PIM thickness varied in the range was 28-32 μm. Each experiential point was repeated 4 times, i.e. membrane formed by immobilization, thickness measured and transport parameters calculated. Experimental reproducibility was high with standard deviation below 1% of the measured values.

2.3. Transport studies

Transport experiments were carried out in a permeation cell described in an earlier paper [15-22]. The membrane film (surface area 4.9 cm²) was tightly clamped between two cell compartments. Both the source phase and the receiving aqueous phase (45 cm³ each) were mechanically stirred at 600 rpm. Metal chlorides were used in the source phase, whereas the receiving phase was deionized water. The PIM transport experiments were carried out at 20 ± 0.2°C. Small samples of the aqueous receiving phase were taken periodically from the sampling port equipped with a syringe and analysed by atomic absorption spectroscopy (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA) to determine Cu(II), Zn(II), and Cd(II) concentrations. The pH of the source phase equaling 5.5 was kept constant using tetra-methyl-ammonium hydroxide.

The kinetics of transport across the PIMs was described as a first-order process with respect to the metal-ion concentration [25] expressed by equation (1):
\[
\ln \left( \frac{c}{c_0} \right) = -kt
\]  

(1)

where: \(c\) is the metal ions concentration (M) in the source aqueous phase at a given time, \(c_0\) is the initial metal ions concentration in the source phase, \(k\) is rate constant values, and \(t\) is the time of transport (s).

In order to calculate the value of \(k\), \(\ln(c/c0)\) versus time was plotted. The rate constant values for two independent transport experiments were averaged and the standard deviation was calculated. The correlation between \(\ln(c/c0)\) and time was linear, which was confirmed by the high correlation coefficient \((R^2)\) ranging from 0.9906 to 0.9974. The permeability coefficient \((P)\) was calculated according to equation (2):

\[
P = -\frac{V}{A} \cdot k
\]  

(2)

where: \(V\) is the volume of the aqueous source phase (m\(^3\)), and \(A\) is an effective membrane area (m\(^2\)). The initial flux \((J_0)\) is equal to:

\[
J_0 = P \cdot c_0
\]  

(3)

The selectivity ratio \((S)\) was defined as the ratio of initial fluxes for \(M_1\) and \(M_2\) metal ions, respectively:

\[
S = \frac{J_{0,M1}}{J_{0,M2}}
\]  

(4)

In order to describe the efficiency of metal removal from the source phase, the recovery coefficient \((RF)\) was calculated:

\[
RF = \frac{c_0 - c}{c_0} \cdot 100\%
\]  

(5)

The reported values correspond to the average values of three replicates, with deviations within 5%.

3. Results and discussion

3.1. Membrane characterization

An AFM image of PIM doped with DDMI in three-dimensional forms in a 5.0 x 5.0 μm format is shown in figure 2.
Calculated by atomic force microscopy (AMF) the porosity and roughness of PIM doped with DDMI was 23.7 and 5.8, respectively. Effective pore sizes for membrane was 0.065 \( \mu \text{m} \), respectively.

3.2. Separation of Cu(II), Zn(II) and Cd(II) ions from their equimolar solution across PIMs

Findings on the transport of non-ferrous metal ions from chloride solutions, across PIMs containing DDMI as ion carrier are discussed below. The concentration of the ion carrier in the membrane was 1.0 M (relative to the plasticizer) since earlier studies [15-22] indicate that the concentration is optimum for that group of carriers. The studies were carried out from single- or multi-component solutions, containing metals each at a concentration of 0.001 M. The initial flux values and selectivity coefficients for the metal ion transport across the PIM’s are shown in table 2.

### Table 2. Initial fluxes (\( J_0 \)), selectivity order and selectivity coefficients (S) for the competitive transport of Cu(II), Zn(II), and Cd(II) ions across PIMs doped DDMI.

| solutions | metal ion  | \( J_0, \mu\text{mol/m}^2\text{s} \) | \( S_{\text{Cu(II)/M(II)}} \) |
|-----------|------------|-----------------------------------|-------------------------------|
| I         | Cu(II)     | 10.82                             | -                             |
| II        | Cu(II)     | 8.56                              | Cu(II) > Zn(II)               |
|           | Zn(II)     | 5.84                              | 1.5                           |
| III       | Cu(II)     | 8.91                              | Cu(II) > Zn(II)               |
|           | Cd(II)     | 0.63                              | 13.5                          |
| IV        | Cu(II)     | 7.21                              | Cu(II) > Zn(II) > Cd(II)      |
|           | Zn(II)     | 4.57                              | 1.6                           |
|           | Cd(II)     | 0.26                              | 27.7                          |

It follows from the data shown in table 2 that the initial flux value for Cu(II) ion transport from a unary solution is higher than that from multi-component solutions. For a ternary mixture, the initial fluxes of metal ions transport across PIMs containing DDMI decrease in the following order: Cu(II) > Zn(II) > Cd(II). Selectivity coefficients (S) Cu(II)/Zn(II) and Cu(II)/Cd(II) were equal 1.5 and 13.5, respectively for binary solutions and 1.6 and 27.7 for ternary solution.

