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THE USE OF 1-ALKYLIMIDZOLES FOR SELECTIVE SEPARATION OF ZINC IONS IN THE TRANSPORT PROCESS ACROSS A POLYMERIC INCLUSION MEMBRANE

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Abstract: The transport of Zn(II) ions from different aqueous nitrate(V) source feeding phases ($c_{Me} = 0.001 \text{ mol/dm}^3$, pH 6.0) across polymer inclusion membranes (PIMs) doped with 1-alkylimidazole as an ion carrier was reported. Alkyl substituents in position 1 of imidazole ring have an effect on hydrophobic properties of the carriers and the initial flux of the transported metal ions. The membranes were characterized by an atomic force microscopy (AFM). The results show that the Zn(II) ions could effectively be separated from other transition metal cations such as Co(II) and Ni(II) from different equimolar ion mixtures. Also, the thermal stability of PIM doped with 1-decylimidazole was studied in replicate experiments. The highest separation coefficients for the Zn(II)/Co(II) and Zn(II)/Ni(II) systems, equal to 9.4 and 11.9 were recorded for the equimolar Zn(II)-Co(II)-Ni(II) mixture for 1-hexylimidazole as a carrier, while using 1-decylimidazole resulted in the highest values of initial flux of the Zn(II) ions transport across the polymeric membrane.

Keywords: *polymer inclusion membrane (PIM), separation ions, cobalt(II), nickel(II), zinc(II), alkylimidazole*

Introduction

Non-ferrous metals recovering from ores and metal-bearing wastes such as flue dusts, melting losses, slimes and spent technological liquors is based either on pyrogenic or hydrometallurgical (wet) technologies. Selection of an appropriate manufacturing process depends on a useful metal content. In a typical wet process, among the four basic technologies, i.e. leaching, phase separation, extraction of metal ions from aqueous solutions and deposition of the ions from the aqueous phase, of particular interest is separation of the ions in an aqueous solution, which has direct bearing on

the purity of a final product. In a modern wet process of non-ferrous metals recovery, separation of the ions is usually conducted by solvent extraction or ion-exchange (Habashi, 1999; Bartsch and Way, 1996). The separation of the non-ferrous metal ions in aqueous solutions or industrial waste waters in a laboratory scale is carried out using membrane-based techniques. A characteristic feature of liquid membranes is that both the extraction and re-extraction steps can be conducted simultaneously, which enabled the implementation of a continuous process eliminating the need of intermediate operations. The combined extraction-reextraction regime, also named a pertraction process, offers a considerable advantage, as compared to that of solvent extraction (Bond et al., 1999). The liquid membranes, as far as their constructional features are concerned, can be divided in four basic categories: thick-layer (BML), immobilised liquid (SCM), emulsion liquid (ELM) and polymeric inclusion (PIM) membranes.

