### Application of a deep eutectic mixture and ionic liquid as carriers in polymer adsorptive membranes for removal of copper(II) and zinc(II) ions from computer scrap leachates

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### ABSTRACT

This paper describes the results of the application of Aliquat 336 ionic liquid (IL-A) and a deep eutectic mixture consisting of diacetamide and Aliquat 336 (DEM-DA) as carriers in polymer adsorptive membranes (PAMs) used to remove copper(II) and zinc(II) ions from aqueous solutions obtained by leaching computer pins with strong acids. The wettability of the formulated PAMs containing poly(vinyl chloride) as a polymer matrix and bis(2-ethylhexyl) adipate as a plasticizer was examined. Using DEM-DA-containing polymer membrane recovered approximately 97% of copper(II) and 96% of zinc(II) ions after 1 h of separation processes, whereas application of IL-A-containing PAM allowed the removal of similar amounts of copper(II) and zinc(II) ions after 3 h. The high efficiency of PAMs was confirmed by the analysis of their chemical composition after the separation processes by wavelength-dispersive X-ray fluorescence spectroscopy. The use of PAMs containing a deep eutectic mixture (DEM) as an ion carrier allows for a reduction of the separation time, which can be of significant economic importance, especially in case of processes carried out on a larger scale. Due to its properties, DEM is considered safe for the natural environment, and its use as a carrier in PAMs represents the so-called "Green Chemistry".

*Keywords:* Polymer adsorptive membranes; Deep eutectic mixtures; Ionic liquids; Copper(II) ions; Zinc(II) ions; Computer scrap

#### 1. Introduction

The dynamic development of industries related to the production of various electrical and electronic equipment and the introduction of digital technologies on an increasingly wide scale result in a systematic increase in the amount of waste electrical and electronic equipment (WEEE) generated. E-scrap is a heterogeneous group of waste that includes, but is not limited to, used batteries, fluorescent tubes, printed circuit boards, photovoltaic modules, or computers and contains various metals, including precious metals (e.g., gold, palladium, platinum, silver), non-ferrous metals (e.g., copper, zinc), or rare earth metals [1–3]. Recovery of valuable components from e-scrap, presently treated as a secondary source of many valuable metals, is vital for environmental protection and sustainability, so methods are being developed to recover them faster, more cost-effectively, and efficiently [4,5]. The recovery of valuable metals from e-scrap primarily employs various hydrometallurgical methods due to, among other things, lower energy requirements, lower operating costs, and the ability to selectively recover metals with high efficiency. In the first stage of the hydrometallurgical process, suitably prepared WEEE (disassembled, segregated, crushed) is usually treated with various leaching agents (e.g., cyanide, acid, alkali, halide, thiosulphate, thiourea, etc.) to extract metals and transfer them to the solution. A combination of leaching agents or chemical inhibitors is often required to ensure adequate process

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performance. Then, metal ions from the solution obtained by WEEE leaching are removed using such methods as solvent extraction, membrane processes, adsorption, selective precipitation, electrowinning, etc. [6–9].

Of particular interest are metal ions removal methods relying on various polymer membranes, such as polymer adsorptive membranes and polymer inclusion membranes (PIMs) [10-12]. This is due not only to such advantages of membranes as usually high selectivity and high efficiency of removal of various metal ions from aqueous solutions (e.g., strongly acidic or alkaline) but also to the ability to easily modify their composition to be optimal for specific process conditions. Polymer membranes are often modified in terms of the carriers used, which should bind well to the metal ions removed from the solution while being non-toxic and safe for the environment [13,14]. The group of such carriers includes, among others, ionic liquids (ILs) and deep eutectic mixtures. ILs are liquid substances consisting only of ions, well extracting various organic and inorganic substances (i.e., metal ions), characterized by high thermal stability, good ionic conductivity, negligible vapour pressure, non-flammability, as well as electrochemical stability [15]. Various ILs have been successfully used as carriers in polymer membranes to remove or recover many types of metal ions from solutions, including copper(II) and zinc(II) ions [16,17]. In addition, it has been shown that Cyphos IL 101 ionic liquid used as a carrier in a polymer film enables efficient, simultaneous

