# Selective transport of copper(II) ions across polymer inclusion membrane with aromatic β–diketones as carriers

**Elżbieta Radzymińska-Lenarcik, Katarzyna Witt, Daria Bożejewicz**

Faculty of Chemical Technology and Engineering, UTP University of Sciences and Technology, Seminaryjna 3, PL-85326 Bydgoszcz, Poland

Corresponding author: elaradz@utp.edu.pl (Elżbieta Radzymińska-Lenarcik)

**Abstract:** The transport of Cu(II) ions from an equimolar mixture of Co(II), Ni(II), and Cu(II) ions as well as from solutions containing only Cu(II) ions in the feed phase through polymer inclusion membranes (PIMs) with aromatic β–diketones as carriers has been investigated. The polymer membranes consisted of polyvinylchloride (PVC) as the support, bis(2-ethylhexyl)adipate (ADO) as plasticizer, and aromatic β–diketones (benzoylacetone (**1**) and dibenzoylmethane (**2**)) as ion carriers. The transport selectivity of PIMs with **1** and **2** was: Cu(II) > Co(II) > Ni(II). The highest recovery factors of Cu(II) ions were observed for **1** (94.0%), whereas for Co(II) and Ni(II) the factors were 21.4 and 7.3%, respectively. The Cu(II)/Co(II) and Cu(II)/Ni(II) selectivity coefficients were equal to 8.9 and 33.7 (for **1**), 6.4 and 28.3 (for **2**), respectively.

*Keywords: β-diketones, polymer inclusion membrane, metal ion separation, copper(II), cobalt(II), nickel(II)*

## 1. Introduction

For many years, there has been an increase in the use of non-ferrous metals such as Cu, Cr, Zn, Ni, etc. (Cote, 2000), which resulted in the increase of prices of these metals. As a result, the metallurgical industry needs new sources of these metals. Such additional sources may be poor off-balance sheet ores and solid, semi-solid and liquid industrial waste (ashes, slags, dusts, sludge and sewage) (Szyczewski et al., 2009; Radzyminska-Lenarcik et al., 2015a). These metallic raw materials are usually mixtures of many metals and because of their low content, they can only be recycled using hydrometallurgical processes, e.g. extraction, ion exchange or membrane techniques. These techniques utilize differences in the formation and structure of metal complexes with appropriately selected reagents (extractants/carriers).

The polymer-based membrane concept, which has been known for over 40 years, was proposed as an alternative to conventional solvent extraction (Almeida et al., 2012). Such membranes have been termed polymer inclusion membranes (PIMs) and have shown excellent stability and versatility, in particular when compared to other liquid membrane types, e.g. supported liquid membranes (SLMs) (Bartsch and Way, 1996). The membrane processes are also characterized by a better use of the ion carrier in the organic phase (membrane) in comparison with conventional extraction systems (Wieczorek, 2007; Baczynska et al., 2013).

The PIMs are usually composed of an extractant (carrier), a base polymer (cellulose triacetate (CTA) or polyvinyl chloride (PVC)) and a plasticizer or modifier. Such membranes are highly stable during the transport of metal ions (Walkowiak et al., 2000; Nghiem et al., 2006; Sgarlata et al., 2008; Almeida et al., 2012). The carrier is essentially a complexing agent or an ion-exchanger, responsible for binding with the species of interest and transporting it across the PIM.

Actually, the application of PIMs is focused mainly on the transport of metal cations. It has been shown in many papers that this type of membranes is able to transport different metal cations with high selectivity and good efficiency. De Gyves et al. (2006) described the removal of Cu(II) ions from a

Cu(II)-Zn(II)-Fe(III) mixture in chloride and sulfate medium across PIMs containing LIX® 84-I as the metal ion carrier.