The efficiency of separation of metal ions using liquid membranes depends mainly on the type and concentration of the ion carriers. Commercial carriers used in laboratory experiments ensure the effective separation of the ions but their selectivity is rather poor. Therefore, new complexing reagents are sought enabling the effective separation of the ions from aqueous solutions. During the past few years, macrocyclic compounds, such as laryate ethers, calixarenes, calixcrowns and cyclodextrins were successfully used as the ion carriers (Ulewicz, 2001, 2008; Walkowiak and Kozłowski, 2009; Nghiem et al., 2006). Moreover, other organic compounds, e.g., imidazole and its derivatives were also used for the purpose. Imidazole (1,3-diazole) belongs to a class of five-member heterocyclic bases known as azoles. According to the Pearson's classification, imidazole is a medium-class base with pK_a of 7.14 (Barszcz and Lenarcik, 1989). It forms stable complexes with soft Lewis acids (Schaekers and du Preez, 2004). The substitution of an alkyl to position 1 of the azole only slightly strengthens the basicity of the electron-donating nitrogen atom of 1-alkylimidazoles ($pK_a = 0.0222n + 7.165$, where n is the number of the carbon atoms in the alkyl substituent) (Lenarcik and Ojczenasz, 2002). At the same time, the stability of their metal complexes is slightly enhanced. Water-insoluble alkylimidazoles were used for the solvent extraction of a number of metal ions, e.g., Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} (Cuprey, 1974; Lenarcik and Barszcz, 1977, 1979; Lenarcik et al., 1977; Schaekers and du Preez, 2004; Lenarcik and Ojczenasz, 2004; Lenarcik and Kierzkowska, 2004; Lenarcik and Rauckyte, 2004; Radzaminska-Lenarcik, 2007,2008). 1-Decylimidazole was used for extraction of Co^{2+} , Ni^{2+} and Cu^{2+} from their chlorate(VII), chloride and thiocyanate solutions (du Preez et al., 2001). Moreover, azocrown ethers and thiaazocrown ethers were also reported as the ion carriers of Pb^{2+} , Zn^{2+} , Cd^{2+} , Ni^{2+} and Co^{2+} in the transport processes across the polymeric inclusion membranes (Ulewicz et al., 2007a,b, 2009), and 1-vinylimidazole was used for separation of the Cu^{2+} and Fe^{3+} ions (Ajjji and Ali, 2010). Recently, the imidazole derivatives were used by Ulewicz and Radzaminska-Lenarcik (Ulewicz and Radzaminska-Lenarcik, 2011, 2012; Radzaminska-Lenarcik and Ulewicz, 2012a) for

separation of the Cu^{2+} ion from the equimolar mixtures in the $\text{Cu}^{2+}\text{-Co}^{2+}\text{-Zn}^{2+}\text{-Ni}^{2+}$ systems.

A metallurgical waste is subjected to recovery processes, as far as these are technologically feasible and cost-effective. By the end of 2007 year, about 8.9 Tg of waste came from the copper metallurgy processes. The post-neutralization deposits of a waste-water treatment plant (80 Mg/24 hours) were found to contain 11.5% of zinc. Hence, our interest is zinc recovery. In the literature, there are many reports on the processes of zinc and other metals recovery (Beniot et al., 1996; Cuprey, 1974; Schaekers and du Preez, 2004).

The present article deals with a competitive transport of the zinc(II) ions from the dilute aqueous solutions using PIM doped with 1-alkylimidazoles. The initial fluxes and selectivity coefficients of zinc(II), cobalt(II) and nickel(II) ions transport across PIM doped with 1-alkylimidazole from the aqueous source phase containing equimolar mixture of all metals are also investigated.

Experimental

Preparation of polymeric inclusion membranes

The polymeric inclusion membranes (PIM) were synthesized using the following solutions: 1.25 g of cellulose triacetate (CTA) in 100 cm^3 of dichloromethane, 10% plasticizer solution (o-nitrophenyl pentyl ether, o-NPPE; FLUKA) in dichloromethane and 0.10 mol/dm^3 1-alkylimidazoles (ion carrier) (Fig.1) solution in dichloromethane. The carrier was synthesized using a literature procedure (Pernak et al. 1987).

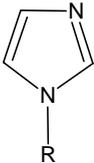
	No	R-:	pK _a
	<u>1</u>	-C ₆ H ₁₃	7.30
	<u>2</u>	-C ₇ H ₁₅	7.32
	<u>3</u>	-C ₈ H ₁₇	7.34
	<u>4</u>	-C ₉ H ₁₉	7.39
	<u>5</u>	-C ₁₀ H ₂₁	7.43