removal of multiple heavy metal ions (Co, Ni, Cu, Zn, Sn, and Pb) from the solution obtained by WEEE leaching [18]. deep eutectic mixtures (DEMs) represent mixtures containing at least one compound that is a hydrogen bond acceptor (HBA) and one that acts as a hydrogen bond donor (HBD). The mixtures that are liquid at room temperature are used in various separation processes as deep eutectic solvents (DESs), which is in line with the green chemistry principles. DESs are considered green solvents because they are not toxic, present low vapour pressure, have high thermal stability, and have a high ability to separate organic and inorganic compounds [19]. Great potential was found for the use of deep eutectic mixtures in separation processes due to the process duration, as well as the simple synthesis of these compounds. To date, deep eutectic solvents have been used to remove cobalt, zinc, nickel, and manganese ions [20] by solvent extraction and lithium ions [21-23] by both extraction and membrane processes. In addition, deep eutectic mixtures have been used in membrane processes to remove copper(II) [24], silver(I) [25], gold(III) [26] and platinum(IV) ions [27]. As mentioned above, deep eutectic solvents generally include a hydrogen bond acceptor and a neutral hydrogen bond donor, and the properties of the resulting mixture determine their subsequent application [28]. Given the above, there are many possible DES combinations. Fig. 1 shows some commonly used HBD and HBA in deep eutectic liquids. Depending on their composition, deep eutectic mixtures have also found



Fig. 1. Selected chemical compounds which can be used as hydrogen bond donor and hydrogen bond acceptor in deep eutectic solvents [4,7,30–33].

applications in metal processing, that is, metal electrodeposition, metal electropolishing, metal extraction, metal oxide processing, biocatalysis and organic chemistry, pharmaceuticals and medicine, as well as nanoengineering [29,30].

Ionic liquids and deep eutectic solvents share several common features, and it is believed that DESs initially represented the so-called new generation of ionic liquids. DESs are distinguished from ILs by their low cost and much lower environmental impact, as ILs often exhibit poor biodegradability and often are not biocompatible. In addition, the method of obtaining DESs is simple and does not generate waste (the synthesis involves mixing the components of a deep eutectic liquid). The ionic liquids produced by the multi-step synthesis consist exclusively of ions that interact through ionic bonds, while DESs are the result of complexation between HBA and HBD [34].

This article presents the results of a comparison of the effectiveness of polymer adsorptive membranes containing Aliquat 336 ionic liquid or a deep eutectic mixture of diacetamide and Aliquat 336 (in a 2:1 molar ratio) as ion carriers for the removal of copper(II) and zinc(II) ions from aqueous solutions obtained by leaching computer waste with concentrated acids. Polymer adsorptive membranes were used because they enable selective and efficient recovery of metal ions [35], but to date, they have not been used with IL-A and deep eutectic mixture consisting of diacetamide (DEM-DA) carriers to remove copper(II) and zinc(II) ions from acidic WEEE leachates. The research focused on copper(II) and zinc(II) ions, as these metals are commonly used in electrical and electronic equipment industries (e.g., for cables, wires, batteries, etc.) and are usually found in relatively large quantities in WEEE. The results confirm the effectiveness of the developed methods in removing copper(II) and zinc(II) ions, but show that the efficiency of the membranes depends significantly on the time of the adsorption process.

#### 2. Materials and methods

### 2.1. Reagents

Aliquat 336 was purchased from Thermo Scientific (St. Louis, MO, USA), and diacetamide from Sigma-Aldrich (Poznan, Poland). Concentrated nitric acid was purchased from Avantor (Gliwice, Poland). Poly(vinyl chloride) (PVC) in suspension with an average molecular weight of 72,000 was obtained from Anwil (Włocławek, Poland). Bis(2ethylhexyl) adipate (ADO) and tetrahydrofuran (both of analytical grade) were sourced from Avantor (Gliwice, Poland).