The permeation of copper ions through PIMs containing di-(2-ethylhexyl)phosphoric acid (D₂EHPA) was investigated by Kavitha and Palanivelu (2012). High Cu(II) ion concentration in the feed phase leads to an increase in the flux values from $0.53 \times 10^{-6}$ to $4.48 \times 10^{-6}$ mol/m² ·s at pH 4.5. Also alkyl derivatives of imidazole: 1-heptyl-2- or 4-methylimidazole (Radzyminska-Lenarcik and Ulewicz, 2015b), 1-hexyl-2-methylimidazole (Ulewicz and Radzyminska-Lenarcik, 2012a); 1-decyl-2-methylimidazole (Ulewicz and Radzyminska-Lenarcik, 2012b), and 1-alkyl-2-methylimidazole (Radzyminska-Lenarcik and Ulewicz, 2017) were used as selective carriers for the recovery of Cu(II) ions from quaternary mixtures (Cu(II)-Zn(II)-Co(II)-Ni(II) or Cu(II)-Zn(II)-Cd(II)-Ni(II)). The best result for Cu(II) removal was obtained for the most hydrophobic alkylimidazoles (94.5%), while the selectivity ratios Cu(II)/M(II) decreased.

The hydrophobic β–cyclodextrin polymers have been used as macrocyclic ion carriers for the separation of metal ions from dilute aqueous solutions by transport across PIMs. In the case of competitive transport of Cu(II), Co(II), Ni(II) and Zn(II) ions through such PIMs, the selectivity order was: Cu(II) > Co(II) > Ni(II) > Zn(II) (Kozlowski et al., 2005).

The transport of Zn(II), Fe(II) and Fe(III) ions from chloride aqueous solutions across PIMs and supported liquid membranes (SLMs) containing one of three phosphonium ionic liquids: Cyphos IL 101, Cyphos IL 104 and Cyphos IL 167 as an ion carrier was reported (Baczyńska et al., 2016a, 2016b). The results showed that Zn(II) and Fe(III) are effectively transported through all of the investigated PIMs and SLMs, while the transport of Fe(II) is not effective. The highest values of initial flux and permeability coefficient of Zn(II) were reported for SLM containing Cyphos IL 167.

The use of 1-hexyl-4-methylimidazole as the carrier in PIMs enables the separation of 98.5% Zn(II) from a single component solution and 96.9% from a four-component solution of Zn(II)-Cd(II)-Co(II)-Ni(II) after running the process for 24 hours (Ulewicz and Radzyminska-Lenarcik, 2015).

Ulewicz et al. (2007) investigated the transport selectivity of the PIMs with five derivatives of imidazole azocrown ethers for a Pb(II)-Zn(II)-Cd(II) mixture. The transport selectivity coefficients varied in the following order: Pb(II) > Zn(II) > Cd(II). The best selectivity coefficient for Pb(II)/Cd(II) amounted to 46. Pb(II) ions present in the diluted feed solutions pH 3.0 were quantitatively removed (about 99%) in about 180–200 min. during the transport across membranes consisting of 50% D₂EHPA/50% PVC (w/w) (Gherisim et al., 2011). Aliquat 336/PVC-based PIMs enable the selective extraction of Cd(II) from chloride solutions (Xu et al., 2004; Annane et al., 2015) and can be also used to separate the Cd(II)-Cu(II) aqueous mixture (Wang and Shen, 2005; Upitis et al., 2009; Peterson and Nghiem, 2010). PIMs are also suitable for the preferential extraction of Co(II) ions from their acid solution containing Co(II)-Ni(II) because extraction of Ni(II) in the experimental conditions was not observed (Blitz-Raith et al., 2007). Moreover, there is a potential for the application of the PIMs with Cyanex 301 for Co(II) recovery from acidic leach liquor solutions from spent lithium ion batteries (Pospiech, 2013).

In most cases, the typical organic donors which form stable complexes with transition metal ions – commonly used in the extraction processes as extractants – are used as metal carriers, e.g.: crown ethers, quaternary ammonium salts, tertiary amines, pyridine derivatives, phosphoric acid derivatives, hydroxyoximes, and β-diketones (Almeida et al., 2012; Regel-Rosocka and Alguacil, 2013).

