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Facilitated selective transport of Co(II), Ni(II), Zn(II) and Cd(II) across polymer inclusion membranes containing 1-decyl-imidazole as a carrier

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Abstract

The work aimed to investigate the possibility of selective separation of Co(II), Ni(II), Zn(II) and Cd(II) ions from chloride solution with variable chloride ion concentration (0.25, 0.5 and 1.0 M) using polymer inclusion membranes. In the studies, polymer inclusion membranes were used, with cellulose triacetate as the matrix, *o*-nitrophenyl octyl ether as the plasticizer, and 1-decylimidazole as a metal ion carrier. The receiving phase was demineralized water. The results of the studies on the transport of metal ions through polymer inclusion membranes with 1-decylimidazole as an ion carrier indicate a strong influence of the chloride ion concentration in source phase on the transport rate, and their separation properties. The kinetic parameters such as the transport flux, the recovery factor, as well as the separation coefficients were determined for the experimental data. It was found that zinc(II) ions were the easiest to separate from the aqueous chloride solution. The

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recovery rates (%) of zinc ions, for chloride ion concentrations of 0.25 M, 0.5 M, and 1.0 M, were 71%, 88%, and 65%, respectively. The lowest recovery observed was for nickel(II) ions, which did not exceed 2%. In contrast, cadmium ions had removal recovery rates ranging from 5.5% to 6.5%, and for cobalt ions – from 2.5% to 14.5%, depending on chloride anion concentration in the source phase. The separation coefficient for zinc ions was the highest compared to the other ions. The results from studies on the transport of nickel(II), cobalt(II), cadmium(II), and zinc(II) ions through polymer inclusion membranes with 1-decylimidazole suggest that this process can be effectively used for the selective separation of Zn(II) ions from a multi-metal aqueous solution.

Keywords: polymer inclusion membranes, 1-decylimidazole, separation, selectivity, metal ions

1. INTRODUCTION

Transition group metals are of particularly high economic importance. Nickel and cobalt are widely used, inter alia, as steel additives, in alloys with non-ferrous metals, as coatings with high resistance and strength, hard sintered materials, soft and hard magnets, pigments, catalysts and in batteries and cells, including in hybrid vehicles (Hassan et al., 2025). Zinc is primarily used for anti-corrosion coatings. However, it is also used in cells and batteries. Cadmium is a toxic metal which, if present in waste or wastewater, needs to be removed.

The ever wider and more intensive use of transition group metals in various fields makes it necessary to search for new sources of raw materials. The growing use of heavy metals is generating an increasing amount of waste and used components containing these metals. Due to the presence of heavy metals, this waste poses a major threat to the environment and has to be managed due to environmental requirements (Alrwashdeh et al., 2025; Chen et al., 2021). It is therefore necessary to dispose of this type of waste. However, this waste can be an additional source of raw materials of great potential importance.

The search for new sources of metallic raw materials makes it necessary to manage various, often poor and usually polymetallic ores with specific chemical compositions. Another important new source of raw materials is the waste generated during pyrometallurgical processing of primary raw materials, e.g. slags, dust and sludge, as well as post-refining electrolytes withdrawn from circulation (Liu et al., 2023; Wei et al., 2023). The management of secondary raw materials such as metallic scrap, used catalysts from the oil or food industry, used batteries and many others is also of great practical importance (Oghabi et al., 2020). All the raw materials listed here can be a valuable source of metals. They are, however, characterised by the fact that they are mostly polymetallic raw materials containing many valuable metals but in relatively small quantities. In addition, in the case of secondary raw materials, the quantity of these materials at their place of origin or collection may be small. In such a situation, the use of typical pyrometallurgical methods appears to be inefficient. If secondary raw materials were used, they would have to be transported long distances to where the relevant processing plants are located. For these reasons, it is very important to develop technological processes that enable the economically viable processing of small quantities of multi-component metallic raw materials at their place of origin. Considering the rapid development of hydrometallurgical methods observed over the last few decades, it seems that these technologies will be the most suitable (Li et al., 2018; Li et al., 2020).

Hydrometallurgical processes include solvent extraction, ion exchange, and membrane transport processes. They can be either one of the stages of larger technological processes for obtaining metals from ores and secondary raw materials, or a stand-alone alternative to pyrometallurgical methods (Li et al., 2024). Literature reports indicate that hydrometallurgical processes are particularly important in the processing of polymetallic and low-metal-content raw materials, such as poor ores, semi-finished products, industrial waste, and secondary raw materials (Jaramillo et al., 2025).