# 2.2. Preparation and characterization of deep eutectic mixture DEM-DA

A DEM-DA deep eutectic mixture containing diacetamide as a hydrogen bond donor and Aliquat 336 as a hydrogen bond acceptor was prepared by mixing the components in a 2:1 molar ratio. After adding solid diacetamide to liquid Aliquat 336 (IL-A), the mixture was heated to 76°C–78°C and heated for 15 min at this temperature. After cooling to room temperature a liquid DEM-DA was obtained. In order to confirm the correct DEM-DA composition, <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of the deep eutectic mixture were obtained using a Bruker Avance III 400 MHz spectrometer (with DMSO-d<sub>6</sub> solution).

#### 2.3. Leaching procedure

The processor pins were separated from the printed circuit boards with a soldering torch. The computer pins probably contained copper-tin alloy with a gold coating or bath. All experiments were carried out with solutions produced by leaching 1 g of computer pins from old computer processors with 50 mL of concentrated nitric acid and allowed to stand for 24 h. After leaching, gold flakes were released on the surface of the solution, and undissolved precipitate. The gold flakes were next separated, and the solution was filtered. PVC/ADO/DEM-DA and PVC/ADO/IL-A membranes were immersed in 10 mL of the obtained solution to separate the metal ions contained in the solution. The metal ions concentration in the aqueous phase was determined by atomic absorption spectrometry (AAS 240FS Spectrometer, Agilent, Santa Clara, CA, USA).

#### 2.4. Preparation of polymer adsorptive membranes

#### 2.4.1. Membrane PVC/ADO/DEM-DA composition

The PVC/ADO/DEM-DA membrane consisted of 60 wt.% poly(vinyl chloride), 20 wt.% DEM-DA, and also 20 wt.% ADO.

#### 2.4.2. Membrane PVC/ADO/IL-A composition

The PVC/ADO/IL-A membrane consisted of 60 wt.% poly(vinyl chloride), 20 wt.% IL-A, and also 20 wt.% ADO.

#### 2.4.3. Polymer adsorptive membranes preparation

To prepare a PVC/ADO/DEM-DA membrane, a solution consisting of 0.473 g of polymer matrix (PVC), 0.154 g of carrier ions (DEM-DA), and 0.157 g of plasticizer (ADO) was prepared in 10 mL of tetrahydrofuran (THF). In the case of PVC/ADO/IL-A membrane, a solution consisting of 0.501 g of PVC, 0.166 g of IL-A, and 0.165 g of ADO was formed in 10 mL of THF. The solutions prepared this way were poured into glass rings with a diameter of 4.5 cm. The glass rings were covered with filter paper and watch glasses to allow THF to evaporate over 1 d slowly. After complete evaporation of THF the membranes were obtained (Fig. 2). Then, the membranes were carefully separated from the glass plates and conditioned in distilled water for 24 h. According to the described procedure, circular membranes with a diameter of 4.5 cm and a thickness of 0.245 nm in the case of PVC/ADO/ DEM-DA and of 0.238 nm in the case of PVC/ADO/IL-A were obtained. The PVC/ADO/DEM-DA and PVC/ADO/ IL-A membranes had an average mass of  $0.748 \pm 0.001$  g and  $0.832 \pm 0.001$  g, respectively.

#### 2.5. Wettability - contact angle measurement

The static water contact angle on the surfaces of polymer adsorptive membranes was measured by the sessile drop method at the ambient temperature using a contact angle goniometer (T-1, DSA100E - Drop Shape Analyzer, Krüss). A membrane sample was washed thoroughly with distilled water and mopped with filter paper to remove the moisture content prior to the contact angle (CA) measurements. Next, 5  $\mu$ L of a deionized water droplet was placed onto the membrane surface and within 3 s of the addition of the water drop the CA was measured. The measurement temperature was 23°C. The contact angle was measured at three random locations for each sample, and the average value was reported.

#### 2.6. Membrane separation processes

The separation of the copper(II) and zinc(II) ions by polymer adsorptive membranes was conducted per the procedure: membranes were immersed in a beaker containing 10 mL of the solution obtained from leaching computer pins. The initial concentration of copper(II) and zinc(II) ions in this leachate was 0.102 and 0.302 mg/L, respectively. The separation processes were run at  $25^{\circ}$ C ± 0.2°C. The solution samples were taken at regular intervals and diluted using nitric acid. Then, the concentration of metal ions was determined using atomic absorption spectroscopy.