The complex-forming properties of β-diketones are used for the separation of metal ions from solutions by means of solvent extraction as well as PIMs (Miyake et al., 1990; Regel-Rosocka and Alguacil, 2013; Witt et al., 2016). LIX type extractants commercially used for the recovery of copper include 1-phenyl-3-isoheptyl-1,3-propanedione (LIX-54) (Kyuchoukov et al., 1998) or a mixture of a number of components, for instance, six isomeric 1-phenyldecane-l,3-diones (LIX 54-100) (Bermejo et al., 2000; Regel-Rosocka and Alguacil, 2013; Gotfryd and Pietek, 2013; Wejman-Gibas et al., 2017). Moreover, LIX 54 enables the separation of zinc (Alguacil and Cobo, 1998a) and nickel ions (Alguacil and Cobo, 1998b) from weakly basic media. Both, the LIX 54 and LIX 54-100 are also used as metal carriers in liquid membranes (Kyuchoukov et al., 1998).

However, a majority of commercial extractants, which were previously used as non-ferrous metal ion carriers during the transport through liquid membranes, do not have sufficient selectivity towards

a number of metals. Therefore, it is necessary to find new, selective carriers, which enable the separation of metal ions from aqueous solutions.

The aim of this study was to investigate the suitability of aromatic β-diketones to the selective transport of Cu(II), Co(II), and Ni(II) from model aqueous solutions using PIMs that consisted of polyvinyl chloride PVC (matrix) and bis(2-ethylhexyl)adipate ADO (plasticizer). The benzoylacetone (**1**) and dibenzoylmethane (**2**) were used as carriers. The values of three parameters: initial flux ($J_0$), selectivity coefficient ($S_{M(1)/M(2)}$), and recovery factor of a given metal after 60 hours (RF) were selected for the comparative analysis of the transport process.

## 2. Material and methods

### 2.1 Reagents

The inorganic chemicals, i.e. copper(II), cobalt(II) and nickel(II) nitrates, as well as tetramethylammonium hydroxide and hydrochloric acid were of analytical grade and were purchased from POCh (Gliwice, Poland). The aqueous solutions were prepared with double distilled water, the conductivity of which was 0.1 μS/m. The pH-meter was calibrated using the commercial buffer solutions (Radiometer) having a pH of 7.00±0.01 and 9.21±0.01, respectively.

The organic reagent, i.e. polyvinyl chloride (PVC) in suspension with an average molecular weight of 72000 was obtained from the Anwil company, Poland. The bis(2-ethylhexyl)adipate (ADO) and tetrahydrofuran (both of analytical grade) were purchased from POCh (Gliwice, Poland) and were used without further purification. The β-diketones (Fig. 1) were synthesized as described by Staniszewski and Urbaniak (Staniszewski and Urbaniak, 2009). Their characteristics is shown in Table 1.
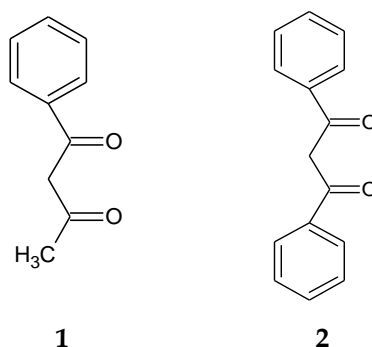


Fig. 1. Structures of benzoylacetone (**1**) and dibenzoylmethane (**2**)

Table 1. Physicochemical parameters of carriers

| Carrier | Molecular formula | Molecular mass, [g/mol] | Melting point [°C] | Boiling point [°C] | Physical state |
|---|---|---|---|---|---|
| benzoylacetone **1** | $C_{10}H_{10}O_2$ | 162.18 | 54-56 | 260-261 | white to off-white crystalline powder |
| dibenzoylmethane **2** | $C_{15}H_{12}O_2$ | 224.25 | 77–79 | 219–221 | white to yellow crystalline powder |

### 2.2 Polymer inclusion membrane preparation

A solution of polyvinylchloride (PVC) as a support, ADO as aplasticizer and β–diketone (**1**, **2**) as an ion carrier in tetrahydrofuran was prepared. A specified portion of the solution was poured into a membrane mould which was composed of a 9.0 cm diameter glass ring fixed on a glass plate with a PVC-tetrahydrofuran glue. After a slow evaporation of the solvent overnight, the resulting polymer

inclusion membrane was peeled off from the glass plate. Then the PIM was immersed for 12 hours in distilled water to make it homogeneous. In order to repeat the process in the same conditions two samples of the PIMs were cut out from the same membrane film for duplicate transport experiments. The average PIM thickness was 30-35 μm.

