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The potential of polystyrene-*block*-polybutadiene-*block*-polystyrene triblock co-polymer as a base-polymer of polymer inclusion membranes (PIMs)

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Abstract

The use of polystyrene-*block*-polybutadiene-*block*-polystyrene triblock co-polymer (SBS) as the base-polymer of polymer inclusion membranes (PIMs) is studied for the first time. SBS is an inexpensive and accessible thermoplastic elastomer which possesses the required properties to be used as a base-polymer in PIMs, namely mechanical strength and high resistance to acids/bases. Its compatibility with commonly used extractants in PIMs was assessed and it was observed that successful PIMs could be obtained when di(2-ethylhexyl)phosphoric acid (D2EHPA), LIX84I or tri-*n*-octylamine (TOA) were used as the extractants. The performance of these PIMs was investigated for the extraction of Zn(II), Cu(II) and Cr(VI), respectively, although only the TOA-based PIMs did not perform well. Both D2EHPA- and LIX84I-based PIMs were characterized by water contact angle measurements, atomic force microscopy, differential scanning calorimetry, and Fourier transform infrared spectroscopy. In comparison with PIMs containing other base-polymers, the SBS-based PIMs were found to extract faster and more Zn(II) or Cu(II), and moreover, the LIX84I-based PIM did not require the inclusion of an expensive plasticizer unlike its counterparts containing other commonly used base-polymers. The stability of these PIMs was also assessed over three transport cycles (i.e., simultaneous extraction and back-extraction), and it was observed that the transport rate decreased significantly when using D2EHPA-based PIMs, and in the case of LIX84I-based membranes it stabilized after the first cycle.

Keywords: polymer inclusion membrane (PIM); polystyrene-*block*-polybutadiene-*block*-polystyrene triblock co-polymer (SBS); LIX84I; di(2-ethylhexyl)phosphoric acid (D2EHPA); extraction

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1. Introduction

Industrial separation of metal ions (e.g., zinc, copper, rare earth metals) is still currently performed mainly by solvent extraction, as it provides high selectivity and high enrichment factors [1]. However, this separation technique involves the use of large volumes of often toxic and volatile solvents, and moreover the extraction and back-extraction processes of the target species have to be performed in separate steps. Hence, greener, safer, inexpensive, and time-efficient alternative technologies are desirable.

Separation involving liquid membranes is an attractive alternative to conventional solvent extraction because it minimizes and even eliminates the use of solvents, reduces separation costs by drastically decreasing the amounts of extractants used and integrates the extraction and back-extraction processes into a single step by conducting these two processes simultaneously at the corresponding sides of the membrane [2]. The most frequently used liquid membranes are supported liquid membranes (SLMs) [3]. Polymer inclusion membranes (PIMs) are a type of liquid membranes which visually resemble SLMs and combine their advantages with improved long-term stability [4, 5]. These membranes have two main components, namely an organic liquid phase and a base-polymer. The membrane liquid phase usually contains an extractant (also referred to as carrier), responsible for forming a complex or ion-pair with the chemical species of interest, and sometimes a plasticizer or modifier is also added to the membrane composition to improve the performance of the membrane by increasing its flexibility or the solubility of the extracted target chemical species – carrier adduct in its liquid phase, respectively. The base-polymer holds the liquid phase between its entangled chains and provides mechanical strength to the membrane. The two most commonly used base-polymers in PIMs are cellulose triacetate (CTA) [6-12] and poly(vinyl chloride) (PVC) [13-16] because they are commercially available and have good compatibility with a wide range of extractants [17]. More recently, poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) has also been used to prepare PIMs successfully, and moreover it has been demonstrated that the PIMs containing this co-polymer performed better than most CTA- or PVC-based PIMs in terms of extraction rate and stability [18, 19]. This enhancement in performance could be attributed to the PVDF-HFP chains being more flexible, thus promoting better membrane permeability. However, PVDF-HFP is significantly more expensive than PVC and CTA, which can be viewed as a disadvantage in scaling-up of PIM fabrication for industrial applications.

In this context, the aim of this work was to assess the feasibility of poly(styrene-*block*-butadiene-

block-styrene) triblock co-polymer (SBS) as a base-polymer since it is significantly cheaper than PVDF-HFP and is readily available commercially. SBS (Figure 1) is a thermoplastic elastomer with excellent mechanically strength (over 10 MPa tensile strength) and flexibility (over 1000% stretching ability) [20]. Moreover, it has good resistance to both acidic and basic media and is soluble in common organic solvents (e.g., tetrahydrofuran) [21]. All these features indicate that SBS is a promising candidate as a base-polymer of PIMs and its use could reduce the cost of industrial PIM-based separation.

The present study examined the compatibility of SBS with commonly used extractants and compared the extraction and transport properties of successfully prepared SBS-based PIMs with PIMs containing common used base-polymers. The SBS-based PIMs were also characterized by water contact angle measurements, atomic force microscopy, differential scanning calorimetry, and Fourier transform infrared spectroscopy. The stability of the newly developed SBS-based PIMs was also studied.