## 2.7. Characterization of polymer adsorptive membranes by wavelength-dispersive X-ray fluorescence spectroscopy

Additionally, after the binding of metal ions by analyzed polymer adsorptive membranes, the wavelength-dispersive X-ray fluorescence spectroscopy (WD-XRF) qualitative spectra of these membranes were recorded. A qualitative spectral analysis was performed with WD-XRF by identifying spectral lines and determining their possible coincidence. On this basis, analytical lines were selected. Semi-quantitative analysis was developed using the SQX calculation program (fundamental parameter method). The analysis was performed in the fluorine-uranium (F-U) range, and the concentrations of the determined elements were normalized to 100% using CH as the balance.

#### 3. Results

## 3.1. Characterization of investigated deep eutectic mixture DEM-DA

After conducting <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments for the obtained DEM-DA deep eutectic mixture, the following results were obtained: the yield was 84.96%. <sup>1</sup>H NMR: 400 Hz, DMSO, δ 0.8887–0.8473 (6H, m), 1.2914–1.2607 (25H, t), 1.3999–1.3835 (2H, d), 1.6044 (4H, s), 2.1252 (9H, s), 2.9347 (2H, s), 3.1673–3.2090 (4H, q). <sup>13</sup>C NMR: 101 Hz, DMSO, δ 171.4866, 61.1825–61.0137, 47.9990, 40.6399–39.3886, 33.0079, 31.7439–31.6184, 29.3760–28.8483, 26.2382–25.9708, 25.1711, 22.5464–22.5090, 21.7901, 14.3951.

Based on the literature data, it can be assumed that, most likely, the chloride anion of the ionic liquid (IL-A, HBA) does not interact directly with the diacetamide (HBD) chain but only solvates and stabilizes the HBD/anion complexes formed as a result of hydrogen interactions (Fig. 3). DEM-DA was obtained by solvation of the chloride anions of IL-A [36,37].



Fig. 2. Membranes containing 20 wt.% DEM-DA (a) or IL-A (b) as ions carriers before membrane separation processes.



Fig. 3. DEM-DA formation [36,37].

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## 3.2. Contact angle measurement of an investigated polymer adsorptive membranes

The sessile drop experiments, where the liquid is supplied from below through a hole in the solid surface using a motorized syringe device, were described in the literature [38]. The produced sorption material is hydrophilic. The contact angle of membrane containing DEM-DA was approx. 48.8°, with an average deviation of 0.4 (Fig. 4a). Therefore, the obtained polymer membrane can be successfully used to separate metal ions from aqueous solutions. When the CA is less than 90°, the material is hydrophilic. The contact angle explains the wetting properties of the material. The more hydrophobic the surface of the material is, the greater the contact angle will be, which makes it difficult to form a fluid layer on the surface of the fiber and hinder fluid adsorption [39]. Furthermore, the contact angle of membrane PVC/ADO/IL-A was approx. 7.3°, and the average deviation was 1.2 (Fig. 4b).

## 3.3. Separation of copper(II) and zinc(II) ions from e-scrap acidic leachate by adsorptive membranes processes

The tested PVC/ADO/DEM-DA and PVC/ADO/IL-A adsorptive membranes were immersed in an e-scrap acidic

leachate solution. Metal ions were adsorbed on the membranes surfaces. After membrane separation processes, the percentage of removal of metal ions from the solutions ( $\%R_s$ ) and the sorption capacity ( $q_i$ ) were determined.

The adsorption equilibrium studies were carried out for 24 h. Fig. 5 shows that the equilibrium was reached before 60 min for the PVC/ADO/DEM-DA membrane and after 3 h in the case of the PVC/ADO/IL-A membrane. This is probably due to the decrease in the number of active sites in membrane after this time [40]. In both cases, the sorption reactions proceeded quickly, leading to a state of equilibrium. The highest removal of metal ions using a polymer adsorptive membrane with a deep eutectic mixture (DEM-DA) as a carrier was 96.85% and 95.94% for copper(II) and zinc(II) ions, respectively. While the highest percentage of copper(II) and zinc(II) ion removal by a membrane containing ionic liquid (IL-A) as a carrier was 96.63% and 95.42%, respectively.

