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APPLICATION OF POLYMER INCLUSION MEMBRANES DOPED WITH 1-HEXYL-4-METHYLIMIDAZOLE FOR PERTRACTION OF ZINC(II) AND OTHER TRANSITION METAL IONS

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Abstract: Transport of Zn(II) from unary aqueous chloride solutions and from solutions which contain mixtures of Cd(II), Co(II) and Ni(II) ions in source phases ($c_{\mathrm{Me}} = 0.001$ mol/dm^3, pH = 6.0) across polymer inclusion membranes (PIMs) doped with 1-hexyl-4-methylimidazole as ion carrier was studied. The use of 1-hexyl-4-methylimidazole enables the separation of 98.5% Zn(II) from a unary solution and 96.9% from a quaternary solution of Zn(II)-Cd(II)-Co(II)-Ni(II) after running the process for 24 hours. Using that ion carrier, the metals are transported in the following order: Zn(II) > Cd(II) > Ni(II) > Co(II), and the selectivity coefficients of Zn(II)/Cd(II), Zn(II)/Ni(II), and Zn(II)/Co(II) are 12.9, 23.4 and 40.8, respectively. Findings of atomic force microscopy (AFM) examinations as well as thermograms of a polymer inclusion membrane containing 1-hexyl-4-methylimidazole are also presented. A membrane with 1.0 mol/dm^3 of carrier has a porosity of 15.8%, and roughness of 6.6 nm. The membranes remain thermally stable at temperatures up to 200°C. The findings were compared with earlier-reported results for 1-hexylimidazole.

Keywords: *polymer inclusion membrane, PIM, metal ions separation, zinc(II), transition metal ions, imidazole derivatives*

Introduction

A variety of techniques are known for non-ferrous metal ion separation from aqueous solutions in commercial facilities or in a bench scale. Such techniques include liquid-liquid extraction, ion exchange, ion flotation and sorption on polymer resins. The choice of the suitable technique depends on the scope of concentrations of the

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components in the solution and on the properties of the compounds to be separated. Apart from conventional methods for the separation of metal ions, much attention has been paid for some time to the processes of transport across liquids membranes. A liquid membrane is a hydrophobic organic liquid which separates two aqueous phases, i.e., the feed solution and the receiving solution. Regardless of their type, liquid membranes have one feature in common: the steps of extraction and re-extraction run concurrently (pertraction process). This enables the process to be carried out in a continuous manner, without any intermediate operations. The pertraction process selectivity depends on the structure of the membrane and its physicochemical properties, on the properties of the substances to be separated, as well as on the nature of their interactions with ligands which carry the ions (Bartsch and Way, 1996; Kislik, 2010; Araki and Tsukube, 1990; Sastre et al., 1998; Noble and Stem, 1995; Nghiem et al., 2006, Walkowiak and Kozlowski, 2009).

The efficiency of metal-ion transport across liquid membranes largely depends on the right choice of carrier. The metal-ion carriers used in the transport across liquid membranes are usually the same organic compounds as those used in extraction processes, that is, organic acids, tertiary amines, quaternary ammonium salts, or macrocyclic compounds (Nghiem et al., 2006; Ulewicz, 2011; Walkowiak et al., 2002, 2009). In the commercial practice, a majority of extractants which have been used in the laboratory scale as metal-ion carriers in the transport across liquid membranes enable the efficient separation of non-ferrous metal ions only. In addition, their selectivity is low, especially for metal ions with similar physico-chemical properties. Therefore, their application is rather limited. At present, a number of research works have been dedicated to searching new organic compounds which have highly efficient separation properties and which are applicable as metal-ion carriers in the transport across liquid membranes. The studies are dedicated to the use of such compounds as imidazole derivatives, for instance, imidazole derivatives of aza- and azothiocrown ethers, for that purpose (Ulewicz et al., 2007[a,b], 2009; Luboch et al., 2006).