Polymer inclusion membranes (PIMs) have become very popular. A typical PIM consists of a polymer matrix, a plasticiser, and a carrier. The most commonly used polymer matrices are cellulose derivatives, mainly cellulose triacetate (CTA), polyvinyl chloride (PVC), and polyvinylidene fluoride (PVDF). The addition of a plasticizer to the polymer membrane improves the ability of the ion carrier to mix with the polymer and increases the elasticity of the membranes. The most commonly used plasticisers are nitrophenylalkyl ethers with different substituent lengths. Some metal ion transporters can also act as plasticisers: tributyl phosphate (TBP) or di(2-ethylhexyl)phosphoric acid (DEHPA). Thanks to this membrane structure, PIMs have better mechanical properties and chemical resistance than supported liquid membranes (SLMs) (Kaczorowska et al., 2023; Keskin et al., 2021; Senila, 2025; Zhao et al., 2023)

The use of membranes for the selective separation and extraction of heavy metal ions from aqueous solutions allows for the elimination of significant amounts of flammable and often toxic compounds used in typical extraction processes. An additional benefit is the ability to use small amounts of carrier. This makes it possible to use relatively expensive but effective carriers in a PIM, which are not economically viable in typical extraction and re-extraction processes (Kaczorowska, 2022).

One group of compounds that can act as effective metal ion carriers in membrane processes using PIMs are imidazoles (Radzyminska-Lenarcik et al., 2020; Szczepański et al., 2021).

Imidazoles belong to a large group of five-membered heterocyclic aromatic compounds containing one to five nitrogen atoms in their molecule. Such compounds, referred to as azoles, may also contain oxygen or sulphur atoms. Due to the presence of a nitrogen atom with a free electron pair, they can form complexes with transition group metals such as Cu, Ni, Co or Zn (Wang et al., 2024). The stability of these complexes depends on the metal cation. These types of aromatic amines are significantly less protonated than aliphatic amines. It can therefore be expected that they will be more selective as metal ion carriers than aliphatic amines (Zhu et al., 2022)

Imidazoles are weak bases. Their pKa depends only slightly on the length of the alkyl substituent chain and varies from about 7.2 to about 7.5 units (Tolomeu and Fraga, 2023). Imidazoles have two aromatic nitrogen atoms in positions 1 and 3 of their molecule. In imidazoles used as metal ion transporters, one of the nitrogen atoms is substituted and, due to steric hindrance, does not participate in the formation of complexes, while the other, which is not substituted and has a free electron pair, can enter the hydration zone of divalent metal ions such as Cu(II), Co(II) or Ni(II), forming complexes with the general formula MCl_2L_2 in aqueous solutions containing chloride ions (Li et al., 2023).

Various imidazole compounds, especially 1-alkylimidazole derivatives, have been used in PIM technology as selective extractants or metal ion carriers (Radzyminska-Lenarcik and Ulewicz, 2019a; Radzyminska-Lenarcik and Ulewicz, 2019b; Radzyminska-Lenarcik et al., 2022; Szczepański et al., 2021; Ulewicz and Radzyminska-Lenarcik, 2020).

Given the nature of the complexes formed by 1-alkylimidazoles with metal ions, it can be expected that the concentration of chloride anions will have a significant effect on the selectivity of the separation process using PIM.

2. EXPERIMENTAL

2.1. Reagents/Materials

The following substances were used in the study: $CoCl_2$, $NiCl_2$, dichloromethane (Chempur, Poland), $CdCl_2$, $ZnCl_2$, and NaCl (STANLAB, Poland). Additionally, cellulose triacetate (CTA, >98%, Sigma-Aldrich) and ortho-nitrophenyloctyl ether (ONPOE, Fluka) were included. For the synthesis of 1-decylimidazole, the reagents used were imidazole, 1-bromodecane, sodium (Sigma-Aldrich), and methanol (Chempur).

All reagents used were of analytical purity. Demineralised water was used to prepare aqueous solutions.

2.2. Synthesis of 1-decylimidazole

The study used 1-decylimidazole (IMI10) obtained by reacting imidazole with the corresponding 1-bromodecane (Figure 1), in accordance with the procedure described earlier (Emel'yanenko et. al., 2011).

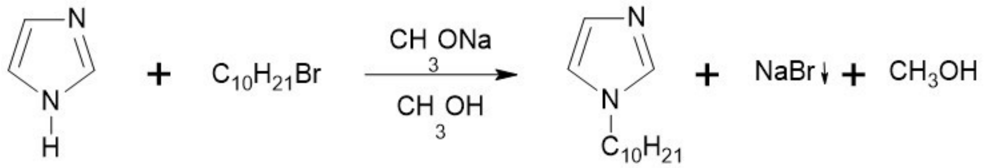

Figure 1. Reaction scheme of alkylation with imidazolibromoalkanes.

