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Zinc recovery from model and waste solutions using polymer inclusion membranes (PIMs) with 1-octyl-4-methylimidazole

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ABSTRACT

The recovery of Zn(II) ions from chloride and sulfate solutions by the transport of a binary Zn(II)–Ni(II) and a quaternary Zn(II)–Cd(II)–Ni(II)–Pb(II) mixture ions through polymer inclusion membranes (PIMs) doped with 1-octyl-4-methylimidazole as an ion carrier was studied ($c_{M(II)}$ = 0.001 M; pH 6.0). The membranes were also used for the separation of metal ions from galvanic tailings. After 24 h, the separation efficiency of the ions from the tailings was higher than 95%, whereas that from the model chloride and sulfate solutions were 96% and 83%, respectively. The selectivity coefficients of Zn(II)/Ni(II) in the transport across PIMs doped with the imidazole derivative were higher for the *o*-nitrophenyloctyl ether (*o*-NPOE) than for the *o*-nitrophenylpentyl ether (*o*-NPPE) as plasticizers, due to an increased viscosity of the former. Membranes based on the *o*-NPOE plasticizer are characterized by higher porosity (23%) and lower roughness (7.7 nm), compared with those based on *o*-NPPE. Irrespective of the plasticizer used, the PIMs with 1-octyl-4-methylimidazole were characterized by high strengths and high thermal resistances (up to 200°C).

Keywords: Polymer inclusion membrane; Recovery of zinc; Imidazole derivatives; Electroplating wastewater

1. Introduction

The dynamic development of metallurgic industry and metal processing leads to a considerable environmental pollution. Hence, industrial waste management, including liquid waste, becomes an urgent necessity and constitutes an important component of sustained development [1,2]. In the European Union approximately 150,000,000 kg/year of this type of sludge are produced [3] which are mainly disposed on landfill, causing real threat to the environment. Moreover in galvanization processes and other hydro-metallurgical processes, a large amount of wastewater containing significant concentrations of various heavy metals are generated, which do not meet the wastewater limit discharge criteria. Recovery of precious metals from liquid waste, including galvanic ones, enables economizing on huge amounts of natural resources [4–6].

Separation of non-ferrous metal ions from aqueous solutions and liquid industrial waste on the laboratory scale is usually carried out using solvent extraction or membrane-based techniques involving simultaneous extraction and re-extraction steps [6–15]. A liquid membrane constitutes an organic phase separating two aqueous phases.

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The membrane-based processes are characterized by a more effective utilization of an ion carrier (extractant) imbedded in the organic phase (a membrane), as compared with the conventional extraction system [17]. Among the types of liquid membranes used, polymer inclusion membranes (PIMs) are distinguished by the highest mechanical strength and allow easy increase of the interfacial area. These systems also feature a small volume of liquid membrane relative to the surface compared with bulk and emulsion liquid membrane systems, which is an important advantage and allows the use of expensive and selective carriers. Molding the PIM allows for obtaining a membrane of different composition and thickness of the membrane. The selectivity and performance of liquid membranes depend mostly on physico-chemical characteristics of the plasticizer and ion carrier. Most of the commercial extractants used so far as non-ferrous metal ion carriers in the process of transport across liquid membranes do not ensure satisfactory selectivities towards a number of metal ions. Therefore, it seemed justified to search for new selective carriers enabling the separation of metal ions from aqueous solutions.

Recently, imidazole derivatives have also been proved useful in the solvent extraction of such metals as Co(II), Ni(II), Cu(II), Zn(II), Fe(III) and Cd(II) [18–24]. Moreover, a number of imidazole derivatives of azo- and thiaazo-crown ethers have been used for the separation of non-ferrous metal ions, Zn(II), Cd(II), Co(II), Cu(II), Ni(II) and Pb(II) in the process of transport through liquid membranes [25,26]. The Pb(II) ions could also be selectively separated from a solution containing the Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Ag(I) ions in the process of transport through thick-layered liquid membranes doped with pyrrole azocrown ethers [27]. Imidazole derivatives were also used for selective separation of the Cu(II) ions [28–32] from chloride and nitrate solutions in transport through liquid membranes.

Moreover, 1-alkylimidazoles as metal ion carriers included in the membranes enable the selective separation of the Zn(II) ions from an equimolar nitrate solution of the Zn(II)–Co(II)–Ni(II) ions [33]. The possibility of using imidazole derivatives for the separation of the Zn(II) ions from a chloride solution was demonstrated in the literature [33–36] (Table 1). It was shown that with elongation of the chain of substituent R in the imidazole ring, the initial flux of the ions increased while the separation coefficient decreased. However, up to the present, the usefulness of those compounds for the selective separation of metal ions from sulphate solutions has not been investigated. Therefore, the authors of this paper chose to present the results of their studies on the separation of the Zn(II) ions from model chloride and sulphate solutions and from a liquid galvanic waste in transport through PIMs with 1-octyl-4-methylimidazole. The methyl substituent in position 4 of the imidazole ring increases the basicity of the 1-octyl-4-methylimidazole molecule ($pK_a = 8.10$) in comparison with that of 1-octylimidazole ($pK_a = 7.36$) [18].