Imidazole and its alkyl derivatives, have also been useful in the solvent extraction of such metals as Co(II), Ni(II), Cu(II), Zn(II), Fe(III) and Cd(II) (Gheaedi et al., 2008; Radzymińska-Lenarcik, 2008[a], du Preez et al., 2004; Lenarcik et al., 1989, 1999; Lenarcik and Kierzkowska, 2004[a,b], 2006; Lenarcik and Rauckyte, 2004; Lenarcik and Ojczenasz, 2004) and in the process of transport of nonferrous metal ions across liquid membranes (Ajji and Ali, 2010; Ulewicz and Radzyminska-Lenarcik, 2011, 2012[a,b]; Radzyminska-Lenarcik and Ulewicz, 2012, 2014). Alkyl derivatives of imidazole are a convenient group of bases in which the complex-forming properties in respect of transition metals may be predicted and programmed in order to differentiate their extraction properties so as to improve the selectivity of recovery of selected metals (Radzymińska-Lenarcik, 2007[a,b], 2008; Lenarcik and Rauckyte, 2004, Gheaedi et al., 2008; Lenarcik and Kierzkowska, 2006; Lenarcik et al., 1999).

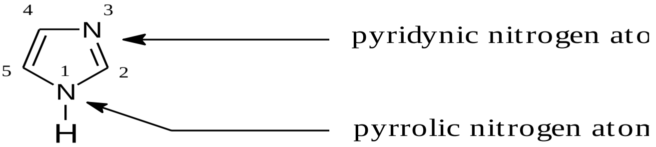
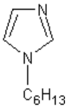
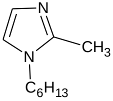
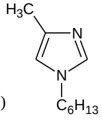


Fig. 1. Molecule of imidazole

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

Ligand	Metal ions	log β_1	log β_2	log β_3	log β_4
1-hexylimidazole	Co(II) [2]	3.47	5.64	7.14	8.38
	Cu(II) [3]	4.15	7.57		
	Zn(II) [4]	3.36	5.87	8.07	
$pK_a = 7.30^{(1)}$	Ni(II) [5]	3.29	5.34	7.07	7.95
1-hexyl-2-methylimidazole	Co(II) [6]	1.96	2.18	3.02	5.61
	Cu(II) [7]	3.52	6.63	8.98	
	Zn(II) [8]	3.48	5.80	8.30	10.10
$pK_a = 8.32^{(1)}$	Ni(II) [9]	2.08	4.62		
1-hexyl-4-methylimidazole	Co(II) [10]	1.40	2.04	3.02	5.61
	Cu(II) [11]	3.72	4.55	6.53	
	Zn(II) [12]	2.95	5.60	6.30	
	Cd(II) [10]	2.20	3.93	5.11	5.81
$pK_a = 8.01^{(1)}$	Ni(II) [10]	1.74	3.00	3.92	

data from: (1) Lenarcik and Ojczenasz, 2002; (2) Lenarcik and Ojczenasz, 2004; (3) Radzyminska-Lenarcik, 2007b; (4) Lenarcik and Kierzkowska, 2004a; (5) Lenarcik and Rauckyte, 2004; (6) Radzyminska-Lenarcik and Witt, 2014; (7) Radzyminska -Lenarcik, 2007a; (8) Lenarcik and Kierzkowska, 2006; (9) Lenarcik et al., 1999; (10) Lenarcik et al., 1989; (11) Radzyminska-Lenarcik, 2010; (12) Lenarcik and Kierzkowska, 2004b

Although a weaker base than ammonia, imidazole (Fig. 1) (pK_a = 7.12 (Sundberg and Martin, 1974)) forms more stable complexes with transition metal cations due to back-donation, therefore, it is classified as a soft base according to the HSAB theory (Pearson, R.G., 1968). Its basicity and complex stability with metal ions may be somewhat improved by substituting an alkyl group in position 1 (Lenarcik and Ojczenasz, 2002). On the other hand, when introduced in position 2 or 4, even small alkyl group will increase the basicity of a pyridine nitrogen atom by as much as one order of magnitude but will also reduce the contribution of the $\pi_{M \leftarrow L}$ bond component. When placed in such positions, the alkyl groups constitute a steric hindrance making it difficult to form a stable coordination bond with metal cations (Radzyminska-Lenarcik, 2007a, 2008a,b, 2009, 2010; Lenarcik and Kierzkowska, 2004b, 2006; Lenarcik et al., 1986, 1999; Lenarcik and Barszcz, 1980). As a result of the two effects, the 6-coordination (octahedral) complexes with 2 or 4 substituted alkylimidazoles have lower stability constants (Table 1). The phenomenon is observed especially for metal cations with a rigid, octahedral structure of the coordination sphere which is hard to deform, for instance Ni(II).