In order to obtain 1-decylimidazole, 250 ml of methanol was poured into a three-necked flask equipped with a stirrer, dropping funnel and reflux condenser, and then

0.3 moles of metallic sodium were added in portions. Once the sodium had completely reacted, 0.3 mole of imidazole was introduced into the flask. The mixture was stirred vigorously until the introduced imidazole dissolved completely. Then, 0.33 moles of 1-bromodecane were added to the flask. The reaction was carried out at a temperature of 64 °C in the presence of the resulting sodium methoxide for 4 hours. The sodium bromide released during the reaction was drained off and then the solvent was distilled off. For the removal of small amounts of unreacted imidazole, the residue was extracted three times with distilled water at 50 °C. The product was subjected to double vacuum distillation (1 Torr) to obtain 1-decylimidazole with a yield of 91%. The purity of the resulting imidazole derivative was assessed using a Hewlett Packard 5890 Series II gas chromatograph equipped with an HP-5 capillary column, a flame ioniser and a Hewlett Packard 3390A Integrator. The purity of the obtained product was about 99.9%.

^{1}H NMR (600 MHz, DMSO-d_6, TMS): δ [ppm] = 0.83–0.88(t, J = 6,9 MHz, 3H); 1.26–1.29(m, 14H); 1.67–1.72(m, 2H); 3.77–3.82(t, J = 6.6 MHz, 2H); 7.85(s, 1H); 7.88(s, 1H); 9.35 (s, 1H).
^{13}C NMR (150 MHz, DMSO-d_6, TMS): δ [ppm] = 12.63; 13.71; 22.27; 26.24; 28.81; 28.83; 29.05; 29.36; 30.41; 31.44; 118.53; 126.58; 143.73.

2.3. Membrane preparation

The following solutions were used for the synthesis of polymer inclusion membranes (PIM): 1.25 % CTA in dichloromethane (w/v), 10% vol. ONPOE as a plasticiser in dichloromethane and 0.10 mol/dm^3 ion carrier solution (IMI10) in dichloromethane. The measured volumes of CTA solution, plasticiser and carrier (in the ratio CTA:ONPOE:IMI10 = 3:1:1 v/v) were mixed thoroughly and poured onto a Petri dish with a diameter of 4.0 cm placed on a flat horizontal surface. The surface area of the membrane was 12.6 cm^2. The dish was left for 24 hours to allow the solvent to evaporate. The membrane was then weighed and its thickness was measured to an accuracy of ±0.1 μm by a digital ultrameter of the A2002M model from Inco-Veritas). The thickness was measured at 17 points. Its thickness was 24.9 ± 0.9 μm. The composition of the membrane was (% by weight): CTA –

23.1%, ONPOE – 64.1%, IMI10 – 12.8% Each membrane was conditioned in demineralised water for 24 hours before being used in the transport process.

2.4. Transport experiments

The measuring vessel for testing metal ion transport across PIM consisted of two chambers, each with a volume of 50 cm^3, separated by a membrane with a working area of 4.91 cm^2 (Fig. 2). The feed phase consisted of solutions containing one- (Zn), and four-component mixtures of cobalt(II), nickel(II), zinc(II) and cadmium(II) chlorides at concentrations of 0.01 mol/dm^3. Variable concentrations of chloride anions (0.25, 0.5 and 1.0 mol/dm^3) were obtained by adding the appropriate amount of NaCl. During the tests, the pH of the feed phase was controlled, which was about 5.5±0.2. Since the transport of metal ions across the tested PIM involved co-transport rather than counter-transport of protons, there was no need to adjust the pH of either the feed or receiving phases during the tests. The receiving phase was demineralised water. The measuring vessel was placed in a water bath at a fixed temperature of 20±1 °C.

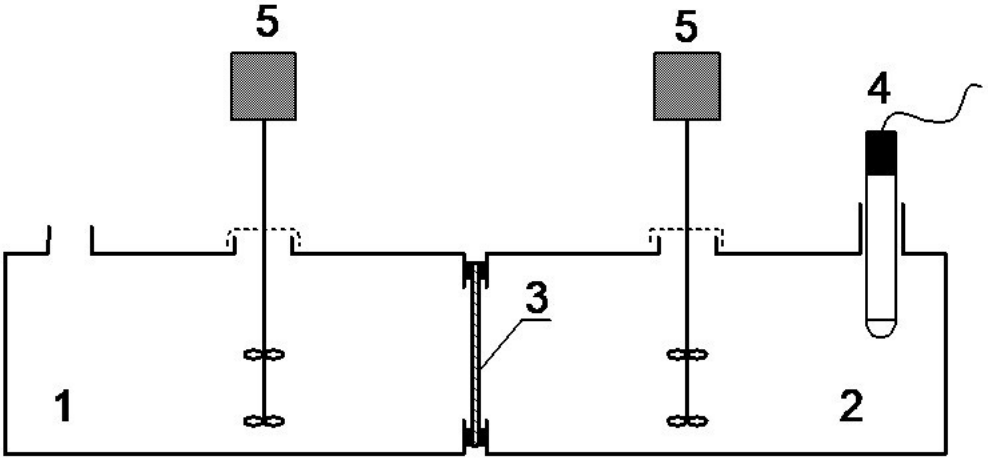

Figure 2. Measuring system for metal ion transport through PIM membranes; 1 - receiving phase 2 - feed phase, 3 - membrane, 4 - pH electrode, 5 – stirrers.