Fig. 1. Formulas of 1-alkylimidazoles

To prepare a membrane, the CTA solution was mixed with the plasticizer solution and that of the carrier and the mixture was poured into a mould consisting of a glass ring (6 cm in diameter). The membrane was formed after solvent evaporation during 12 hours at ambient temperature and subsequently it was conditioned in distilled water for further 12 hours. For preparation of the membrane, 2.67 cm^3 of o-NPPE/1.0 g of CTA and 1.0 mole of 1-alkylimidazoles, based on the weight of the plasticizer, were used. A fresh membrane was prepared for each experiment. Highly magnified images of the polymeric membranes were recorded using an atomic force microscopy (AFM)

MultiMode instrument (Veeco) equipped with type E scanner with the maximum scanning area of $10 \times 10 \times 2.5 \mu\text{m}$. The NanoScope IIIa and Quadrex control systems were employed. The equipment was operated as the atomic force microscope in the Tapping Mode. The HA_NC Etalon probes manufactured by NT-MDT were used and a resonance frequency was set at 110 KHz. In the separation process, distilled water (conductance of $5 \mu\text{S/m}$) was the receiving phase. The thermal stability of the polymeric inclusion membranes was determined over the range of $20 - 700^\circ\text{C}$ under nitrogen, in ceramic crucibles. An empty crucible served as a reference. The apparatus used was a SDT 2960 simultaneous DSC-TGA-TA instrument operated at a heating rate of 10°C/min and a nitrogen flow rate of $100 \text{ cm}^3/\text{min}$. The sample weight was 10 mg throughout.

Investigation of transport across polymeric inclusion membranes

The following metal nitrate(V) solutions were used for preparation of the aqueous solutions: $\text{Zn}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and NaNO_3 (all of analytical reagent grade, purchased from POCh, Gliwice, Poland). The transport of the metal ions across PIM was determined in equimolar solutions (0.001 mol/dm^3 each), containing the following ion systems: Zn(II)–Ni(II), Zn(II)–Co(II), and Zn(II)–Co(II)–Ni(II) placed in a cell fitted with a membrane separating both aqueous phases (feeding and receiving), stirred at 600 rpm. The metal ion concentrations were determined by an atomic absorption spectrometry using a Solaar 939 (Unicam) spectrometer.

The efficiency of the ionic transport was estimated using the following quantities.

- Initial flux:

$$J_0 = -\frac{V}{A} k c_0 \quad (1)$$

where J_0 is the flux at $t = 0$ ($\text{mol/m}^2\text{s}$), A an effective surface area of the membrane (m^2), V volume of the feeding phase (m^3), and c_0 is the initial concentration of the metal ion (mol/dm^3). The rate constant, k (s^{-1}) for the first-order kinetics was defined as:

$$\ln \frac{c}{c_0} = -kt \quad (2)$$

High correlation coefficients R^2 falling in the range of 0.971–0.997 indicated a linear relationship of $\ln(c/c_1)$ against time t .

- The separation factor of ions was defined as:

$$S_{M1/M2} = \frac{J_{0,M1}}{J_{0,M2}} \quad (3)$$

where $J_{0, M1}$ and $J_{0, M2}$ are initial fluxes of metal ions M_1 and M_2 , respectively.

- The percentage of the metal ions transport from the feeding to receiving phase, RF, was defined as:

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

where c_i is the initial concentration of metal ion in the receiving phase and c is the concentration in that phase after time t .

Results and discussion

The selectivity of transport of metal ions across the liquid membranes depends both on physicochemical characteristics of solutions, such as the metal ion concentration in the feeding phase, its pH and the presence of extraneous ions, the characteristics of membrane and plasticizer used and concentration of the carrier (Ulewicz et al., 2007a,b; 2009; Ajji and Ali, 2010; Ulewicz and Radzaminska-Lenarcik, 2011, 2012). One of the crucial factors affecting the selectivity of membrane is the ion carrier

Table 1. Initial flux, selectivity order and selectivity coefficients for competitive transport of Zn(II), Co(II), and Ni(II) ions across PIM doped with 1-alkylimidazole; membrane: 2.6 cm³ *o*-NPPE /1g CTA and 1.0 M carriers calculated on plasticizer; source phase: [Me(II)] = 0.001M each, receiving phase: deionized water. * data from Radzaminska-Lenarcik and Ulewicz (2012b)