The steric effect much less hinders the formation of tetrahedral complexes of 1-alkyl-2-methylimidazoles and 1-alkyl-4-methylimidazoles with cations which have an ability to change the shape of a coordination polyhedron from an octahedron to a tetrahedron (Eqs. 1 and 2) (Radzyminska-Lenarcik, 2007a, 2008a, 2010; Lenarcik and Kierzkowska, 2004b, 2006; Lenarcik et al., 1986, 1999):

$$[M(H_2O)_6]^{2+} + nL + 2A^{-} \leftrightarrow [M(H_2O)_{6-n}L_n]A_2 + nH_2O \qquad (1)$$

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

where L denotes the carriers molecule.

The reactions, described by Eq. 2 and involving a change in the coordination number, are typical for Zn(II), Cd(II), Cu(II) and Co(II), especially for the fourth stage of complexation (n=4) (Radzyminska-Lenarcik, 2007a, 2008a,b, 2010; Lenarcik et al., 1986, 1999; Lenarcik and Kierzkowska, 2004b, 2006). In such cases, configuration equilibria are established (Equation 3) between ML_n complexes, which have different coordination sphere structures, for instance:

$$[M(H_2O)_2L_4]^{2+} \leftrightarrow [ML_4]^{2+} + 2H_2O. \qquad (3)$$

The occurrence of configuration equilibria in the *n*-th stage of complexation will lead to higher values of its corresponding stability constant, β_n (Table 1), because it is a sum of the stability constant of the tetrahedral complex, β_t, and the octahedral complex β_o ($\beta_n = \beta_t + \beta_o$) (Radzyminska-Lenarcik, 2008a; Lenarcik and Kierzkowska, 2004b, 2006; Lenarcik et al., 1986).

There was a decrease in the stability of all the metal complexes due to steric hindrance, which in turn, depends on the kind of the central ion.

As seen in Table 1 the stability constants for 1-hexylimidazole complexes with all metal ions are the highest. Stability constants of the Cu(II) complexes are considerably higher than those for Co(II), Ni(II), and Zn(II). This may be explained in terms of a larger contribution of the $\pi_{M\rightarrow L}$ back donation to interaction of Cu(II) with the imidazole ring (Radzyminska-Lenarcik, 2007a,b, 2008a).

Phenomena which change the structure and the values of stability constants of metal complexes may affect the process of competitive transport of metal cations through PIM (Radzyminska-Lenarcik and Ulewicz, 2014; Ulewicz and Radzyminska-Lenarcik, 2012a,b).

In this work, the authors present the results of investigation of the competitive transport of nonferrous metal ions as zinc(II), cobalt(II), cadmium(II) and nickel(II) ions across polymer inclusion membranes doped with 1-hexyl-4-methylimidazole from dilute chloride solutions. The results were compared with results previously published for the transport of Zn(II), Co(II), and Ni(II) ions across PIM doped with 1-hexylimidazole (Radzyminska-Lenarcik and Ulewicz, 2014).

Experimental

Reagents

The inorganic chemicals, i.e., zinc(II), cadmium(II), nickel(II), cobalt(II) chlorides and tetramethylammonium hydroxide, were of analytical grade and were purchased from POCh (Gliwice, Poland). The organic reagents, i.e., cellulose triacetate (CTA), *o*-nitrophenylpentyl ether (*o*-NPPE) having a density 1.098 g/cm^3 and dichloromethane were also of analytical grade and were purchased from Fluka and used without further purification. 1-hexyl-4-methylimidazole (formula in Table 1) was synthesized according to a method reported in the literature (Pernak et al., 1987).

Preparation of polymer inclusion membranes and its characterization

The polymer inclusion membranes were prepared according to the procedure reported in the previous paper (Ulewicz and Radzyminska-Lenarcik, 2011, 2012a,b; Radzyminska-Lenarcik and Ulewicz, 2012). A solution of cellulose triacetate as the support, plasticizer and 1-hexyl-4-methylimidazole as ion carrier in dichloromethane was prepared. The plasticizer used was *o*-nitrophenylpentyl ether, which penetrates into the polymer molecules and neutralizes the polar groups of the polymer with its own polar groups, thus making the membrane more flexible. 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 cellulose triacetate-dichloromethane glue. After a slow evaporation of the solvent overnight, the resulting polymer inclusion membrane was peeled off from the glass plate by immersion in cold water. Then the polymer inclusion membrane was soaked for 12 hours in distilled water to achieve its homogeneity.