Decyl substituents at position 1 of the imidazole ring distinctly affect the hydrophobic properties of the molecule. An additional two methyl substituents at position 2 and 4 of the imidazole ring has been found to increase basicity by one order of magnitude, compared with that of 1-decylimidazole (pK\(_a\) = 7.39 [26]).
Ion carriers embedded in the membrane interact with metal ions in the diffusion-controlled water phase to form complexes. These form electrically neutral ion pairs with anions that penetrate the membrane in the co-transport:

$$M^{2+} + L + 2A^- \leftrightarrow (ML)_2A_2$$

(6)

where $M^{2+}$ is the metal ion, $L$ is the carrier, and $A^-$ is the co-transported anion (Cl$^-$).

### Table 3. Comparison of the stability constants $\beta_n$ of Cu(II), Zn(II), and Cd(II) complexes with DDMI, at 25°C, ionic strength 0.5 M (KNO$_3$) [23].

| metal ion | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ | $\log \beta_4$ |
|-----------|-----------------|-----------------|-----------------|-----------------|
| Zn(II)    | 2.17            | 4.48            | 6.39            | 9.87            |
| Cu(II)    | 3.95            | 7.18            | 9.42            | 11.69           |
| Cd(II)    | 2.53            | 4.21            | 5.68            | 7.56            |

The stability constants, $\beta_n$, of the studied metal complexes with DDMI are collected in table 3. The presence of the substituent at position 2 or 4 of the imidazole ring hinders the formation of each metal complex (steric effect). The stability constants of Cu(II), Zn(II) and Cd(II) complexes increase in the following order: Cd(II) > Zn(II) > Cu(II) (table 3).

In aqueous solutions, cations of Zn(II), Cd(II) and Cu(II) exist in the form of octahedral aqua complexes $(M(H_2O)_6)^{2+}$. Owing to the effect of ligands (extractants), octahedral aqua complexes of certain cations tend to change their coordination number (c.n.) from 6 to 4 and they change their coordination sphere into tetrahedral flat or, depending on the structure of their d-electron layer. The process is illustrated by the equation.

$$(M(H_2O)_{6-n+1}L_{n-1})^{2+} + L \leftrightarrow (M(H_2O)_{4-n}L_n)^{2+} + (n+2)H_2O$$

(7)

The steric effect of the substituent at position 2 decreases the stability constants of octahedral complexes of all the metals studied though it does not hinder the formation of tetrahedral species [23]. The formation of tetrahedral complexes with 1-alkylimidazoles has been proven for the Zn(II) and Cu(II) ions [27,28]. The Cu(II) ions were transported across PIMs most effectively. Perhaps the reason for this is the coordination sphere Cu(II), which is the most flexible, i.e. easier to deform [29]. It seems (compare tables 2-3) that the initial flux values correspond to those of the stability constants of the complexes.

### 3.3. Recovery of metal

The recovery factor (RF) of Cu(II) transport across PIMs from chloride solutions of Cu(II), Zn(II), and Cd(II) into deionized water is presented in fig. 3.
The highest recovery factors (RF) were found for Cu (II) ions for unary solution. The RF values of Cu(II) ions from binary Cu(II)-Zn(II) and Cu(II)-Cd(II) solutions are almost the same. In the case of a ternary Cu(II)-Zn(II)-Cd(II) mixture, the RF for Cu(II), Zn(II) and Cd(II) were 96, 60, and 3.5 percent, respectively.

The lowest RF values were obtained for Cd(II) ions, which are the slowest transported by this type of membrane. Practically, Cd(II) ions remain in the feeding phase.

3.4. Membrane diffusion coefficients of Cu(II), Zn(II), and Cd(II) complexes with DDMI
In figure 4, the correlation graphs \( (M^{2+})_0 - (M^{2+})_t \) versus time of metal ions transport across PIM doped with DDMI is presented.
The diffusion coefficient of M(II) was calculated from the equation:

$$D_0 = \frac{d_0}{\Delta_0}$$  \hspace{1cm} (8)

where: $d_0$ is the thickness of the membrane (0.003 cm) and $\Delta_0$ could be evaluated by plotting $(M^{2+})_{0-}$, $(M^{2+})_{t}$ vs. time.

The corrected (normalized) membrane diffusion coefficient $D_{o,n}$ [30], which considers the morphological features inside the membrane ($\varepsilon$ - porosity and $\tau$ - tortuosity), was calculated from equation:

$$D_{o,n} = D_0 \cdot \left(\frac{\varepsilon}{\tau}\right)$$  \hspace{1cm} (9)

where: $\varepsilon$ - porosity and $\tau$ – tortuosity.