2. Experimental setup

2.1. Reagents

The inorganic chemicals, that is, $ZnCl_2$, $NiCl_2$, $CdCl_2$, $ZnSO_4$, $NiSO_4$, $CdSO_4$ and $Pb(NO_3)_2$ as well as tetramethylammonium hydroxide (each of them of analytical grade) were purchased from POCH (Gliwice, Poland). The liquid waste resulting from zinc electroplating, of which the composition is shown in Table 2, was obtained from an electroplating enterprise located in the Silesian province. Wastewater was taken after the preliminary purification in the galvanizing plant.

The organic reagents, that is, cellulose triacetate (CTA), *o*-nitrophenylpentyl ether (*o*-NPPE), *o*-nitrophenyloctyl ether (*o*-NPOE) and dichloromethane (each of them of analytical grade) were purchased from Fluka- Sigma-Aldrich Chemie

Table 2
Physico-chemical characteristics of galvanic waste

Investigated galvanic waste	Initial concentration, mg/dm^3
Cl^-	2,000–2,500
SO_4^{2-}	868–892
Zn(II)	670
Ni(II)	7.9
Cd(II)	<0.02
Pb(II)	<0.03
Cu(II)	<0.06
Cr(III)	<0.09
Colour	Light brown
pH	6.3

Table 1
Zn(II) ions transport across supported liquid membrane (SLM) and polymer inclusion membrane (PIM) doped imidazole derivatives from chloride solutions reported in the literature

Carriers	Target solutions	Type LM	J_i, mmol/m^2×s	RF, %	Reference
1-Alkylimidazole	Cu(II), Zn(II), Co(II), Ni(II)	PIM	1.70–2.15	–	[33]
1-Hexyl-4-methylimidazole	Zn(II), Co(II), Ni(II), Cd(II)	PIM	3.64	96.9	[34]
1-Hexyl-4-methylimidazole	Zn(II), Co(II), Cd(II)	PIM	3.73	98.5	[34]
1-Heptyl-4-methylimidazole	Cu(II), Zn(II), Co(II), Ni(II)	PIM	1.31	61.2	[35]
1-Decyl-4-methylimidazole	Zn(II), Co(II), Ni(II), Cd(II)	SLM	3.37	95.8	[36]
1-Decyl-4-methylimidazole	Zn(II), Co(II), Ni(II), Cd(II)	PIM	3.72	96.9	[36]

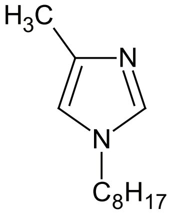


Fig. 1. Chemical structure of 1-octyl-2-methylimidazole.

GmbH (Munich, Germany) and used without further purification. The CTA, *o*-NPPE and *o*-NPOE plasticizers were chosen for this test because they make possible, as a result of previous work, the highest removal of the metal ions during transport across the PIMs. 1-Octyl-4-methylimidazole (Fig. 1) was synthesized according to a method reported in the literature [37].

2.2. Preparation and characterization of polymer inclusion membranes

The PIMs were prepared according to the procedure reported in the previous research papers [25–27,38]. A solution of CTA as the support, plasticizer and 1-octyl-4-methylimidazole as ion carrier in dichloromethane was prepared. A specified portion of the solution was poured into a membrane mould composed of a 9.0 cm diameter glass ring fixed on a glass plate with a CTA–dichloromethane glue. After a slow evaporation of the solvent overnight, the resulting PIM was peeled off from the glass plate by immersion in cold water. Then the PIM was soaked for 12 h in distilled water. Two samples of the PIM membranes were cut from the same membrane film for duplicate transport experiments. A surface characterization study of the PIMs was performed by atomic force microscopy (AFM) according to the procedure described in our earlier paper [28]. The analysis of surface pore characteristics of the PIM was made using the NanoScope v.5.12 AFM image processing program, which enabled the calculation of two parameters: roughness (R_q) and porosity (ε). The PIM's thermal analysis in nitrogen atmosphere (150 cm^3/min) was done using TG 209 F3 Tarsus, Netzsch GmbH (Selb, Germany). Scanning speed was 10°C/min.

2.3. Transport studies

The transport experiments were carried out in a permeation module cell where the feed and receiving phase was separated by the PIM. The PIM film having a surface area of 4.9 cm^3 was tightly clamped between two cell compartments. Both the source and the receiving aqueous phases (45 cm^3 each) were mechanically stirred at 600 rpm. The receiving phase was double distilled water (conductivity 5 µS/m). The PIM transport experiments were carried out at a temperature of 20°C ± 0.2°C (controlled by thermometer in air-conditioned room). Metal concentration was determined by withdrawing small samples (0.1 cm^3 each) of the aqueous receiving phase at different time intervals and analyzed by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam). The source phase pH in model solution was kept constant (pH = 6.0) by adding tetramethylammonium hydroxide and controlled by pH meter (CX-731, Elmetron, Zabrze, Poland), with a combination pH electrode (ERH-126, Hydromet, Poland).