Fig. 6 shows the polymer adsorptive membranes after the membrane separation processes. The surfaces of produced membranes before the membrane separation processes were colorless, whereas membranes changed colors after the sorption processes. This was probably due to the binding of metal ions by carrier molecules contained in the structure of the membranes and creating complexes.



Fig. 4. Contact angle of polymer adsorptive membranes containing DEM-DA (a) or IL-A (b) as ion carriers.



Fig. 5. Percentage of copper(II) and zinc(II) ion removal by membranes with DEM-DA or IL-A. The average value  $%R_s$  of all experiments are ±0.01.



Fig. 6. Membranes containing 20 wt.% DEM-DA (a) or IL-A (b) as metal ion carriers after removal of copper(II) and zinc(II) ions from an e-scrap acidic leachate solution.

Table 1 Sorption capacities of PVC/ADO/DEM-DA and PVC/ADO/IL-A membranes against the removal of copper(II) and zinc(II) ions over time

Adsorptive membrane	PVC/ADO/DEM-DA		PVC/ADO/IL-A	
Metal ions	Cu(II)	Zn(II)	Cu(II)	Zn(II)
T (min)	$q_t (mg/g)$	$q_t (mg/g)$	$q_t (mg/g)$	$q_t (\mathrm{mg/g})$
10	9.6486	9.3336	2.8179	2.5656
30	10.7760	9.6129	3.2404	2.4478
60	15.6341	9.2928	5.2371	2.5123
180	15.5011	14.0241	5.1977	4.6829
1,440	15.5216	13.9720	5.2010	4.6608

Average values  $q_t$  of experiments are ±0.0001.

The sorption capacity of the investigated polymer adsorptive membranes (PVC/ADO/DEM-DA and PVC/ADO/IL-A) increased over time. The highest  $\%R_s$  after 1 h of sorption of the copper(II) ions ( $q_t$  = 15.6341 mg/g,  $\%R_s$  = 96.85%) and zinc(II) ions ( $q_t$  = 9.2928 mg/g,  $\%R_s$  = 95.94%) was observed for the PVC/ADO/DEM-DA membrane. While the maximum sorption capacity during the removal of copper(II) ions after 1 h of the process was  $q_t$  = 5.23 mg/g ( $\%R_s$  = 64.03%). In the case of zinc(II) ions ( $q_t$  = 4.6829 mg/g,  $\%R_s$  = 95.42%), the highest sorption capacity was achieved after 3 h of the process with the PVC/ADO/IL-A membrane (Fig. 5). Detailed results of the sorption capacity of the adsorptive membranes tested are shown in Table 1.

To confirm the sorption capacity of the adsorptive membranes tested, the membranes yielded from the process were subjected to qualitative XRF analysis.

#### 3.4. Characterization of polymer adsorptive membranes PVC/ ADO/DEM-DA and PVC/ADO/IL-A after membrane separation processes

After membrane separation of copper(II) and zinc(II) ions from the solution obtained as a result of acidic leaching of computer pins, XRF qualitative spectra of the investigated polymer membranes (PVC/ADO/DEM-DA and PVC/ADO/ IL-A, respectively) were designated. These spectra (Fig. 7a and b) confirmed the presence of copper(II) and zinc(II) ions on the surfaces of tested polymer adsorptive membranes (PAMs). Thus, information from XRF experiments confirmed the sorption efficiency of tested polymer adsorptive materials.