Carrier	Metal ions	J, μmol/m ² ·s	S _{Zn(II)/Me(II)}
1	Zn(II)	1.79	Zn(II) > Co(II) > Ni(II) 9.4 11.9
	Co(II)	0.19	
	Ni(II)	0.15	
2	Zn(II)	1.86	Zn(II) > Co(II) > Ni(II) 7.4 9.3
	Co(II)	0.25	
	Ni(II)	0.20	
3	Zn(II)	1.95	Zn(II) > Co(II) > Ni(II) 6.9 8.1
	Co(II)	0.28	
	Ni(II)	0.24	
4	Zn(II)	2.29	Zn(II) > Co(II) > Ni(II) 6.7 7.0
	Co(II)	0.34	
	Ni(II)	0.29	
5*	Zn(II)	2.50	Zn(II) > Co(II) > Ni(II) 6.4 7.8
	Co(II)	0.39	
	Ni(II)	0.32	

nature. Therefore, the kind of substituent at the imidazole molecule on the separation efficiency of the Zn(II), Co(II) and Ni(II) ions from their equimolar mixture was studied. The initial fluxes of ions J_o and their transportation selectivity rank orders depending on the carrier used are presented in Table 1. Table 1 shows that the Zn(II) ions are transported from the feeding to receiving phase faster than the Co(II) and Ni(II) ions. Irrespective of the substituent chain length, the selectivity of transport of the ions across polymeric membranes doped with 1-alkylimidazole declines in the order Zn(II) > Co(II) > Ni(II).

This finding can be interpreted in terms of the kinetic factors involved in a complex formation of metal ions at the membrane/feeding phase interface. The stability constants of the Zn(II) complexes are higher than those of the Co(II) and Ni(II) (Table 2). With increasing chain length from $-C_6H_{13}$ to $-C_{10}H_{21}$, associated with pK_a increase of the carrier, the initial fluxes of metal ions increase, while the selectivity coefficients of Zn(II) against those of the remaining metals decrease. This decrease is due to faster increase in the transportation fluxes of remaining metals as compared with the increasing transportation fluxes of the Zn(II) ions.

The differences in the transport efficiency of metal ions can be explained by structural features of their complexes with 1-decylimidazole. This compound forms Zn(II) complexes of distorted tetrahedral geometry just at the first complexation steps ($n = 1, 2..$) (Lenarcik and Kierzkowska, 2004) according to equation:



where L denotes the 1-decylimidazole molecule.

The tetrahedral Zn(II) complexes are more compact than the octahedral, thus there are more readily transported across the pores of membranes. The Co(II) ions form tetrahedral complexes in the 3rd and 4th complexation steps at high alkylimidazole concentrations (Lenarcik and Ojczenasz, 2004). Consequently, much more readily are formed more bulky complexes of those ions. Under these conditions, the Ni(II) ions form exclusively 6-coordinate species (Lenarcik and Rauckyte, 2004).

Table 2. Comparison of stability constants β_n of Co(II), Ni(II), and Zn(II) complexes with 1-alkylimidazoles. x denotes a number of carbon atoms in alkyl chain at position 1 in the 1-alkylimidazoles. Data from: * Lenarcik and Ojczenasz (2004), ** Lenarcik and Rauckyte (2004), *** Lenarcik and Kierzkowska (2004)

$\log \beta_n$	Co(II)*	Ni(II)**	Zn(II)***
$\log \beta_1$	$y = 0,302x + 1,653$	$y = 0,161x + 2,631$	$y = 0,229x + 1,986$
$\log \beta_2$	$y = 0,342x + 3,592$	$y = 0,164x + 5,290$	$y = 0,229x + 4,500$
$\log \beta_3$	$y = 0,377x + 4,881$	$y = 0,164x + 7,233$	$y = 0,229x + 6,700$
$\log \beta_4$	$y = 0,434x + 5,780$	$y = 0,166x + 8,653$	