### 2.3 Transport studies

The transport experiments were carried out in a permeation module cell. The membrane film (having the surface area of 4.4 cm²) was tightly clamped between two cell compartments. Both phases: the feed and receiving aqueous phases (45 cm³ each) were mechanically stirred at 600 rpm. The 0.5 M HCl was used as a receiving phase. The PIMs transport experiments were carried out at 20±0.2 °C. Small samples of the aqueous receiving phase were taken periodically via a sampling port equipped with a syringe and analyzed by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam) to determine the copper(II), cobalt(II) and nickel(II) concentration. The feed phase pH (7.8) was kept constant using tetramethylammonium hydroxide and controlled by pH-meter (pH meter, CX-731 Elmetron, Poland), with a combination pH electrode (ERH-126, Hydromet, Poland).

The transport across PIMs fits the first-order kinetics in relation to the metal-ion concentration (Danesi, 1984-85), which can be described by equation 1:

$$\ln \frac{c}{c_0} = -kt \tag{1}$$

where $c_0$ – initial concentration of metal ions in the feed phase [M], $c$ – concentration of metal ions in the feed phase after time $t$ [M], $k$ – rate constant, [h$^{-1}$], $t$ – time of transport [h].

To calculate the value of $k$, the graph of $\ln(c/c_0)$ versus time was plotted. The rate constant values for two independent transport experiments were averaged and a standard deviation was calculated. The permeability coefficient ($P$, [m/s]) was calculated as follows:

$$P = -\frac{V}{A} k \tag{2}$$

where $V$ – volume of the aqueous phase, and $A$ – an effective area of membrane.

The initial flux ($J_0$, [mol/m²·s]) was determined as equal to:

$$J_0 = P \cdot c \tag{3}$$

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

$$S = J_{0,M1} / J_{0,M2} \tag{4}$$

To describe the efficiency of metal ions transport from the feed phase, the recovery factor ($RF$) was calculated:

$$RF = \frac{c_0 - c}{c_0} \cdot 100\% \tag{5}$$

### 3. Results and discussion

In the first series of the experiments, the authors investigated the transport of Cu(II) from nitrate aqueous solutions containing metal ions at a 0.001 M concentration through PIMs with aromatic β–diketone and ADO into 0.5 M hydrochloric acid aqueous solutions. No transport was detected after running the blank experiment for more than 60 hrs. The relationship between $\ln(c/c_0)$ and the time of Cu(II) transport across PIMs containing **1** or **2** β–diketone is shown in Fig. 2. The correlation between $\ln(c/c_0)$ and time was linear, as confirmed by the high correlation coefficient (R²) ranging from 0.915 to 0.986.
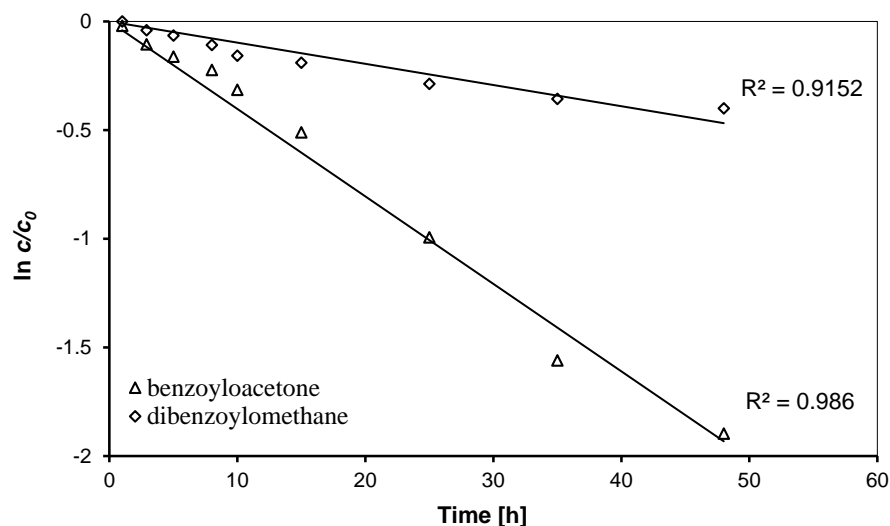
Fig. 2. Kinetics of Cu(II) ions transport across PIMs containing 0.05 M benzoylacetone (**1**) and dibenzoylmethane (**2**) from aqueous solutions. Feed phase: $c_M$ = 1 mM, pH = 7.8, receiving phase: 0.5 M HCl, Membrane: 0.5 g PVC, 0.2 g ADO, and 60% carrier calculated on PVC