The permeability coefficient (P, m/s) of metal ions across the membranes was described by the following equation:

$$\ln\left(\frac{c}{c_i}\right) = -\frac{A}{V}\cdot P\cdot t \tag{1}$$

where c is the metal ions concentration (M) in the source aqueous phase at a given time, c_i is the initial metal ions concentration in the source phase, t is the time of transport (s), V is the volume of the aqueous source phase (m^3) and A is an effective membrane area (m^2) [39].

A linear dependence of $\ln(c/c_i)$ in the source phase vs. time was obtained and the permeability coefficient was calculated from the slope of the straight line that fits the experimental data. The initial flux (J_i) was determined as being equal to:

$$J_i = P\cdot c_i \tag{2}$$

The selectivity coefficient (S) was defined as the ratio of initial fluxes for $M1$ and $M2$ metal ions, respectively:

$$S_{M1/M2} = J_{i,M1} / J_{i,M2} \tag{3}$$

To describe the efficiency of metal removal from the source phase, the recovery factor (RF) was calculated as follows:

$$\mathrm{RF} = \frac{c_i - c}{c_i}\cdot 100\% \tag{4}$$

The recovery factor calculated using concentration of the metal ion in the source phase after a given time was insignificant (0.5%), but which is higher than calculated using concentration of the metal ion in the receiver phase after a given time. Therefore, the content of the metal in the polymer membrane after process was not taken into account in the discussion of results (this allows to compare obtained results with other work).

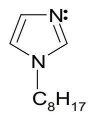
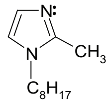
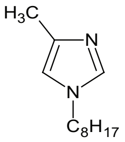
The reported values correspond to the average values of three replicates, with a standard deviation within 5%.

3. Results and discussion

The selectivity of the transport of ions through a PIM depends both on the physico-chemical characteristics of a solution (ion concentration in the feed phase, its pH and the presence of extraneous ions) as well as the structure of the membrane itself (type and concentration of the plasticizer and of the carrier). Therefore in this paper, the derivative of imidazole as complexing reagents (ion carriers) is investigated. Alkylimidazoles have been found to be a prospective group of stable heterocyclic aromatic bases with complexing and extractive properties which could be modified by changing the bulkiness and position of substituents in the imidazole ring. The modifications affect not only the basicity (electron-donating properties) and solubility of the molecules but also can provide steric hindrance during complexation. Owing to those features, both the stability and structure of the alkylimidazole complexes with metal ions could be varied.

When placed in position 2 or 4, even small alkyl groups are able to hinder the formation of a stable coordination bond with metal ions [18–24,28,30,32,34–36]. Owing to the steric effect, 6-coordinate (octahedral) complexes with 2- or 4-substituted alkylimidazoles have lower stability constants in comparison with those of 1-alkylimidazoles (Table 3). The phenomenon is especially evident in metal cations of the rigid octahedral structure of their coordination sphere which can hardly undergo deformation, for instance Ni(II).

Table 3
Comparison of the stability constants (β_n) of Cd(II), Ni(II) and Zn(II) complexes with 1-octyl-, 1-octyl-2-methyl- and 1-octyl-4-methylimidazole at 25°C, ionic strength 0.5 mol/dm^3 (KNO_3)

Ligand	Metal ions	log β_1	log β_2	Reference
1-Octylimidazole	Zn(II)	3.82	6.33	[18]
	Ni(II)	3.92	6.60	[18]
	Cd(II)	2.81	4.04	[18]
1-Octyl-2-methylimidazole	Zn(II)	4.45	6.80	[18]
	Ni(II)	2.03	3.49	[23]
	Cd(II)	2.44	3.81	[23]
1-Octyl-4-methylimidazole	Zn(II)	5.10	7.75	[22]
	Ni(II)	3.54	3.68	[24]
	Cd(II)	1.95	2.21	[24]

The steric effect is much less evident during the formation of tetrahedral complexes of 1-alkyl-2-methyl- and 1-alkyl-4-methylimidazoles [18,20–24,29,30,32,34–36] with cations which have an ability to change the shape of the coordination polyhedron from an octahedron to a tetrahedron (Eqs. (5) and (6)):

$$[M(H_2O)_6]^{2+} + nL + 2A^- \leftrightarrow [M(H_2O)_{6-n}L_n]A_2 + nH_2O \quad (5)$$

$$[M(H_2O)_6]^{2+} + nL + 2A^- \leftrightarrow [M(H_2O)_{4-n}L_n]A_2 + (n+2)H_2O \quad (6)$$

where L, A^- denote the carrier's molecule, and the anion denotes the metal's salt, respectively.