Table 3. Kinetic parameters and selectivity factors for the transport of the metal ions across polymeric membranes doped with 1-hexylimidazole (**1**) and 1-decylimidazole (**5**).
* data from Radzimska-Lenarcik and Ulewicz (2012^b)

Carrier	Mixture	Ions	J, $\mu\text{mol}/\text{m}^2\cdot\text{s}$	$S_{\text{Zn(II)/Me(II)}}$
1	Zn(II)/Co(II)	Zn(II)	1.98	Zn(II) > Co(II)
		Co(II)	0.21	9.4
	Zn(II)/Ni(II)	Zn(II)	2.04	Zn(II) > Ni(II)
		Ni(II)	0.19	10.7
5 *	Zn(II)/Co(II)	Zn(II)	2.65	Zn(II) > Co(II)
		Co(II)	0.30	8.8
	Zn(II)/Ni(II)	Zn(II)	2.67	Zn(II) > Ni(II)
		Ni(II)	0.28	9.5

The selectivity of separation of Zn(II) from binary solutions was studied during the transportation process across polymeric membranes doped with carriers **1** and **5**, i.e. those exhibiting respectively the highest and lowest selectivity of separation of the Zn(II) ions from the equimolar ternary mixture, Zn(II) – Co(II) – Ni(II). The results are given in Table 3. The highest separation factor among the Zn(II)/Me(II) systems was 10.7 for the Zn(II) – Ni(II) pair using carrier **1** and 9.5 for carrier **5**. From the Zn(II) – Co(II) – Ni(II) mixture, the separation efficiency for the Zn(II) ions was 89.3% and from the binary ion mixtures it exceeded 90% (Fig. 2). By comparing data from Tables 1 and 3, it can be seen that the Zn(II) ions were transported most effectively from all the investigated mixtures.

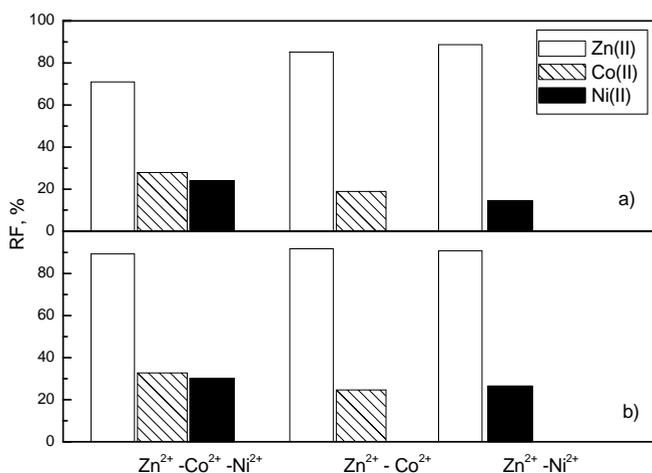


Fig. 2. Transport of metal ions from feeding phase after 24 hours, from different mixtures, during transport across the 1-hexylimidazole (a) and 1-decylimidazole (b) doped PIM