The experiment was conducted for 8 hours. Both solutions were stirred at a rate of 600 rpm. During transport, 0.2 cm^3 of the feed and receiving phases were collected for analysis every hour, and, after dilution, subjected to quantitative analysis for metal content using an Agilent emission spectrometer, in which microwave-induced nitrogen plasma at a temperature of 5000 K is used to excite the elements. Each sample was analysed three times. The average value was used for further calculations. The analysis error, taking into account instrument error and the scatter of results expressed as measurement uncertainty (standard deviation for the mean), did not exceed 3%.

The concentration of chloride anions in the receiving phase was determined using a Dionex DX-100 ion chromatograph with an AS4SC column, an AG4SC guard column and an ASRS-II suppressor. A solution of 1.7 M Na_2CO_3 + 1.8 M $NaHCO_3$ was used as the eluent.

2.5. Mathematical model

When conducting the study, it can be assumed that in the initial period, the rate of metal ion transport across PIM is directly proportional to the difference in metal ion concentrations in the feed and receiving phases. With this assumption, the concentration of metal ions in the feed phase can be described by a first-order kinetic equation (Danesi, 1984; St John et al., 2013):

$$\frac{dc}{dt} = -k(c - c_0) \tag{1}$$

where: c [mol/dm^3] – concentration of metal ions on the feed side at time t, c_0 [mol/dm^3] – initial concentration of metal ions on the feed side. In this equation, the transport rate coefficient k [1/s] takes into account all processes occurring during the transport process.

By integrating the above equation with the initial condition $c = c_0$ for $t = 0$, the following relationship is obtained:

$$ln\left(\frac{c}{c_0}\right) = -kt \tag{2}$$

This relationship is linear in the initial period of the study. Therefore, using linear regression analysis methods, the transport rate coefficient k can be determined.

As a quantity characterising the transport of metal ions across the PIM, the initial flux, J_0 [mol/(m^{2}s)], was determined from the following relationship:

$$J_0 = \frac{V}{A}kc_0, \tag{3}$$

where V [m^3] – volume of the feed phase, A [m^2] – working area of the membrane.

Additionally, in order to quantitatively describe the process of metal ion separation during transport across the PIM, selectivity coefficient was calculated, defined as the ratio of the initial flux of metal I ions to the initial flux of metal II ions:

$$S_{M_I/M_{II}} = \frac{J_{0,M_I}}{J_{0,M_{II}}}, \text{ gdzie } J_{0,M_I} > J_{0,M_{II}} \tag{4}$$

and the recovery factor R (%) indicating the efficiency of metal ion separation from the feed phase, defined as:

$$R(\%) = \frac{c_0 - c}{c_0} \cdot 100\% \tag{5}$$

3. RESULTS AND DISCUSSION

The carrier under study is a 5-membered heterocycle consisting of an amine and an imine nitrogen atom in positions 1 and 3, respectively. The molecule is aromatic with electrons distributed over 5 ring atoms but concentrated on the nitrogen atoms. Slightly higher electron densities in positions 4 and 5 offer potential sites for electrophilic substitution; position 2 is slightly electropositive and therefore more susceptible to nucleophilic substitution (2). A stable structure is formed upon protonation of the imine nitrogen, with imidazole having a pKa of approximately 7 (3). Like water, imidazole is both a good proton acceptor and donor and forms a network of hydrogen bonds that provides a means of proton transfer (3) (Eicher and Hauptmann, 2003; Every and Zawodzinski, 2004).

3.1. Chloride ions transport

Our previous studies suggest that only inert MCl_2 molecules (Gajda and Bogacki, 2012; Gajda et al., 2011), where M are divalent transition metal cations, are transported across the PIM with imidazole derivatives as the carrier. This hypothesis was verified by studying the transport of zinc across the PIM with IMI10 as the carrier. In the tests, a single-component solution containing 0.01 mol/dm^3 $ZnCl_2$ and 0.5 mol/dm^3 Cl^- ions was used on the feed side. On the receiving side, demineralised water was used. During the study, the concentration of chloride ions and zinc(II) ions was measured on the receiving side. The experiment was conducted for 8 hours. The test results are shown in Figures 3 and 4.