Reaction (6), describing the change in the coordination number, is typical of the Zn(II), Cd(II), Cu(II) and Co(II) ions [18,20–24,29,30,32,34–36]. In this case, a configuration equilibrium is established in the solution (Eq. (7)) between ML_n complexes having different structures of the coordination sphere, for instance:

$$[M(H_2O)_2L_4]^{2+} \leftrightarrow [ML_4]^{2+} + 2H_2O \quad (7)$$

The occurrence of configurational equilibriums at the n-th stage of complexation would lead to higher values of the corresponding stability constants, β_n, because it makes up a sum of the stability constant of the tetrahedral complex, β_t, and the octahedral complex, β_o ($\beta_n = \beta_t + \beta_o$) [18,20–24,29,30,32,34–36]. The formation of the 4-coordinate and 6-coordinate species facilitates the extraction of a metal into the organic phase, because the less hydrated compound is more easily extracted than the more hydrated one.

The stability constants of the Cd(II), Ni(II) and Zn(II) complexes with 1-octyl-4-methylimidazole shown in Table 3 increase in the following order: Cd(II) < Ni(II) < Zn(II). The initial fluxes (J_i) shown in Table 4 increase in the same sequence. The Pb(II) ions do not form complexes with imidazole or its alkyl derivatives [40], although they do form weak

Table 4
Values of initial fluxes, selectivity order and selectivity coefficient for competitive transport of metal ions through PIMs. Source phase: $c_M = 0.001$ M, pH = 6.0; receiving phase: H_2O; membrane: 2.60 cm^3 o-NPPE/1.0 g CTA, $c_{\text{carrier}} = 1.0$ M based on plasticizer volume

Solutions	Mixture	M(II)	J_i (mmol/m^{2}s)	Selectivity order and selectivity coefficients
Cl^-	I	Zn(II)	3.98	Zn(II) > Ni(II)
		Ni(II)	0.13	30.6
	II	Zn(II)	3.71	Zn(II) > Cd(II) > Ni(II) > Pb(II)
		Cd(II)	0.31	12.0 28.5 41.2
		Ni(II)	0.13	
		Pb(II)*	0.09	
SO_4^{2-}	I	Zn(II)	2.09	Zn(II) > Ni(II)
		Ni(II)	0.07	29.9
	II	Zn(II)	1.97	Zn(II) > Cd(II) > Ni(II) > Pb(II)
		Cd(II)	0.19	10.4 21.9 32.8
		Ni(II)	0.09	
		Pb(II)*	0.06	

*$Pb(NO_3)_2$.

complexes with ammonia (log $\beta_1 = 1.5$) [41]. The initial fluxes for these ions are negligible, that is, the ions are retained in the feed phase.

3.1. Comparison of Zn(II) ions transport across PIM from chloride and sulphate solutions

In the first step of this study, the selectivity of separation of the Zn(II) ions from model chloride and sulphate solutions was determined in the process of transport through PIMs doped with 1-octyl-4-methylimidazole as the carrier and either *o*-NPPE or *o*-NPOE as the plasticizers. The experiments were conducted for both the model and the liquid galvanic waste aqueous solutions at a fixed carrier concentration (1.0 M) in the membrane based on the volume of the plasticizer. That concentration of the imidazole derivatives (1-alkylimidazole and 1-decyl-4-methylimidazole) had previously been found as optimal (it allowed to get the highest removal of the metal ions from the feed phase) [33,36]. It was thus expected that the concentration of the carrier used would be effective for the separation of the Zn(II) ions from the solutions. Taking into account the presence of metal ions in the liquid waste, two model solutions were prepared, a binary Zn(II)–Ni(II) solution (I) and a quaternary Zn(II)–Ni(II)–Cd(II)–Pb(II) solution (II). In each of these models, the initial concentrations of the particular metal ions were 0.001 M. A nitrate salt of lead was used while preparing these solutions.