As a result of the excitation of the polymer membranes tested with X-rays, the composition of the PVC/ADO/ DEM-DA and PVC/ADO/IL-A adsorptive membrane was confirmed based on the XRF spectra produced. Analysis of the elemental composition of the PVC/ADO/DEM-DA membrane revealed both 82.4218% CH<sub>2</sub> and 17.4912% Cl, likely confirming the presence of the PVC polymer in the membrane, as well as copper(II) and zinc(II) ions with percentages of 0.0023% and 0.0679%, respectively, confirming the binding of these metal ions by the membrane containing DEM-DA as ions carrier. Similarly, chlorine (15.9458%) and CH<sub>2</sub> ions with a content of 84.0008% were observed in the PVC/ADO/IL-A membrane, and copper(II) (0.0043%) and zinc(II) (0.02191%) ions were adsorbed.

#### 4. Discussion and conclusions

Despite the great interest in the ionic liquid Aliquat 336 for removing metal ions from aqueous solutions, this compound has not been used in a deep eutectic mixture utilized as a carrier of metal ions in a polymer membrane. In separation processes, Aliquat 336 was used, for example, to remove copper(II), cadmium(II), zinc(II), chromium(VI), iron(II), or vanadium(V) ions [41–46]. Table 2 shows example applications of Aliquat 336 in PIMs to remove selected metal ions.



Fig. 7. X-ray fluorescence spectroscopy spectra of polymer adsorptive membranes PVC/ADO/DEM-DA (a) and PVC/ADO/IL-A (b).

Table 2 Application of Aliquat 336 in polymer inclusion membranes to remove selected metal ions [41–46]

Metal ions removed	Procedure	Literature
Cd(II) and	Pieces of membranes (approx. 0.55 g) were placed in beakers containing	[41]
Zn(II)	100 mL of the feed phase and placed in a temperature-controlled water bath.	
	Feed phase: 50 mg/L of Cd(II) or Zn(II) in 1 M HCl solution.	
Cd(II)	Transport of metal ions across PIM in micro-channel cell. The membrane was	[42]
	placed between the feed and stripping aqueous phases that flow in serpentine	
	microchannels built in Teflon plates.	
Cr(VI)	Transport of metal ions across PIMs.	[43]
	Feed phase: solution of Cr(VI) ions in 0.1 M HCl solution; receiving phase: acetic acid	
	and ammonium acetate solution, pH 5 or 7, with a solution of 0.1 M NaOH.	
	Each solution was mechanically stirred at 1,000 rpm.	
Co(II)	Transport of metal ions across PIMs.	[44]
	Feed phase: 250 mL of cobalt and nickel solution mixed with ammonium thiocyanate,	
	a solution of 1 M acetic acid and 1 M sodium acetate buffer was used to adjust the pH.	
	Stripping phase: a solution of 1 M NH <sub>3</sub> and 1 M TEA.	
Cd(II),	Membrane with a mass of about 0.05 g was placed in beakers containing 150 mL of a	[45]
Zn(II),	solution of each heavy metal. The solution was stirred continuously for 2 h.	
Fe(II)	Feed phase: a solution of 3 ppm of Cd(II) or Zn(II) or Fe(II) ions in 1 M HCl.	
V(V)	PIMs were immersed in feed solutions, the solution was mechanically stirred at	[46]
	200 rpm/min.	
	Feed phase: 50 mL of 50 mg/L solutions containing V(V) ions and 0.2 mol/L sulfate, the	
	pH of these solutions was adjusted to 2.5 by adding sulfuric acid or sodium hydroxide	
	solutions.	
	Metal ions removed Cd(II) and Zn(II) Cd(II) Cr(VI) Co(II) Co(II), Zn(II), Fe(II) V(V)	Metal ions removed Procedure   Cd(II) and Zn(II) Pieces of membranes (approx. 0.55 g) were placed in beakers containing 100 mL of the feed phase and placed in a temperature-controlled water bath. Feed phase: 50 mg/L of Cd(II) or Zn(II) in 1 M HCl solution.   Cd(II) Transport of metal ions across PIM in micro-channel cell. The membrane was placed between the feed and stripping aqueous phases that flow in serpentine microchannels built in Teflon plates.   Cr(VI) Transport of metal ions across PIMs. Feed phase: solution of Cr(VI) ions in 0.1 M HCl solution; receiving phase: acetic acid and ammonium acetate solution, pH 5 or 7, with a solution of 0.1 M NaOH. Each solution was mechanically stirred at 1,000 rpm.   Co(II) Transport of metal ions across PIMs. Feed phase: 250 mL of cobalt and nickel solution mixed with ammonium thiocyanate, a solution of 1 M acetic acid and 1 M sodium acetate buffer was used to adjust the pH. Stripping phase: a solution of 1 M NH <sub>3</sub> and 1 M TEA.   Cd(II), Membrane with a mass of about 0.05 g was placed in beakers containing 150 mL of a solution of each heavy metal. The solution was stirred continuously for 2 h. Fe(II)   Feed phase: a solution of 3 ppm of Cd(II) or Zn(II) or Fe(II) ions in 1 M HCl.   V(V) PIMs were immersed in feed solutions, the solution was mechanically stirred at 200 rpm/min. Feed phase: 50 mL of 50 mg/L solutions containing V(V) ions and 0.2 mol/L sulfate, the pH of these solutions was adjusted to 2.5 by adding sulfuric acid or sodium hydroxide solutions.