Two samples of the PIM membranes (containing 15.8% CTA, 42.1% carriers and 42.1 plasticizer) were cut from the same membrane film for duplicate transport experiments. A surface characterization study of the polymer inclusion membranes was performed by atomic force microscopy (AFM) according to the procedure described in our earlier paper (Ulewicz et al., 2007a). The analysis of surface pore characteristics of the polymer membrane 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).

Transport studies

The transport experiments were carried out in a permeation module cell described in our earlier paper (Ulewicz and Radzyminska-Lenarcik, 2012, 2014; Radzyminska-

Lenarcik and Ulewicz, 2012a,b). The membrane 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 distillated water (conductivity 5 μS/m). The PIM transport experiments were carried out at a temperature of 20±0.2°C. Metal concentration was determined by withdrawing small samples (0.1 cm^3 each) of the aqueous receiving phase at different time intervals and analysing by atomic absorption spectroscopy (AAS Spectrometer, Solaar 939, Unicam). The source phase pH was kept constant (pH = 6.0) using tetramethylammonium hydroxide and controlled by pH meter (pH meter, CX-731 Elmetron, with a combination pH electrode, ERH-126, Hydromet, Poland). The permeability coefficients (P, m/s) of metal ions across polymer membranes was described by the following equation (Danesi, 1984-85):

$$\ln\left(\frac{c}{c_i}\right) = -\frac{A}{V} \cdot P \cdot t \tag{4}$$

where c is the metal ion concentration (mol/dm^3) in the source aqueous phase at some given time, c_i is the initial metal ions concentration in the source phase, t is the time of transport (s), V is volume of the aqueous source phase (m^3), and A is an effective area of membrane (m^2).

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

$$J_i = P \cdot c_i \,. \tag{5}$$

The diffusion coefficient D_o (cm^2/s) of the metal-complex across the organic phase can be determined in the case of absence of diffusion resistances in the aqueous layer source phase/membrane by the following equation (Danesi, 1984-85):

$$c = c_i - \frac{[L]_o \cdot A \cdot t}{n \cdot V \cdot \Delta_o} \tag{6}$$

where $\Delta_o = d_o/D_o$ (s/cm) is the resistance of transport by diffusion across the membrane, d_o (cm) is the thickness of the membrane, n - is the number of moles of the carrier in the complex (in our case $n = 1$), $[L]_o$ is the initial concentration of the extractant in the organic phase (mol/dm^3). Plotting $[Me^{2+}]_i$-$[Me^{2+}]_t$ vs. time gives a slope equal to $([L]_o \cdot A)/(\Delta_o \cdot V)$ and allow access to the diffusion coefficients D_o of the metal complex species in the membrane phase.

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

$$RF = \frac{c_i - c}{c_i} \cdot 100\% . \tag{7}$$

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

Results and discussion

Findings on the transport of non-ferrous metal ions from chloride solutions, across polymer inclusion membranes containing 1-hexyl-4-methylimidazole as ion carrier are discussed below. The concentration of the ion carrier in the membrane was 1.0 mol/dm^3 (relative to the plastifier) since earlier studies (Radzyminska-Lenarcik and Ulewicz, 2014) indicate that the concentration is optimum for that group of compounds. The studies were carried out using single- or multi-component solutions, containing each metal at a concentration of 0.001 mol/dm^3. The initial flux values and selectivity coefficients for the metal ion transport across the PIMs are shown in Table 2.

Table 2. Initial fluxes, selectivity order and selectivity coefficients for the competitive transport of nonferouus ions across PIM containing 1.0 mol/dm^3 of 1-hexyl-4-methylimidazole

Solutions	Metal ions	J_i, μmol/m^2·s	$S_{Zn(II)/Me(II)}$
I	Zn(II)	4.37	-
II	Zn(II)	3.85	Zn(II) > Cd(II)
	Cd(II)	0.41	9.4
III	Zn(II)	3.73	Zn(II) > Cd(II) > Co(II)
	Cd(II)	0.38	9.8 24.9
	Co(II)	0.15	
IV	Zn(II)	3.64	Zn(II) > Cd(II) > Ni(II) > Co(II)
	Cd(II)	0.29	12.9 23.4 40.8
	Co(II)	0.01	
	Ni(II)	0.16	