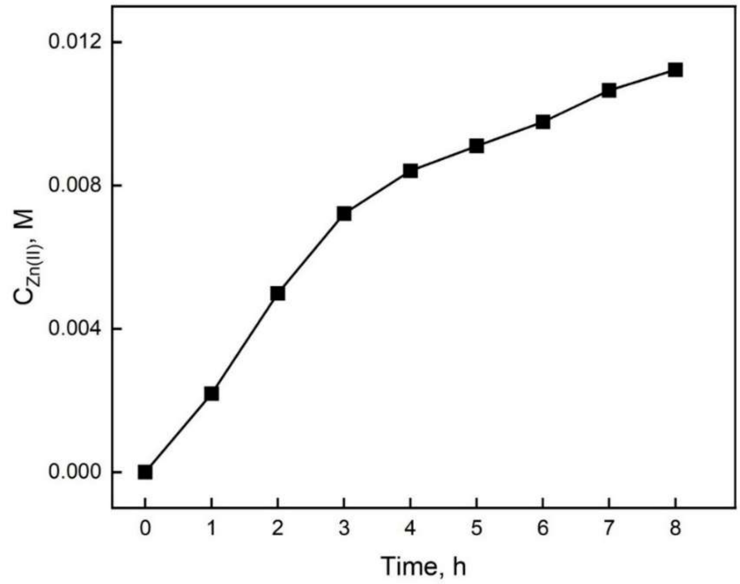

Figure 3. Change in Zn(II) ion concentration over time in the receiving phase. Feed phase: 0.01 M $ZnCl_2$, 0.5 mol/dm^3 Cl^-; receiving phase: demineralised water.

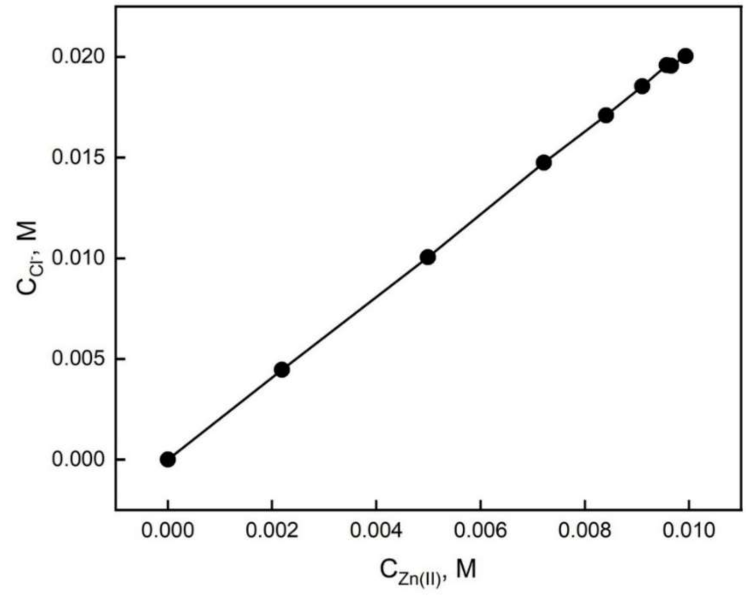

Figure 4. Change in the concentration of chloride anions in the receiving phase as a function of the concentration of Zn(II) ions in the receiving phase. Feed phase: 0.01 M $ZnCl_2$, 0.5 mol/dm^3 Cl^-; receiving phase: demineralised water.

The concentration of zinc(II) ions in the receiving phase increases monotonically (Fig. 3). This increase is accompanied by an increase in the concentration of chloride anions in the receiving phase (Fig. 4), this increase being directly proportional to the concentration of zinc(II) in the solution. The experimental points lie on a straight line $y = a + bx$, where the regression coefficients with standard uncertainty are $a = (4.36 \pm 9.5) \times 10^{-5}$ and $b = 2.036 \pm 0.012$, respectively. This equation is statistically significant, and the correlation coefficient is $R^2 = 0.9998$. Statistical analysis of this model indicates that the free expression a is statistically insignificant. Therefore, a new model $y = bx$ has been determined, where the direction coefficient is $b = 2.041 \pm 0.005$. This model is also statistically significant; the correlation coefficient in this case is $R^2 = 0.9999$.

The above shows that the concentration of chloride anions in the receiving phase is twice as high as that of Zn(II) ions. Therefore, it can be assumed that Na^+ is not transported during the transport across the PIM with IMI10 as the carrier because the ratio of Zn^{2+} to Cl^- is 2:1, and not 1:1 as in the case of Na^+ to Cl^-.

3.2. Metal complexes formation in membrane phase

1-Alkylimidazoles are basic extractants. They form complexes in the form of an ion pair according to the reaction:

$$\mathrm{MCl_2 + 2Im \rightleftarrows MCl_2 \cdot (Im)_2} \tag{6}$$

using the imidazole nitrogen atom for this purpose. Since the two-component solution on the feed side contains only the chlorides $ZnCl_2$, $CdCl_2$ and NaCl, while the receiving side is distilled water, any protonation of this type of ion carrier can be disregarded. In this situation, inert MCl_2 molecules must be carried across the membrane, as shown in reaction 6.

Inert chlorocomplexes of zinc(II) and cadmium(II) are formed in largest quantities at chloride anion concentrations of approximately 1 M. A further increase in the concentration of chlorides in the solution results in a decrease in the concentration of MCl_2 and an increase in the concentration of anionic chlorocomplexes MCl_3^- and MCl_4^{2-}. In line with this observation concerning the distribution of zinc(II) and cadmium(II) chlorocomplexes depending on the concentration of chloride anions, a process of selective transport across the PIM with 1-decyloimidazole as an ion carrier occurs. This may provide indirect confirmation of the assumed composition of the complex of the tested ions with this carrier.