As can be seen from the results displayed in Table 4, Zn(II) were selectively separated from both the chloride and sulphate solutions in the transport through the PIMs doped with *o*-NPPE. The selectivity through the polymer membranes containing 1-octyl-4-methylimidazole from both the chloride and sulphate solutions decreased in the sequence: Zn(II) > Ni(II) > Cd(II) > Pb(II). On the other hand, initial fluxes through the membranes were higher for the chloride than for the sulphate solutions. The selectivity coefficients for the Zn(II)/Ni(II), Zn(II)/Cd(II) and Zn(II)/Pb(II) pairs during the transport for the chloride solutions (mixture II) were 12.0, 26.5 and 123.7, respectively, whereas for the sulphate solutions they were lower (10.4, 21.9 and 98.5, respectively). For the binary model (I), the selectivity coefficients were higher than the chloride and sulphate solutions (30.6 and 29.9, respectively). The recovery factor of the Zn(II) ions from those solutions is considerably higher, amounting to 97.7% and 85.5%, respectively. Whereas the recovery factor of Zn(II) from the quaternary solution (II), at pH 6.0 of the feed phase, were 97.1 and 83.9 for the chloride and sulphate solution, respectively. The recovery factor of zinc(II) using 1-octyl-4-methylimidazole is higher than a previously presented paper by Ulewicz and Radzyminska-Lenarcik [36] during transport across membrane CTA–*o*-NPPE with 1-decyl-4-methylimidazole. The recovery factor of Zn(II) ions during transport across PIM with 1-decyl-4-methylimidazole from different mixtures of cations (Zn(II)–Cd(II); Zn(II)–Ni(II); Zn(II)–Co(II); Zn(II)–Cd(II)–Co(II)–Ni(II)) was above 95% after 24 h [36]. Insignificant higher recovery factor of zinc(II) ions (98.5%) from a quaternary solution of Zn(II)–Cd(II)–Co(II)–Ni(II) after running the process for 24 h was obtained using CTA–*o*-NPPE membrane with 1-hexyl-4-methylimidazole [34].

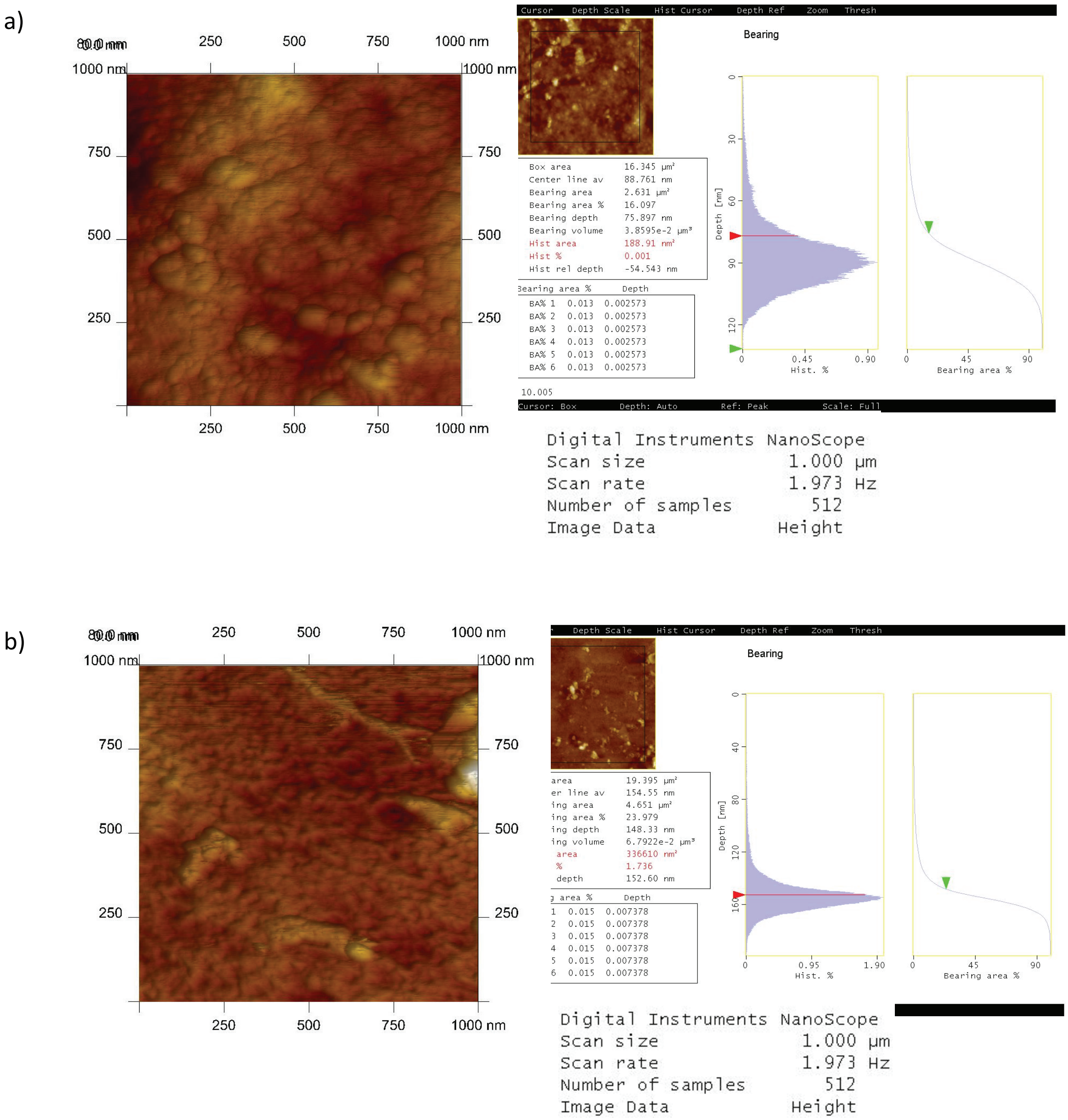
In Table 5, initial fluxes are shown for the transport of the Zn(II) and Ni(II) ions together with separation coefficients of these ions obtained during the transport of the ions through the membranes with *o*-NPOE as the plasticizer. This is because, as demonstrated by Kozlowska et al. [42], using a plasticizer of a higher viscosity resulted in higher separation coefficients of the Pb(II) ions in comparison with those of the Cd(II) ions during their transport through membranes doped with a commercial Cyanex 302 carrier. The viscosity coefficients of the *o*-NPPE and *o*-NPOE ethers are 7.58 and 12.35 mPa s, respectively, and their molar volumes are 193.0 and 243.0 cm^3/mol. This study has been restricted to two ethers only, because as reported in the literature, the relationship between the efficiency of transport and the kind and concentration of the plasticizer in the membrane is very complex and somewhat unclear, while the highest separation efficiency of non-ferrous metal ions could be achieved using *o*-nitrophenylalkyl ethers with alkyl substituents extending from $-C_4H_9$ to $-C_8H_{17}$ [42–44]. A comparison of the results presented in Tables 4 and 5 shows that initial fluxes of the transport of the Zn(II) and Ni(II) ions through polymer membranes with *o*-NPOE as the plasticizer are lower for the chloride and sulphate solutions than those with embedded *o*-NPPE. On the other hand, separation coefficients for the Zn(II)/Ni(II) pair in the transport through polymer membranes based on the ether with higher viscosity, that is, *o*-NPOE, are considerably higher than those based on *o*-NPPE. The selectivity coefficients for that pair through PIM based on *o*-NPOE determined for the sulphate and chloride solutions are 32.3 and 47.3, respectively. The recovery factor (RF) of the Zn(II) from equimolar model sulphate and chloride solutions through those membranes are 83.3% and 96.9%, respectively.