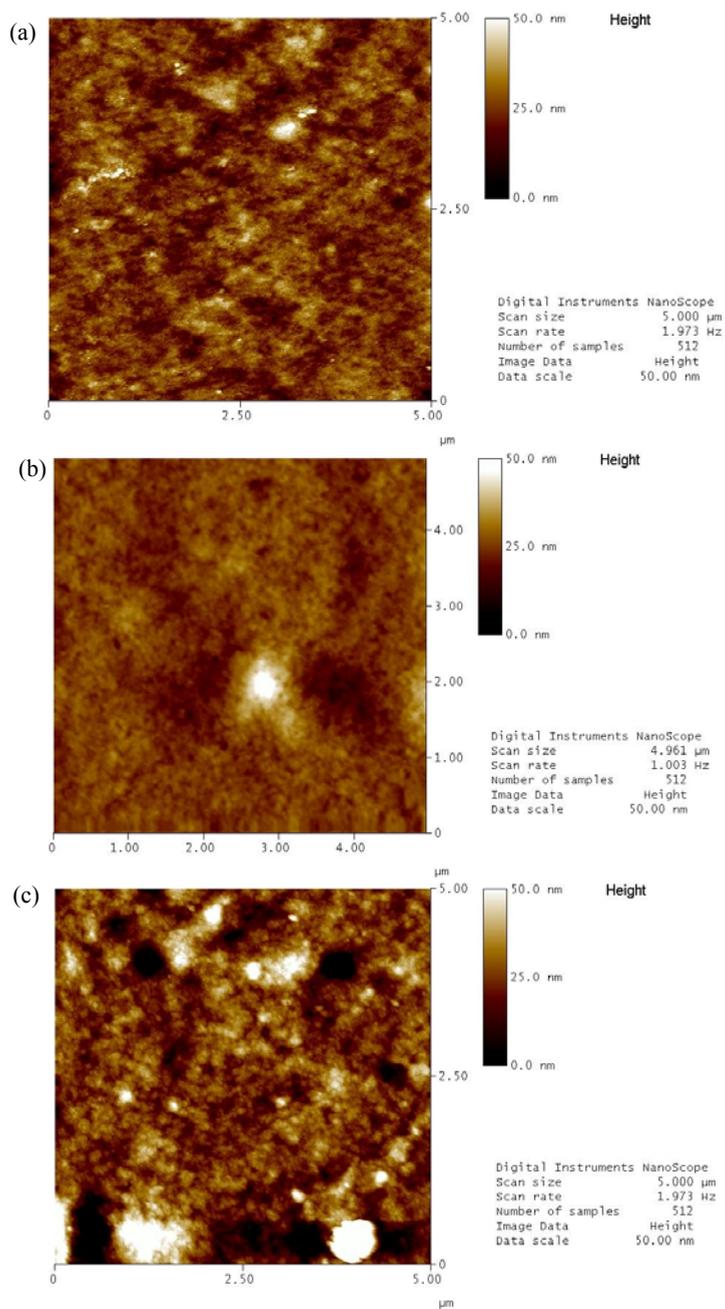


Fig. 3. 2D-view AFM images of the CTA - *o*-NPPE membrane (a), CTA - *o*-NPPE - carrier 1 (b), and CTA - *o*-NPPE - carrier 5 (c)

Since, as demonstrated in many papers (Ulewicz, 2001; Nghiem et al., 2006; Ulewicz et al., 2007a, Arous et al., 2004a), the selectivity of transportation of metal ions is affected by the physicochemical characteristics of the membrane, also the porosity and roughness of membranes were determined. Figure 3 shows the AFM image of the polymeric inclusion membranes doped with 1-hexylimidazole (membrane b) and 1-decylimidazole (membrane c) and, for the sake of comparison, that of a membrane consisting of support (CTA) and plasticizer (*o*-NPPE) only (membrane a).

The calculated mean roughness values, based on Ulewicz et al. (2009), for membranes 3a, 3b and 3c (surface area of 25 μm^2) are respectively 6.8, 8.1 and 3.9 nm. In Figures 3b and 3c the inclusions of organic phase are seen as large pores of 39.9 and 35.5 nm. The degree of porosity of *o*-NPPE-CTA membranes doped with carriers **1** and **5** was 21.1 and 18.7%, respectively.