3.3. Metal transport – four-component systems

The results obtained from the study of metal ion transport across the PIM containing IMI10 as a metal ion carrier indicate a strong influence of chloride ion concentration on the transport rate, the amount of ions transported across the membrane and their separation. There is also a noticeable influence of the composition (presence or absence of individual metal ions) on the transport process. In the feed phase, there was a four-component system of metals with the same concentration, which was transported across the PIM, determining kinetic parameters and separation properties.

The test results for the transport of metal ions across polymer inclusion membranes containing 1-decylimidazole used in the study as carrier indicate a strong influence of chloride ion concentration on the transport rate, the amount of ions transported across the membrane and their separation (Table 1).

Analysis of the results for individual metal ions indicates that the transport of zinc(II) ions is most favoured. In this case, all kinetic parameters are at least one order of magnitude greater than for cobalt(II) and cadmium(II) ions and two orders of magnitude greater than for nickel(II) ions. For cobalt(II) and cadmium(II) ions, the kinetic parameters are comparable. Nickel(II) ions have the worst kinetic values. In this case, the values of these parameters are an order of magnitude smaller than for cobalt(II) and cadmium(II) ions.

The effect of chloride ion concentration on the transport of individual metal ions across the PIM is not identical for each of the ions studied. Thus, in the case of cadmium(II) and zinc(II), an increase in chloride concentration in the feed phase causes a slight decrease in the values of the determined kinetic parameters. In the case of cobalt(II) ions, the values of the kinetic parameters increase with increasing chloride anion concentration from 0.25 to 0.50 M and then decrease. For cobalt(II) ions, the change in chloride anion concentration has practically no effect on the values of kinetic parameters.

The effect of chloride anion concentration on the recovery rate of metal ions is similar. Thus, an increase in chloride anion concentration results in a decrease in this parameter for zinc(II) and cadmium(II) ions, an increase for cobalt(II) ions, and virtually no effect on the recovery rate for nickel(II) ions.

The recovery rate also shows the possibility of selective separation of zinc(II) ions from a polymetallic solution containing all four metal cations under study. Depending on chloride anion concentration, 71, 88 and 65% can be separated from such a solution for chloride anion concentrations of 0.25, 0.5 and 1.0 M, respectively. The lowest recovery was observed for nickel(II) ions – it does not exceed 2%. For cadmium ions, the recovery rate is between 6.5 and 5.5%. For cobalt, however, it rises from an initial value of 5.5 to 14.5 and then falls to 2.5% for chloride anion concentrations of 0.25, 0.5 and 1.0 M, respectively.

3.4. Kinetics Parameter of transport process

A prerequisite for the transfer of a metal ion across the PIM is its complexation with 1-alkylimidazole. The permeability coefficients (P) of the cations are quite consistent with the stability constants of their 1-alkylimidazole complexes. The presence of an alkyl chain in the 1-alkylimidazole molecule increases the donor part of the carrier, thereby increasing the likelihood of Zn(II) and Cu(II) complexes forming according to the equation:

$$[M(H_2O)_6]^{2+} + 4L \rightleftarrows [ML_4]^{2+} + 2H_2O \qquad (7)$$

This phenomenon increases the transport rate and simultaneously suppresses the selectivity coefficients. The addition of chloride ions to the feed phase enables the formation of MCl and MCl_2 complexes, especially with Zn(II) ions. Based on the relationship lnc/ci vs process time, the rate constant k was calculated; Figure 5 shows an example linear relationship for the transport of Zn(II) from 0.5M Cl^- through PIM containing IMI10.

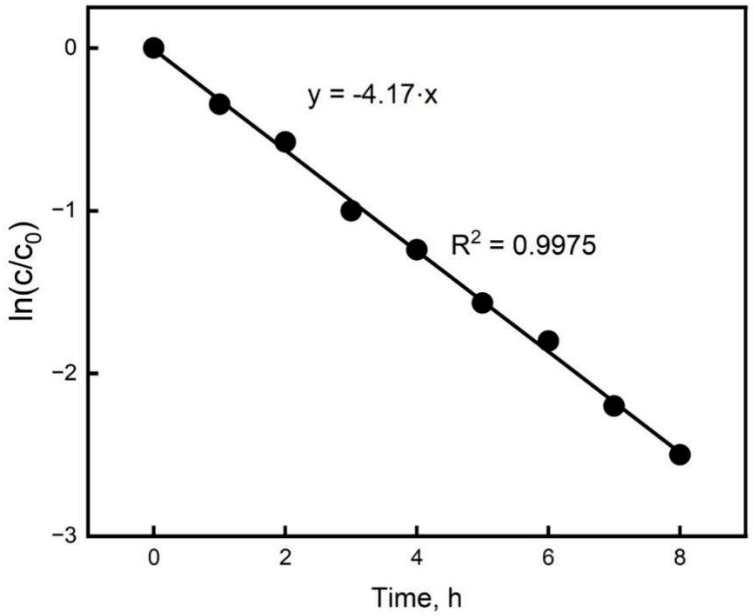

Figure 5. Variation of ln(c/c_0) versus time for zinc ion transport across PIM with cellulose acetate as matrix, carrier – 1-decylimidazole, and plasticizer: ONPOE. Feed phase: 0.5 M Cl

These complexes are more dissociable. This phenomenon increases the permeation flux, but suppresses the selectivity coefficient. Table 1 summarises the kinetic parameters of the transport of the tested metal ions from solutions with different chloride ion concentrations.