3.2. Membrane characteristic

In the next step, the PIMs were examined with respect to their morphology. In Fig. 2, a two-dimensional (2D) 1.0 × 1.0 μm AFM image of a polymer membrane is displayed.

Table 5
The values of initial fluxes, selectivity order and selectivity coefficient for competitive transport of Zn(II) and Ni(II) through PIMs. Source phase: $c_M = 0.001$ M, pH = 6.0; receiving phase: H_2O; membrane: 2.60 cm^3 *o*-NPOE/1.0 g CTA, $c_{carrier} = 1.0$ M based on plasticizer volume

Solutions	M(II)	J_i (mmol/m^2 s)	Selectivity order and selectivity coefficients	RF,%
Cl^-	Zn(II)	3.78	Zn(II) > Ni(II)	96.9
	Ni(II)	0.08	47.3	8.1
SO_4^{2-}	Zn(II)	1.94	Zn(II) > Ni(II)	83.3
	Ni(II)	0.06	32.3	6.3



```
Box area            16.345 µm²
Center line av      88.761 nm
Bearing area        2.631 µm²
Bearing area %      16.097
Bearing depth       75.897 nm
Bearing volume      3.8595e-2 µm³
Hist area           188.91 nm²
Hist %              0.001
Hist rel depth      -54.543 nm
```

```
Bearing area %        Depth
BA% 1   0.013   0.002573
BA% 2   0.013   0.002573
BA% 3   0.013   0.002573
BA% 4   0.013   0.002573
BA% 5   0.013   0.002573
BA% 6   0.013   0.002573

10.005
```

```
Digital Instruments NanoScope
Scan size             1.000 µm
Scan rate             1.973 Hz
Number of samples       512
Image Data            Height
```

```
area                19.395 µm²
er line av          154.55 nm
ing area            4.651 µm²
ing area %          23.979
ing depth           148.33 nm
ing volume          6.7922e-2 µm³
 area               336610 nm²
 %                  1.736
 depth              152.60 nm
```

```
g area %      Depth
1   0.015   0.007378
2   0.015   0.007378
3   0.015   0.007378
4   0.015   0.007378
5   0.015   0.007378
6   0.015   0.007378
```

```
Digital Instruments NanoScope
Scan size             1.000 µm
Scan rate             1.973 Hz
Number of samples       512
Image Data            Height
```

Fig. 2. 2D-view AFM images of the CTA–*o*-NPPE membrane (a), CTA–*o*-NPOE–1-octyl-4-methylimidazole (carrier) (b) with histograms.