Obtained values of diffusion coefficients are presented in table 4.

Values of diffusion coefficient determined in this study are comparable with presented in literature data for different membranes are in the range from $10^{-12}$ to $10^{-6}$ cm$^2$/s and show that limiting step of the process is the transfer of metal complex across membrane barrier. The value of the diffusion coefficient of M(II)-carrier species of $4.64 \cdot 10^{-11}$ - $1.06 \cdot 10^{-9}$ cm$^2$/s is smaller than the value of $1.5 \cdot 10^{-7}$ cm$^2$/s reported for the lead complex with the D$_2$EHPA in PIM’s reported by Salazar-Alvarez et al. [30].

The values of normalized diffusion coefficients (considering membrane porosity and tortuosity) of M(II)-carrier complexes, obtained in the process of transport across PIM’s containing DDMI from the solution Cu(II)-Zn(II)-Cd(II) are in the range $1.90 \cdot 10^{-12}$ - $1.03 \cdot 10^{-10}$ cm$^2$/s. Thus, the rate of transport of non-ferrous metal ions across PIM’s doped with DDMI is determined by the diffusion rate of the complexes M(II)-carrier across the membrane.

| metal ion | $\Delta_0$, s/m | $D_0$, s/m | $D_{o,n}$, s/m |
|-----------|-----------------|------------|----------------|
| Zn(II)    | $10^{6.45}$     | $1.06 \cdot 10^{-9}$ | $1.03 \cdot 10^{-10}$ |
| Cu(II)    | $10^{5.53}$     | $8.85 \cdot 10^{-9}$ | $3.63 \cdot 10^{-9}$ |
| Cd(II)    | $10^{7.81}$     | $4.64 \cdot 10^{-11}$ | $1.90 \cdot 10^{-11}$ |
Table 5. Comparison of solvent and membrane extraction of Cu(II), Zn(II), and Cd(II) complexes using DDMI as extractant/carrier.

| Selectivity Order | Solvent Extraction [23] | Membrane Extraction |
|-------------------|-------------------------|---------------------|
| Cu(II) > Zn(II) > Cd(II) | Cu(II) > Zn(II) > Cd(II) |
| Selectivity Coefficient | | |
| $S_{\text{Cu(II)/Zn(II)}}$ | $S_{\text{Cu(II)/Zn(II)}}$ | $S_{\text{Cu(II)/Cd(II)}}$ | $S_{\text{Cu(II)/Cd(II)}}$ |
| 1.4 | 1.6 | 1.5 | 27.7 |
| Recovery Factor of Cu(II), % | 94 | 96 |

| Solvent | Reaction Conditions |
|---------|---------------------|
| Dichloromethane | Nitrate, ionic strength 0.5 mol/dm$^3$ (KNO$_3$) | Chloride, pH=5.5 |

3.5. Comparison of transport across PIMs with solvent extraction (SX)

Previously, the possibility of Cu(II) ion separation from an equimolar Cu-Cd-Zn tertiary mixture by solvent extraction was investigated [23]. The separation of Cu(II) ions from the mixture of Cu(II)-Cd(II)-Zn(II) ions by solvent and membrane extraction is compared in table 5. In both processes, DDMI was used as the extractant or ion carrier.

It follows from the data shown in table 5 that the selectivity order in both extraction processes was the same. For PIMs selectivity coefficients $S_{\text{Cu(II)/Zn(II)}}$ and $S_{\text{Cu(II)/Cd(II)}}$ increased. Separation of Cu(II)/Zn(II) in both processes was almost the same, while the Cu(II)/Cd(II) separation is definitely better in the case of membrane extraction.

In addition, no toxic solvents are used in the membrane separation.

4. Conclusion

Copper(II) cations can be effectively removed from aqueous chloride solutions in the hydrometallurgical process of polymer inclusion membrane transport with 1-decyl-2,4-dimethylimidazole as ion carriers. With the use of this carrier the competitive transport of metal ions across the PIMs the order is: Cu(II) > Zn(II) > Cd(II). It seems that the initial flux values correspond to those of the stability constants of the complexes. The rate of transport of non-ferrous metal ions is determined by the diffusion rate of the complexes M(II)-carrier across the membrane. The selectivity coefficients of Cu(II)/Zn(II) and Cu(II)/Cd(II) were equal 1.5 and 13.5, respectively for binary solutions and 1.6 and 27.7 for ternary solution. Owing to the high steric effect, 1-decyl-2,4-dimethylimidazole fairly well differentiates the properties of its complexes with Cu(II), Zn(II), and Cd(II). The highest recovery factor (after 24 h) was obtained for Cu(II). In the case of a ternary solution, the RF for Cu(II), Zn(II), and Cd(II) were 96, 60, and 3.5 percent, respectively. The lowest RF values were obtained for Cd(II) ions, which are the slowest transported by this type of membrane.
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