It follows from the data shown in Table 2 that the initial flux value for Zn(II) ion transport from a unary solution is higher than that from multi-component solutions. For a quaternary mixture, the initial fluxes of metal ions transport across PIMs containing 1-hexyl-4-methylimidazole decrease in the following order: Zn(II) > Cd(II) > Co(II) > Ni(II). This is similar to earlier results, obtained for membranes containing 1-decyl-4-methylimidazole and discussed by these authors in (Ulewicz and Radzyminska-Lenarcik, 2014). On the other hand, selectivity coefficients obtained for Zn(II)/Cd(II), Zn(II)/Ni(II) and Zn(II)/Co(II) during the transport across PIMs containing 1-hexyl-4-methylimidazole are higher, compared with those for 1-decyl-4-methylimidazole as ion carrier, for which the respective values were 11.6, 24.8 and 33.8. Shown in Table 3, for comparison, are earlier-reported values of initial fluxes, selectivity order and selectivity coefficients for competitive transport of Zn(II), Co(II), and Ni(II) ions across PIM doped with 1-hexylimidazole (Radzyminska-Lenarcik and Ulewicz, 2014).

Table 3. Initial flux, selectivity order and selectivity coefficients for competitive transport of Zn(II), Co(II), and Ni(II) ions across PIM doped with 1-hexylimidazole$^{(*)}$
membrane: 2.6 cm^3 o-NPPE /1g CTA and 1.0 M carriers calculated on plasticizer

Carrier	Metal ions	J_i, μmol/m^2·s	$S_{Zn(II)/Me(II)}$
1-hexyl-imidazole	Zn(II)	1.79	Zn(II) > Cd(II) > Co(II) 7.4 9.3
	Cd(II)	0.19	
	Co(II)	0.15	

(*) data from Radzyminska-Lenarcik and Ulewicz, 2014

From comparison of the data in Tables 2 and 3, it follows that, in the case of 1-hexyl-4-methylimidazole as ion carrier, the initial fluxes value for Zn(II) ions is twice as high as that for a membrane doped with 1-hexylimidazole, and selectivity coefficients are considerably higher.

After 24 hours, 98.5% of Zn(II) ions was separated from the unary solution, compared with 97.2 and 97.0%, respectively, from Zn(II)-Cd(II) and Zn(II)-Cd(II)-Co(II). The degree of separation from the quaternary solution is 96.9% for Zn(II) ions, 25% for Cd(II) ions, while those of Co(II) and Ni(II) ions are below 12%.

Using alkyl derivatives of imidazole, substituted in positions 1 and 4, the degree of recovery of Zn(II), Co(II) and Ni(II) is higher, compared with membranes doped with 1-hexylimidazole (Radzyminska-Lenarcik and Ulewicz, 2014), for which the degree of recovery was 72%, 30% and 24%, respectively, for Zn(II), Co(II) and Ni(II).

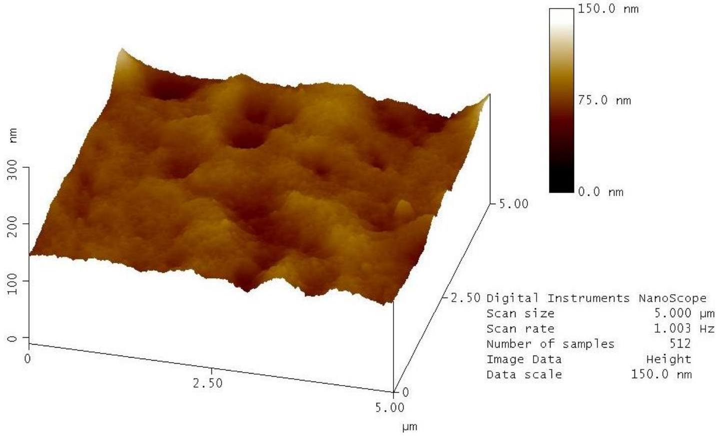


Fig. 2. 3D-view atomic force microscopy for PIM with 1-hexyl-4-methylimidazole

The AFM image of PIM in a two-dimensional form in the format 5.0 x 5.0 μm is shown in Fig. 2. The porosity (ε) and roughness (R_q) of the polymer inclusion membrane were calculated using atomic force microscopy (AFM) data and were equal to 15.8% and 6.6 nm, respectively. The effective pore size was 0.06 μm; thickness membrane 30 μm. The distribution of the carrier in the investigated membrane after evaporation of dichloromethane is homogeneous over the entire surface. The tortuosity of the PIM doped with 1-hexyl-4-methylimidazole was determined also from the relationship developed by Wolf and Strieder (1999) and was found to be equal to 2.85.