As shown in Fig. 2, the transport of Cu(II) across PIMs with β–diketone can be described by first order kinetics in relation to the metal ion concentration changes. It is in accordance with the mathematical model proposed by Danesi (Danesi, 1984-85). The kinetic parameters and recovery factor of Cu(II) are summarized in Table 2 for both carriers **1** and **2**.

Table 2. Kinetic parameters and recovery factors for competitive transport
of Cu(II) across PIM with carriers **1** and **2**. Conditions as in Fig. 2

| Carrier | $P$ [μm/s] | $J_0$ [μmol/m² s] | $RF$ [%] |
|---------|------------|-------------------|----------|
| **1**   | 630.0      | 1.998             | 94       |
| **2**   | 389.6      | 1.239             | 38       |

Both the permeability coefficient and the initial flux are higher for carrier **1** in comparison with **2** (Table 2). Also, the recovery factor of Cu(II) is higher (more than twice as high). Such significant differences are a result of differences in the formation and stability of the Cu(II) complexes with both of the investigated carriers.

The β-diketones exist in the enol form (Eq. 6), making them Broensted acids. Owing to their specific structure, diketones combine with cations of block d and f metals, forming highly stable 6-member chelate complexes (Eq. 7) (Lis et al., 2011). The mechanism of metal ion complexation is very complicated because according to Miyake et al. (1990) both tautomeric forms of β-diketone are reactive towards metal ions. In the case of Cu(II), the reaction mechanism was described by equation 7.



(6)
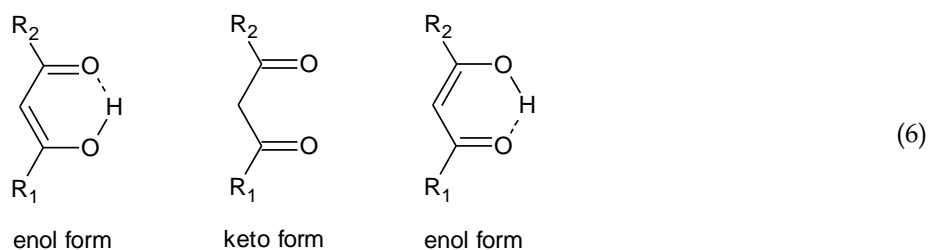
It has been noted that keto form hydrates are easily formed and are more stable in comparison with the hydrates of the corresponding enol forms (Prochaska et al., 1995). The stability constants of complexes of the studied carriers with Cu(II), Co(II) and Ni(II) ions are summarized in Table 3.
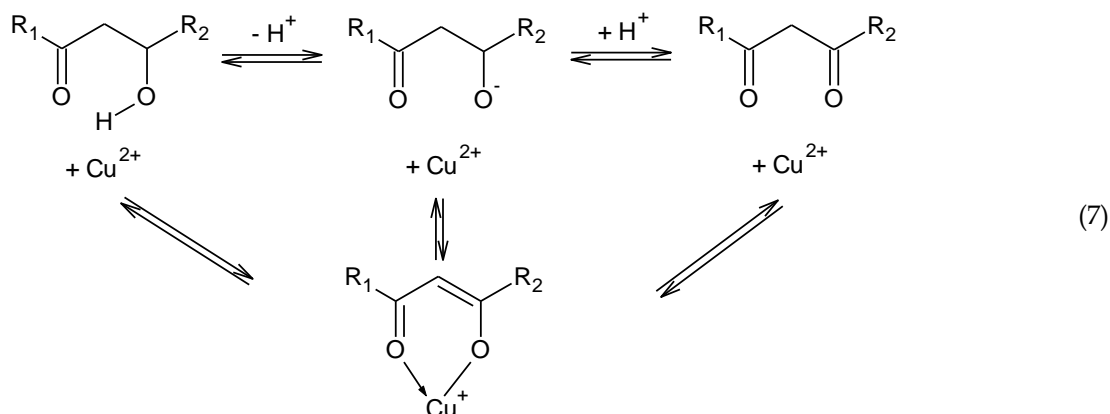