As shown by the data included in Table 2, Aliquat 336 has been successfully used in PIMs with different compositions, confirming that this ionic liquid is compatible with various polymers and plasticizers and allows to obtain membranes with appropriate properties. The obtained polymer adsorptive membranes containing PVC, ADO and

Aliquat 336 or a deep eutectic mixture of Aliquat 336 and diacetamide have a hydrophilic nature (confirmed by the results of contact angle measurement), which, in general, has a beneficial effect on reducing the problem of membrane surface contamination and causes a growth of efficiency and lifetime of PAMs [47,48]. Both formulated PAMs are characterized by high efficiency. However, polymer adsorptive membrane containing DEM-DA compared to membrane with IL-A binds metal ions faster (PVC/ADO/DEM-DA: removal of 96.85% of Cu(II) and 95.94% of Zn(II) after 1 h of the process), which may be economically important, especially when carrying out the process on a larger scale. While to achieve a similar effect in the case of application of ionic liquid as the carrier, the process had to last as long as 3 h (PVC/ADO/IL-A: removal of 96.63% of Cu(II) and 95.42% of Zn(II)). Moreover, formulation of a PVC/ADO/DEM-DA membrane is relatively low-cost and does not require the use of complex equipment. In addition, DEMs are easy to prepare (usually by mixing the reactants and slightly heating their mixtures), and the cost of the starting compounds is also relatively low [49]. They also have better biocompatibility with other membrane components (polymers, plasticizers) and are considered safer for the environment than ILs [50,51]. Many chemical compounds that, due to their structure, could potentially be used to bind metal ions (hydrogen bond donors or acceptors) are often soluble or miscible in water, which means that they cannot be used as carriers in PAMs. However, as components of a deep eutectic mixture, they are insoluble in water, which makes them good candidates for metal ion carriers in membranes. An example is water-soluble diacetamide, used in this work to obtain a deep eutectic mixture containing water-insoluble Aliquat 336. The results may potentially influence a new trend in research related to the application of polymer adsorptive membranes for the removal of various metal ions from e-scrap acidic leachates and may contribute to the broader use of DEMs, which are considered safe for the environment.

#### Symbols

AAS	_	Atomic absorption spectrometry
ADO	_	Bis(2-ethylhexyl) adipate
DEM	_	Deep eutectic mixture
CA	_	Contact angle
<sup>13</sup> C NMR	_	Carbon nuclear magnetic resonance
HBA	_	Hydrogen bond acceptor
HBD	_	Hydrogen bond donor
<sup>1</sup> H NMR	_	Proton nuclear magnetic resonance
IL	_	Ionic liquid
PAM	_	Polymer adsorptive membrane
PM	_	Polymer membrane
PVC	_	Poly(vinyl chloride)
%R	_	Percentage of removal of metal ions from
5		the solutions
THF	_	Tetrahydrofuran
$q_{t}$	_	Sorption capacity
WEEE	_	Waste electrical and electronic equipment
WCA	_	Water contact angle
WD-XRF	_	Wavelength-dispersive X-ray fluorescence
		spectroscopy

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