Table 1. Parameters characterising the transport and separation of nickel(II), cobalt(II), zinc(II) and cadmium(II) ions from chloride solutions. Matrix – cellulose triacetate, carrier – 1-decylimidazole, plasticiser: ONPOE. Chloride anion concentration in the feed phase 0.25 – 1.0 M.

Conc. of Cl^- [M] in source phase	Kinetic parameters	Metal ions			
		Co(II)	Ni(II)	Cd(II)	Zn(II)
0.25	k [s^{-1}]	$1.26 \cdot 10^{-4}$	$7.72 \cdot 10^{-5}$	$1.62 \cdot 10^{-4}$	$1.20 \cdot 10^{-3}$
	P [μm/s]	1.30	0.787	1.65	12.3
	J_0 [μmol/(m^2s)]	14.0	7.58	9.37	89.1
	%R	5.5	<1.0	6	71
0.50	k [s^{-1}]	$1.89 \cdot 10^{-4}$	$7.15 \cdot 10^{-5}$	$1.47 \cdot 10^{-4}$	$1.16 \cdot 10^{-3}$
	P [μm/s]	1.93	0.730	1.50	11.9

	J_0 [µmol/(m^{2}s)]	19.3	7.35	8.54	99.0
	%R	14.5	2	6.5	88
1.0	k [s^{-1}]	$5.01\cdot10^{-5}$	$7.50\cdot10^{-6}$	$5.02\cdot10^{-5}$	$8.45\cdot10^{-4}$
	P [µm/s]	0.51	0.076	0.52	8.62
	J_0 [µmol/(m^{2}s)]	5.32	0.758	2.82	84.4
	%R	2.5	<1	5.5	65

The data in Table 1 indicate that the highest initial fluxes of Zn(II) ions were obtained using IMI10 as a carrier (99.0 µmol/m^{2}s), extracting the metal from a 0.5 M solution of Cl$^-$. For the 4-component Zn-Cd-Co-Ni solution, the initial fluxes of metal ion transport across the PIM containing imidazole decrease in the following order: Zn(II) > Cd(II) > Co(II) > Ni(II). For the 3-component Zn-Cd-Ni solution, for PIMs immobilised with 1-octylimidazole, 1-octyl-2-methylimidazole, 1-octyl-4-methylimidazole or 1-octyl-2,4-dimethylimidazole, the initial fluxes of metal ions decrease in the following order: Zn(II) > Cd(II) > Ni(II) (Radzyminska-Lenarcik and Ulewicz, 2019a).

The transport of zinc(II) from equimolar chloride mixture of four metal ions, each at 0.01 M concentration through PIM with imidazole was also investigated. The changes in the efficiency of Zn separation from other metals from various chloride solutions are shown in Fig. 6.