(7)

Table 3. Stability constants of complexes of benzoylacetone (**1**) and dibenzoylmethane (**2**) with selected metal ions at 30 ºC

| Ligand | Cu(II) | Co(II) | Ni(II) | Reference |
|---|---|---|---|---|
| dibenzoylmethane **2** | 12.98 | 9.97 | 10.46 | (van Uitert et al., 1953a) |
| benzoylacetone **1** | 12.05 | 9.42 | 9.58 | (van Uitert et al., 1953b) |

The stability constants (Table 3) of the complexes with **2** are higher than those of the same metals with **1**. For both carriers, the stability constants of their metal complexes with the metal ions decrease in the following order: Cu(II) > Ni(II) > Co(II).

The increased stabilities of metal ion complexes with **2** impede the process of dissociation of the complex from PIM to the receiving phase. As a result, lower values of the kinetic parameters for carrier **2** were observed – compiled in Table 1. It seems that too high stabilities of the complexes being formed in the membrane reduce transport efficiency. Fig. 3 presents the proposed mechanism of the transport of Cu(II) across PIMs.
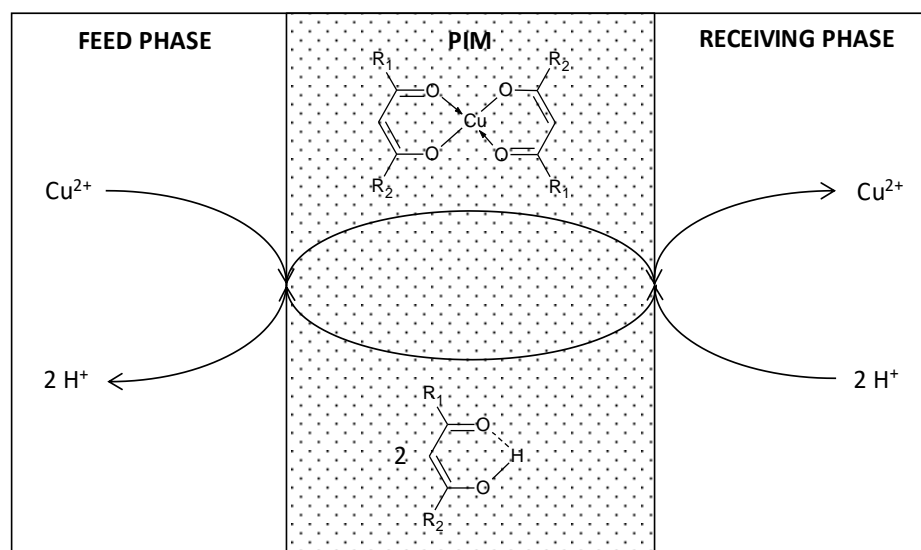


Fig. 3. Schematic transport of Cu(II) ions through the PIM doped with β-diketones

The transport of Cu(II) from an equimolar nitrate mixture of three metal ions (Cu(II)-Co(II)-Ni(II)), each at a 0.001 M concentration, across PIMs with aromatic β–diketone **1** was also investigated. The kinetic parameters and the selectivity order are summarized in Table 4.

The transport rate of Cu(II), Co(II) and Ni(II) across the studied membrane increased in the following order: Ni(II) < Co(II) < Cu(II). The stability constants of the complexes of these ions with **1** are increasing in the same order. Recovery factors for all of the investigated ions are shown in Fig. 4. The recovery factors (Fig. 4) of all ions investigated for PIMs with **1** increased with time. The highest recovery factors 94.0% (after 60 h) were obtained for Cu(II), whereas for Co(II) and Ni(II), the factors were 21.4 and 7.3%, respectively. The transport selectivity (Table 4) of the PIMs with **1** increased in the series: Cu(II) > Co(II) > Ni(II).