The distribution of the carrier in the investigated membrane after evaporation of dichloromethane is homogeneous over the entire surface. The porosity, ε, and roughness, R_q, of the PIM CTA–*o*-NPPE and CTA–*o*-NPPE with 1-octyl-4-methylimidazole were calculated using AFM. The porosity and roughness of the membrane based on *o*-NPPE plasticizer were 16.1% and 8.5 nm, respectively, and for that based on *o*-NPOE, the respective figures were 23.9% and 7.4 nm. In both cases, effective pore sizes were comparable and equal to 0.05 µm. The membranes were 30 µm thick. Also the tortuosity (t) was calculated for the membranes from the Wolf and Strieder's formula [45]: t = 1 – lnε. Tortuosities for the membranes CTA–*o*-NPPE and CTA–*o*-NPPE with 1-octyl-4-methylimidazole were 2.83 and 2.43, respectively. The roughness of investigated PIMs is higher than that found for polymer membrane with di-(2-ethylhexyl)-phosphoric acid (D2EHPA) obtained by Salazar-Alvarez et al. [46], which is equal to 4.6 nm, as well as for PIMs with imidazole azothiacrown ethers (3.6–5.3 nm) [47]. Also low roughness values were obtained for PIM based on *o*-NPPE with 1-hexylimidazole (3.9 nm) [33]. The porosity of this membrane was 23.9% and was slightly higher than for the membrane with 1-hexyimidazole (21.1%) [33].

3.3. Thermogravimetric analysis

Recently, attention has been paid to the thermal stability of PIMs. Generally, the thermal stability of polymers depends, amongst other things, on the polymer's internal structure and cross-linking and on the presence of aromatic rings and degradable functional groups. It has been demonstrated [48,49] that degradation of the CTA membrane proceeds in two steps: the former in the range 292°C–320°C (main step) and the latter in the range 450°C–476°C (carbonization). According to other reports, thermal degradation of a CTA membrane is a single-step process which occurs at 300°C [50] or at 350°C [51,52]. However, addition of a plasticizer and an ion carrier to the CTA matrix affects strongly the thermal stability of the membranes. In Gherrou et al. [48], it was reported that thermal degradation of the CTA–*o*-NPOE crown ether membrane, an intermediate step could be distinguished, assigned to the degradation of the crown ether. The step emerges at 238.2°C, 250.0°C, 298.7°C and 273.4°C for the DB18C6, HT18C6, DA18C6 and HA18C6 crown ethers, respectively. On the other hand, membranes with a cryptand 222 ion carrier undergo thermal degradation at a temperature matching that of a carrier-free membrane composed of CTA and a plasticizer [49].

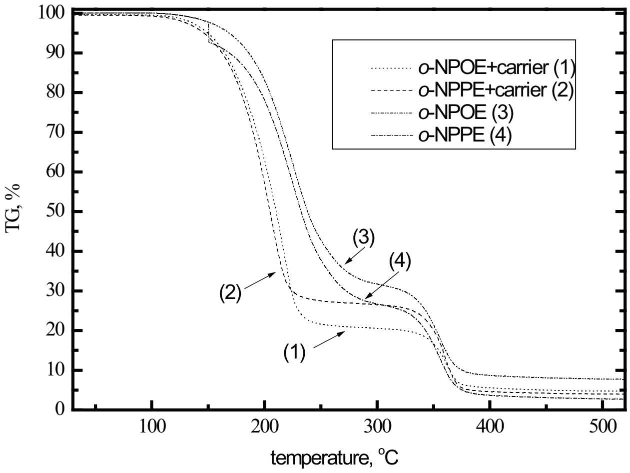


Fig. 3. Thermograms of CTA–*o*-NPPE and CTA–*o*-NPOE membranes without carrier and with 1-octyl-4-methylimidazole.

Table 6
Zn(II) removal from the liquid galvanic waste obtained after 24 h processes of transport across PIMs with 1-octyl-4-methylimidazole

Plasticizer	Metal ions	Initial concentration of metal ions (mg/dm^3)	RF, %
o-NPPE	Zn(II)	670.0	95.4
	Ni(II)	7.9	9.1
o-NPOE	Zn(II)	670.0	95.1
	Ni(II)	7.9	8.9

As seen from Fig. 3, thermal degradation of the membranes made with CTA–*o*-NPPE and CTA–*o*-NPOE with 1-octyl-4-methylimidazole as the carrier proceeds in two steps. With the *o*-NPPE membrane, in the first step at 230°C, weight loss is 80%, and in the second step, at 370°C, weight loss is 15%. On the other hand, with the CTA–*o*-NPOE membrane, the respective weight losses are 60% and 25%. The two-step degradation of the PIMs has been reported for membranes containing 1-hexylimidazole and 1-decyl-4-methylimidazole [29,36]. For the CTA–*o*-NPPE membranes with 1-hexylimidazole and 1-decyl-4-methylimidazole, the respective onsets of degradation occur at 211.3°C and 360.7°C [36] as well as 230.3°C and 342.4°C [29]. Thus, the results enable the conclusion to be drawn that the CTA–*o*-NPPE and CTA–*o*-NPOE membranes with embedded imidazole derivatives show a high thermal resistance (up to approx. 200°C).