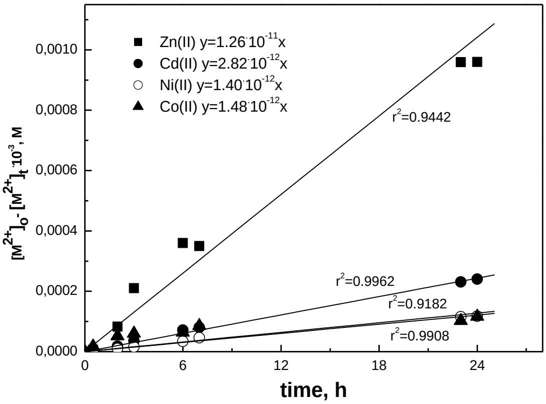


Fig. 3. Relation of $[Me^{2+}]_i$-$[Me^{2+}]_t$ plotted vs. time for Zn(II), Cd(II), Co(II) and Ni(II) transport across PIM membrane doped with 1.0 mol/dm^3 1-hexyl-4-methylimidazole

In Fig. 3, the correlation graphs of $[Me^{2+}]_i$-$[Me^{2+}]_t$ versus time of metal ions transport across PIM doped with 1-hexyl-4-methylimidazole are presented. The diffusion coefficient of Me(II) was calculated, substituting $D_o=d_o/\Delta_o$, where d_o is the thickness of the membrane (0.003 cm) and Δ_o could be evaluated by plotting $[Me^{2+}]_i$-$[Me^{2+}]_t$ vs. time. The corrected (normalized) membrane diffusion coefficient $D_{o,n}$, which considers the morphological features inside the membrane (ε - porosity and τ - tortuosity), was calculated from equation (Salazar-Alvarez et al., 2005): $D_{o,n} = D_o \cdot (\varepsilon / \tau)$. The obtained values of diffusion coefficients are presented in Table 4.

Table 4. Diffusion coefficients normalized for competitive transport of Zn(II), Cd(II), Co(II), and Ni(II) ions through PIM with 1-hexyl-4-methylimidazole

Metal ions	Δ_o, s/m	D_o, cm^2/s	$D_{o,n}$, cm^2/s
Zn(II)	$10^{5.64}$	$6.94\cdot10^{-09}$	$3.85\cdot10^{-10}$
Cd(II)	$10^{7.23}$	$1.56\cdot10^{-10}$	$8.66\cdot10^{-12}$
Ni(II)	$10^{7.54}$	$7.71\cdot10^{-11}$	$4.28\cdot10^{-12}$
Co(II)	$10^{7.57}$	$8.16\cdot10^{-11}$	$4.53\cdot10^{-12}$

Values of diffusion coefficient determined in this study are comparable with data presented in literature for different membranes. They are in the range 10^{-6} to 10^{-12} 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 Me(II)-carrier species of $3.85 \cdot 10^{-10} - 4.28 \cdot 10^{-12}$ cm^2/s is smaller than the value of $1.5 \cdot 10^{-7}$ cm^2/s reported for the lead complex with the D2EHPA in PIM reported by (Salazar-Alvarez et al., 2005).

The values of normalized diffusion coefficients (considering membrane porosity and tortuosity) of Me(II)-carrier complexes, obtained in the process of transport across PIMs containing 1-hexyl-4-methylimidazole from the solution Zn(II)-Cd(II)-Co(II)-Ni(II) are in the range $3.85 \cdot 10^{-10} - 4.28 \cdot 10^{-12}$ cm^2/s. Thus, the rate of transport of non-ferrous metal ions across PIMs doped with 1-hexyl-4-methylimidazole is determined by the diffusion rate of the complexes Me(II)-carrier across the membrane.