Finally, thermal stability was examined for the membranes, which depends, among other things, on the polymer internal structure, its networking, presence of degradable aromatic and functional groups in the plasticizer and ion carrier. It was demonstrated (Gherrou et al. 2004, 2005; Arous et al., 2004b) that the degradation of CTA-made membrane occurs in two steps, the first over the range of 292–320 °C (main step) and the other over the range of 450–476 °C (charring of products). It was also shown that in thermal degradation of the CTA – *o*-NPOE – crown ether membranes, an additional

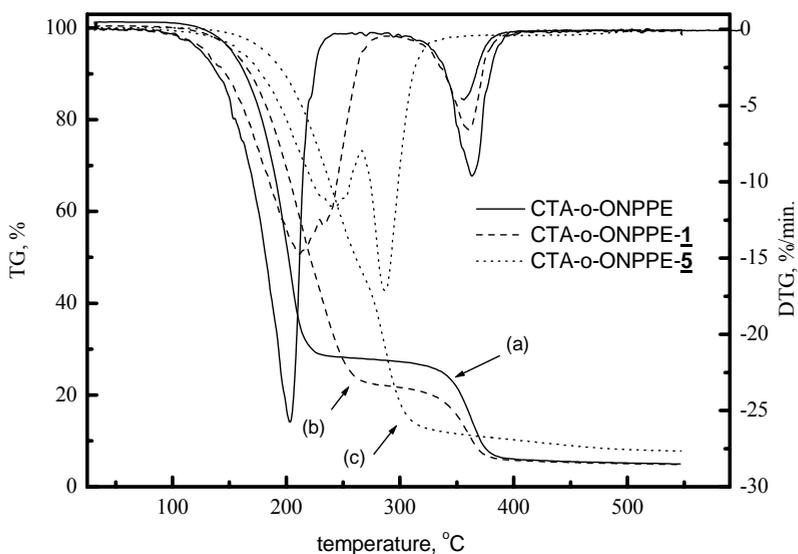


Fig. 4. TG-DTA curves for membranes: CTA-*o*-NPPE and CTA-*o*-NPPE + carrier **1**, and CTA-*o*-NPPE + carrier **5**

step emerges, which is assigned to degradation of the crown ether (ion carrier). For the series of crown ethers this step was recorded at 238.2 °C, 250.0 °C, 298.7 °C, and 273.4 °C for DB18C6, HT18C6, DA18C6, and HA18C6, respectively.

Figure 4 shows the thermograms of CTA-o-NPPE membranes with and without 1-hexylimidazole and 1-decylimidazole. Degradation of the membranes without the carrier occurs in two steps. In the first one, at 203.1 °C, 73.5% loss in mass was recorded, and in the second, at 363.3 °C, the loss was 19.9%. For the 1-hexylimidazole doped membrane corresponding losses of 74.63% and 13.9% occurred at 211.3 °C and 360.7 °C, respectively, while for the 1-decylimidazole doped membrane corresponding losses of 61.3% and 18.9% occurred at 227.7 °C and 358.6 °C, respectively.

Conclusion

The effective transport of the Zn(II) ions across 1-alkylimidazoles doped polymeric membranes was studied from both binary Zn(II) – Ni(II) and Zn(II) – Co(II) mixtures and ternary Zn(II) – Ni(II) – Co(II) mixture. The selectivity of separation declined in the series Zn(II) > Co(II) > Ni(II). The initial flux of the zinc(II) transport across PIM increases slightly with increasing alkyl chain length of the alkyl substituent in a molecule of the carrier in the order: **1** < **2** < **3** < **4** < **5**. The highest separation coefficient for the Zn(II)/Co(II) and Zn(II)/Ni(II) systems, equal 9.4 and 11.9, respectively, were determined for the equimolar Zn(II) – Co(II) – Ni(II) mixture using carrier **1**. Application of this carrier enables also to obtain higher selectivity factors for the Zn(II) ions from equimolar binary systems Zn(II) – Co(II) and Zn(II) – Ni(II). PIMs doped 1-hexyl- and 1-decylimidazole are thermally stable up to 210°C and they enable separation of Zn²⁺ with efficiencies better than 72% and 90% respectively within 24 hours.

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