3.4. Recovery of Zn(II) from technological waste solutions

In the next step, attempts have been made to utilize the PIMs with 1-octyl-4-methylimidazole for the separation of the Zn(II) ions from liquid galvanic waste. The waste has been produced in an electroplating plant during the preparation of the surface for treating industrial goods (degreasing, etching), electroplating (galvanic effluents), as well as during the water exchange in washers. A major volume of the effluents from electroplating plants is caught from the interprocessing washing of goods. The liquid waste studied here was collected in a plant where zinc (periodically nickel) electroplating was performed from chloride and sulphate solutions of average acidity, and after neutralization (solution in Table 3). The solution is treated in a local wastewater treatment plant. As shown in Table 3, the metal concentration (copper(II), lead(II), cadmium(II), chromium(VI)) in solution is below the permissible level according to the Decree of the Minister of Environment (Dz.U. of 2014, No. 1800) which permits their disposal to water. Only the concentration of

Table 7
Comparison of the Zn(II) removal from different liquid galvanic waste

Process separation	Carrier	Removal of Zn(II), %	Reference
Polymer inclusion membrane	1-Octyl-4-methylimidazole	above 95	This paper
Emulsion liquid membrane	Tributyl phosphate (TBP)	46–63	[13]
Membrane Neosepta CMX	Di-(2-ethylhexyl)-phosphoric acid (D2EHPA)	67.6	[16]
Membrane Neosepta CMX	Salicylaldoxyoxime (Acorga P-50)	24.9	[16]
Solvent extraction	Di-(2-ethylhexyl)-phosphoric acid (D2EHPA)	96.0	[9]
Solvent extraction	D2EHPA and CYANEX 272	95.0	[10]
Solvent extraction	Aliquat 336	99.6	[10]

zinc and nickel is above this limit, which makes it necessary to remove these metals from the wastewater.

The results displayed in Table 6 show that the transport of the liquid galvanic waste through the PIMs enables the recovery of more than 96% of zinc(II). The results obtained are better than those shown by Carrera et al. [13] for selective transport of zinc from hot-dip galvanizing effluents across emulsion membranes using tributyl phosphate (TBP). Zinc extraction from the spent pickling solution was 46%–63%. Comparison of the Zn(II) removal from different liquid galvanic waste is presented in Table 7.

The removal of Zn(II) ions from industrial rinse water during transport across a cation-exchange polymer membrane (Neosepta CMX) with D2EHPA or salicylaldoxyoxime (Acorga P-50) as the active extractant/carrier [16] was 67.6% and 24.9%, respectively. The D2EHPA provided a much better removal of zinc(II) ions (96%) in solvent extraction from a sulphuric acid leach solution of galvanic sludge (at pH = 3.0). From these solutions, 63% of Ni(II) ions were removed at a pH of 6.0 [9]. Using D2EHPA and CYANEX 272, zinc was extracted from a real mix electroplating wastewater at pH < 3.0 with 95% efficiency. The Aliquat 336 enabled the removal of Zn(II) at 99.6% [10].

4. Conclusions

The Zn(II) ions can be selectively separated from both the model chloride and sulphate solutions and the liquid galvanic waste during their transport through PIMs using 1-octyl-4-methylimidazole as an ion carrier. For both types of model solutions, the efficiency of separation of metals decrease in the following order: Zn(II) > Ni(II) > Cd(II) > Pb(II). From the binary (Zn(II)/Ni(II)) and quaternary (Zn(II)–Ni(II)–Cd(II)–Pb(II)) chloride solutions, the recovery factor of the Zn(II) ions was higher (>96%) than that from the sulphate solutions (>83%) after 24 h. On the other hand, efficiency obtained from the liquid galvanic solutions was higher than 95%. For the Zn(II)/Ni(II) pair, the selectivity coefficient was higher for the *o*-NPOE plasticizer than for the *o*-NPPE one, due to the increased viscosity of the former. Membranes based on the *o*-NPOE plasticizer had a higher porosity (23%) and a lower roughness (7.7 nm) than those based on *o*-NPPE. Irrespective of the plasticizer used, the PIMs doped with 1-octyl-4-methylimidazole are characterized by high strengths and thermal resistances (up to 200°C).

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Symbols:

R_q — Roughness, nm
ε — Porosity, %
τ — Tortuosity
β_n — Stability constant
pK_a — Dissociation constant
c — Metal ions concentration in the source phase at a given time, mol/dm^3
c_i — Initial metal ions concentration in the source phase, mol/dm^3
k — Rate constant, 1/s
t — Time of transport, s
P — Permeability coefficient, m/s
V — Volume of the aqueous source phase, m^3
A — Effective area of the membrane, m^2
J_i — Initial flux, mmol/m^{2}s
S — Selectivity coefficient
RF — Recovery factor, %

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