Table 4. Kinetic parameters, selectivity order, and selectivity coefficients for competitive transport of Cu(II), Co(II) and Ni(II) ions across PIM with carrier **1**. Conditions as in Fig. 2

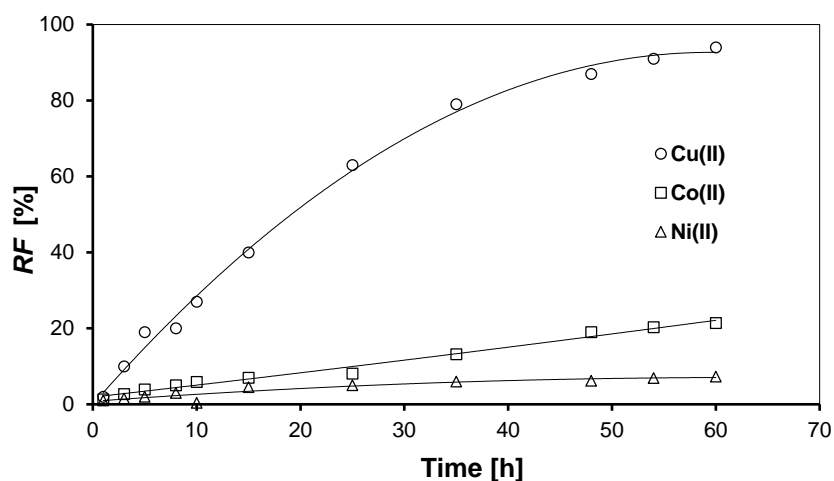| Metal ions | $P$ [µm/s] | $J_0$ [µmol/m²·s] | Selectivity order, and selectivity coefficients |
|---|---|---|---|
| Cu(II) | 106 | 0.337 | Cu(II) > Co(II) > Ni(II) |
| Co(II) | 3.8 | 0.038 | $S_{Cu(II)/Co(II)} = 8.9$ |
| Ni(II) | 1.1 | 0.010 | $S_{Cu(II)/Ni(II)} = 33.7$ |



Fig. 4. Recovery of Co(II), Ni(II), and Cu(II) from feed phase from aqueous solutions in transport across PIMs with β–diketone **1**. Feed phase: $c_M$ = 1 mM, pH = 7.8; receiving phase: 0.5 M HCl; membrane: 0.5 g PVC, 0.2 g ADO, and 60% carrier calculated on PVC
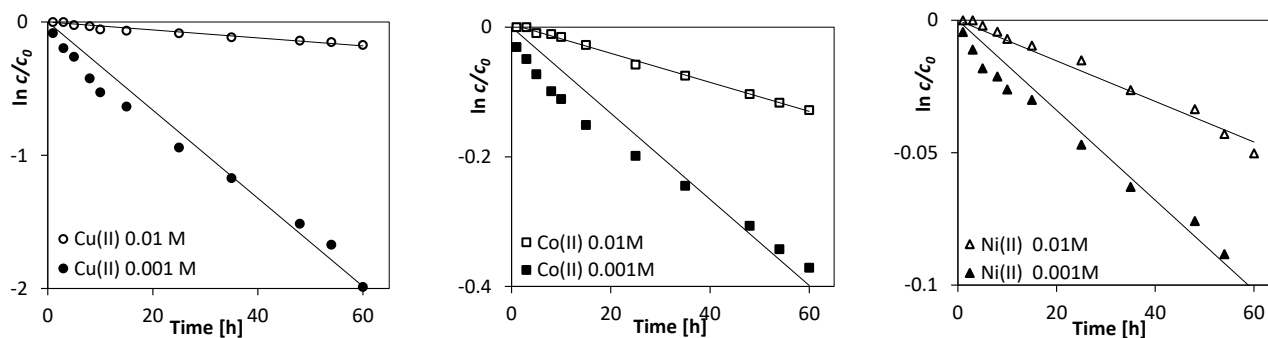