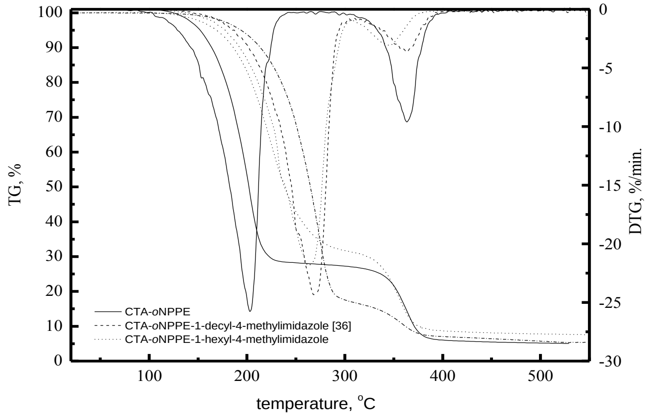


Fig. 4. TGA thermograms of CTA-*o*-NPPE and CTA-*o*-NPPE-carrier: 1-hexyl-4-methylimidazole and 1-decyl -4-methylimidazole

In the final stage of the studies, the thermal stability of the PIM doped with 1-hexyl-4-methylimidazole was determined. Literature reports (Arous et al., 2004; Gherrou et al., 2004, 2005) indicate that degradation of a CTA membrane proceeds in two steps. The first step occurs at temperatures in the range 292-320^{o}C while the second (carbonization) occurs in the range 450-476^{o}C. The membrane thermal stability changes after addition of a plastifier and ion carrier (Gherrou et al., 2004, 2005; Benosmane et al., 2009). Figure 4 shows the thermograms of the membrane CTA-*o*-NPPE–carrier. The diagram indicates that degradation of the membrane made of CTA–*o*-NPPE with 1-hexyl-4-methylimidazole (carrier) proceeds in two steps. In the first step, at 220.1^{o}C, the weight loss is 80.57%, in the second at 327.0^{o}C the weight loss is 5.88%. At a temperature of 547.6^{o}C, the residue is 3.43%. The first and second steps of degradation of a membrane doped with 1-hexyl-4-methylimidazole occur at temperature lower by 10^{o}C, compared with the membrane which contains 1-

decyl-4-methylimidazole, for which the results were reported in (Ulewicz and Radzyminska-Lenarcik, 2014). The first step of degradation of the membrane studied in this work occurs at temperatures higher by 10^oC, compared with that of the membrane doped with 1-hexylimidazole (211.3^oC) – the relevant findings were reported in (Radzyminska-Lenarcik and Ulewicz, 2012), while the second step does at temperatures lower by 33^oC (360.7^oC). The findings obtained lead to the conclusion that PIMs doped with 1-alkyl-4-methylimidazole are thermally stable up to temperatures just below 200^oC.

Conclusions

In the case of alkyl derivatives of imidazole, shown in positions 1 and 4 as ion carriers in PIMs, the initial flux for Zn(II) ions is twice as high as that for a membrane doped with 1-hexylimidazole. Also the selectivity coefficients and degrees of recovery are significantly higher for Zn(II), Co(II) and Ni(II), compared with the membranes doped with 1-hexylimidazole. Polymer inclusions membranes doped with 1-alkyl-4-methylimidazole are thermally stable up to temperatures just below 200^oC.

Zinc(II) cations can be removed effectively from aqueous chloride solutions in the hydrometallurgical process of supported and polymer inclusion membrane transport with 1-hexyl-4-methylimidazole as ion carriers. The use of the ion carrier enables the separation of 98.5% Zn(II) ions from a unary solution and of 96.9% from a quaternary solution of Zn(II)-Cd(II)-Co(II)-Ni(II) after running the process for 24 hours. Competitive transport of metal ions across PIM doped with 1-hexyl-4-methylimidazole showed the following preferential selectivity order: Zn(II) > Cd(II) > Ni(II) > Co(II). The selectivity coefficients of Zn(II)/Cd(II), Zn(II)/Ni(II), and Zn(II)/Co(II) obtained during transport across the polymer membranes are 12.9, 23.4 and 40.8, respectively. Moreover the values of diffusion coefficient of Me(II)-carrier complexes, obtained in the process of transport across PIMs containing 1-hexyl-4-methylimidazole are in the range 10^{-10} to 10^{-12} cm^2/s and show that limiting step of the process is the transfer of metal complex across membrane barrier.

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