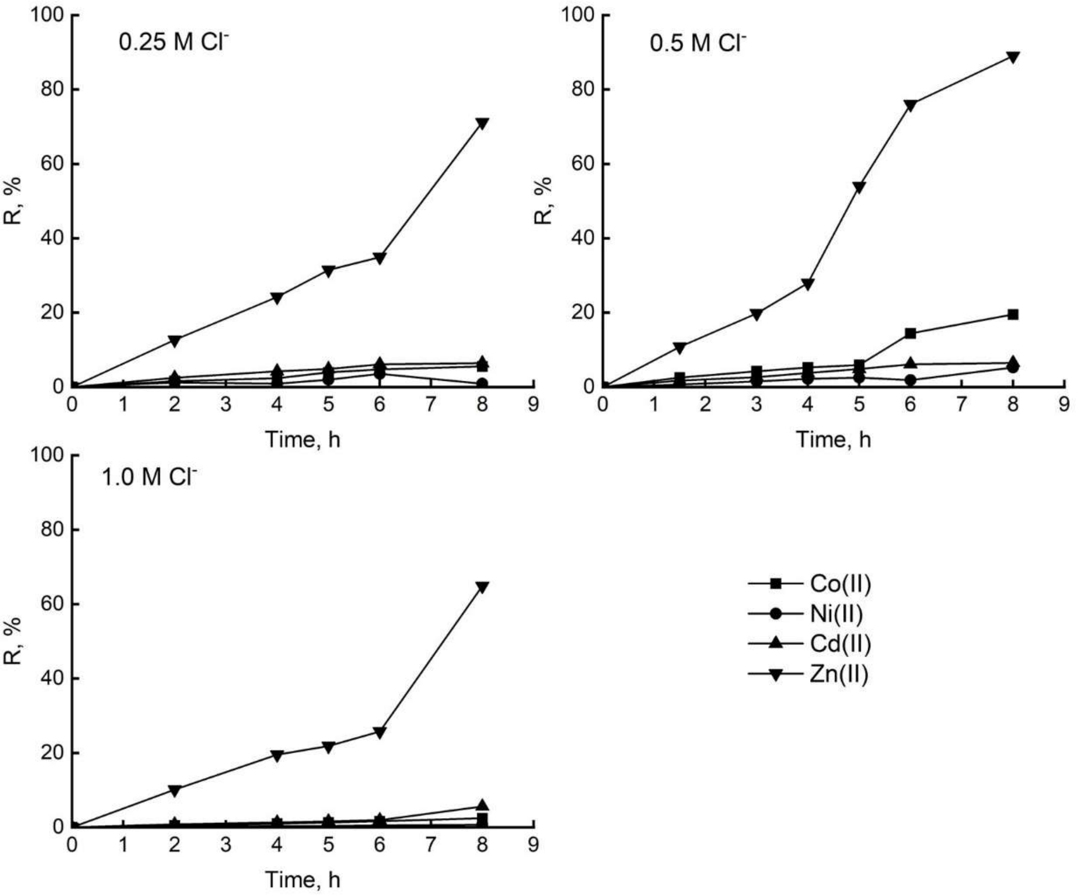

Figure 6. Changes in the recovery rate determined during the transport of Co(II), Ni(II), Zn(II) and Cd(II) ions across the PIM. Matrix – cellulose acetate, carrier – 1-decylimidazole, plasticiser – ONPOE. Chloride anion concentration in the feed phase from 0.25 to 1.0 M.

As seen from this figure, the recovery factors of all investigated ions increase with time. The highest recovery factors – 88% (after 8 h) were obtained for Zn(II) ions, whereas for other metal the factors were below 20%, respectively. The transport selectivity of the polymer inclusion membrane with 1-decyl-imidazole was: Zn(II) >Cd(II)> Co(II)> Ni(II).

3.5. Separation factors

Also of interest are the changes in the separation coefficient calculated for pairs of individual metal cations. The separation coefficient for zinc ions is the highest in relation to other ions (Table 2). Characteristically, its value passes through a minimum for 0.5 M chloride anions. The separation coefficients for nickel(II), cobalt(II) and cadmium(II) ions are several times lower than for zinc(II) ions. Comparing the individual values of the separation coefficients for these three ions, it should be noted that the lowest values were obtained for nickel(II) ions, while the separation coefficients for cobalt(II) and cadmium(II) ions are comparable.

Table 2. Dependence of the separation coefficient of nickel(II), cobalt(II), zinc(II) and cadmium(II) ions on the concentration of chloride anions in the feed phase. Matrix – cellulose triacetate, carrier – 1-decylimidazole, plasticizer – ONPOE.

$S=J_{M1}/J_{M2}$	Concentration of Cl^- ions in source phase		
	0.25 M	0.5 M	1.0 M
Co/Ni	1.84	2.62	7.01
Co/Cd	1.49	2.26	1.88
Cd/Ni	1.24	1.16	3.72
Zn/Co	8.14	4.61	15.9
Zn/Ni	15.0	12.1	111
Zn/Cd	12.2	10.4	29.9

4. CONCLUSIONS

The test results for the transport of nickel(II), cobalt(II), cadmium(II) and zinc(II) ions across the PIM containing 1-decylimidazole as carrier, CTA as matrix and ONNPE as plasticiser indicate that this process can be used for the selective separation and subsequent extraction of these metal ions from a polymetallic solution. Parameters determined on the basis of the tests carried out, such as transport rate across the PIM, recovery coefficient and separation coefficients, indicate that zinc(II) ions should be the easiest to separate from the solution under study. In this case, by selecting the appropriate chloride anion concentration, i.e. 0.5 M Cl^-, it would be possible to separate almost 90% of these ions from the solution. The transport selectivity of the polymer inclusion membrane with 1-decylimidazole was: Zn(II) > Cd(II) > Co(II) > Ni(II).

It may be feasible to employ a second membrane module to enhance separation of the remaining metal ions. Under such conditions, cobalt(II) and cadmium(II) ions - owing to their similar transport kinetics - would likely permeate the membrane, while nickel(II), characterized by its much lower transport rate, could be selectively retained in the feed phase. This approach could provide a pathway for targeted recovery of nickel(II) after initial separation.

Although the PIM shows long-term integrity in the model system, factors such as membrane stability, reusability, matrix effects, ion interferences, and surface deposit formation can impede its efficiency and should be considered when evaluating practical feasibility.

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