Fig. 5. Relationship of ln($c/c_0$) vs. time for Cu(II), Co(II) and Ni(II) transport across PIMs with **2** from the feed phase of different metal ions concentrations; receiving phase: 0.5 M HCl, membrane: 0.5 g PVC, 0.2 g ADO, and 60% carrier **2** calculated on PVC

In order to examine the influence of the metal ions concentration in the feed phase, the transport of the metal ions from two equimolar mixtures of three ions (0.001 and 0.01 M) was performed. The relationship between ln($c/c_0$) and time for Cu(II), Co(II) and Ni(II) transport across PIMs doped with carrier **2** is shown in Fig. 5, whereas the kinetic parameters (calculated for the experimental data) are summarized in Table 5.

Table 5**.** Kinetic parameters for competitive transport of metal ions across PIM with carrier **2**. Conditions - Fig. 5

| Concentration of metal ions [M] | Type of metal ions | $k$ [$h^{-1}$] | $J_0$ [$\mu mol/m^2 \cdot s$] |
|---|---|---|---|
| 0.001 | Cu(II) | 0.0496 | 14.2 |
| | Co(II) | 0.0053 | 2.20 |
| | Ni(II) | 0.0015 | 0.50 |
| 0.01 | Cu(II) | 0.0216 | 0.62 |
| | Co(II) | 0.0022 | 0.089 |
| | Ni(II) | 0.0008 | 0.026 |

It is evident that metal ions are transported across PIMs at a higher rate from solutions of lower concentration. Also, the initial fluxes are higher for thess concentrations (Table 5). For the 0.01 M concentration, the selectivity coefficients Cu(II)/Co(II) and Cu(II)/Ni(II) are equal to 6.95 and 23.5, respectively. For the 0.001 M solutions, the same parameters are 6.43 and 28.3, respectively. For both concentrations, the transport selectivity across the PIM with **2** is ordered as: Cu(II) > Co(II) > Ni(II) (Fig. 5).

The new compounds investigated, i.e. aromatic β–diketones (benzoylacetone (**1**) and dibenzoylmethane (**2**)), can be used for recovering Cu(II) from nearly neutral solutions using PIMs. The commercial extractant LIX 54-100 containing six isomeric 1-phenyldecane-1,3-diones (Dziwinski and Szymanowski, 1996) was used for the extraction of Cu(II) from acidic waste solutions (Gotfryd and Pietek, 2013). According to these authors, the $pH_{1/2}$ corresponding to 50% of copper extraction was 2.2. Bermejo et al. (2000) investigated the membrane extraction (SLMs) of copper from ammoniacal/ammonium sulfate medium by LIX 54-100 dissolved in Iberfluid (kerosene type diluent). According to these authors, the permeability coefficients depend on pH, and at pH 8.8, 9.5, and 10.5 they were 565, 416 and 210 μm/s, respectively. The PIMs with benzoylacetone (**1**) and dibenzoylmethane (**2**) can be used for copper recovery from ammoniacal solutions obtained after leaching waste containing a small amount of copper ions.

## 4. Conclusions

The new PVC-based polymer inclusion membranes, with aromatic β–diketones (benzoylacetone (**1**) and dibenzoylmethane (**2**)) were prepared. Copper(II) can be effectively separated from equimolar aqueous solutions of copper, cobalt, and nickel nitrates with these PIMs.

The separation of metal ions using PIMs with benzoylacetone (**1**) was more effective than those with dibenzoylmethane (**2**). The transport selectivity of the PIMs was ordered as follows: Cu(II) > Co(II) > Ni(II). The highest recovery factors for Cu(II) were observed for benzoylacetone (94.0%), whereas for Co(II) and Ni(II), the factors were 21.4 and 7.3%, respectively. The Cu(II)/Co(II) and Cu(II)/Ni(II) selectivity coefficients of the PIMs were equal to 8.9 and 33.7 (for **1**), 6.4 and 28.3 (for **2**), respectively. The metal ions were transported across the PIMs at higher rates from solutions of lower concentrations.

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