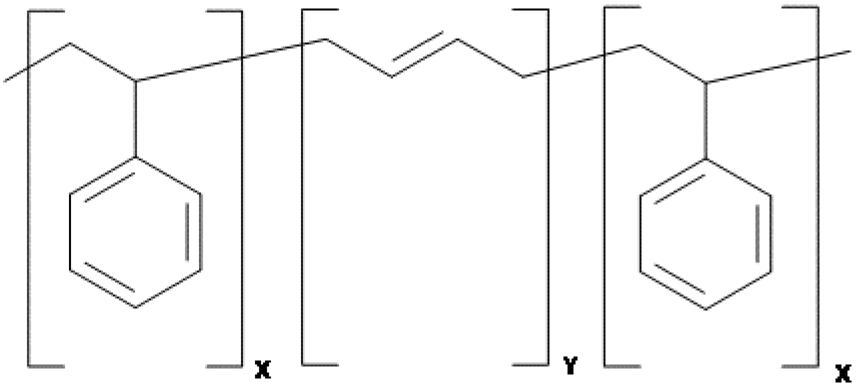

Figure 1. Molecular structure of SBS.

2. Experimental

2.1. Reagents and solutions

Polystyrene-*block*-polybutadiene-*block*-polystyrene triblock co-polymer with styrene (SBS, Lot#MKCF0088, Aldrich) was used as base-polymer, and the following chemicals were used as extractants: di(2-ethylhexyl)phosphoric acid (D2EHPA, 97%, Sigma Aldrich), LIX84I (BASF, ~49% 2-hydroxy-5-nonylacetophenone in a high flash point hydrocarbon diluent, Lot# 0016898649), Aliquat 336 (Aldrich, USA), tri-*n*-butylphosphate (TBP, 97%, Sigma Aldrich), tri-*n*-octylamine (TOA, 98%, Aldrich), trihexyl(tetradecyl)phosphonium chloride (Cyphos® IL 101, >95%, Aldrich), trihexyl(tetradecyl)phosphonium bis-2,4,4-(trimethylpentyl) phosphinate (Cyphos® IL 104, >93%, Strem Chemicals), and bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272, Cytec Australia Limited). 1-Tetradocanol (TDOL) (Aldrich) and 2-nitrophenyl octyl ether (NPOE, Fluka) were used as a modifier and plasticizer, respectively. Polystyrene (MW ~100,000, BDH Chemicals) and polybutadiene (Aldrich) were also trialed as base-polymers. These chemicals were all used as received and were dissolved in tetrahydrofuran (THF, HPLC grade without stabilizer, VWR). Other chemicals used in this work for the preparation of the feed and receiving solutions included KCl (AR, Chem Supply), CH_3COONa (AR, Chem Supply), CH_3COOH (AR, Chem Supply), HNO_3 (70%, Ajax Finechem), $ZnCl_2$ (LR, Asia Pacific Specialty Chemicals Limited), H_2SO_4 (98%, SCI Labscan), HCl (32%, Ajax Finechem), NaOH (AR, Chem Supply), $CuSO_4{\cdot}5H_2O$ (AR, Chem Supply), and $(NH_4)_2SO_4$ (AR, Chem Supply).

Deionized water (resistivity ≥18.2 MΩ cm, Millipore Synergy 185) was used in the preparation of all solutions.

2.2. Membrane preparation

The base-polymer SBS was dissolved in THF to prepare a 10% (w/v) solution, followed by the addition of the extractant and plasticizer/modifier (if used). After magnetically stirring the mixture for over 3 h, the solution was cast into a glass ring (internal diameter of 76 mm), which was positioned on a polytetrafluoroethylene (PTFE) sheet. The glass ring was covered with filter paper to slow down the solvent evaporation. After the solvent evaporated over a 24 h period, the PIM was peeled from the PTFE sheet. Circular segments with a diameter of 45 mm and containing between 70 and 105 mg of SBS were cut from the central section of the PIM to ensure uniform thickness and were subsequently used in the extraction and back-extraction experiments.

The thickness of selected segments was determined as the average of the thicknesses measured at 6 points along the segment cross-section using an optical microscope (CH-2, Olympus) equipped with a calibration slide.

All membrane compositions are expressed in mass percentages.

2.3. Membrane characterization

The water contact angle (CA) of the membranes was determined on a contact angle system (OCA 15EC DataPhysics Instruments) under ambient conditions, using the sessile drop method with a water droplet of 5 μL. At least five independent measurements were averaged in calculating the contact angle of a membrane.

Fourier transform infrared measurements (FTIR, Tensor 27 IR, Bruker) were conducted on PIMs cast on KBr crystal disks.

Atomic force microscopy (AFM, NanoScope V, Bruker) imaging was performed in tapping mode in air at room temperature using silicon cantilevers with 30 nm thick aluminum reflex coatings (Tap 300Al-G, Budget Sensors, Innovative solutions). According to the supplier's datasheet the cantilever spring constant and the resonance frequency were in the range of 1.5 to 15 N/m and 150 ± 75 kHz, respectively. The tip radius was less than 10 nm. The scan rate was set at 1 Hz and the images were captured in height mode with 512 × 512 pixels in JPEG format. Subsequently, all images were flattened by using NanoScope software (Bruker).

The thermal characteristics of the PIMs studied were determined by differential scanning calorimetry (DSC, DSC-7, Perkin-Elmer). Samples of 10 mg were heated from room temperature (25 °C) to 200 °C in pure nitrogen atmosphere at a rate of 5 °C min^{-1}. Temperature and heat flow calibration of the DSC measurements was made by evaluating the melting peak of pure In and Zn. Dry nitrogen was used as a purge gas at a fixed flow rate of 20 mL min^{-1}.

2.4. Extraction and back-extraction experiments

The extraction procedures for Zn(II) and Cu(II) were carried out according to those described by Kolev et al. [22] and Wang et al. [19], respectively. In each extraction experiment a circular membrane segment with a diameter of 45 mm was immersed in a 100 mL aqueous feed solution. The solution was mechanically stirred on an orbital shaker (Platform mixer OM06, Ratek) operating at 150 rpm. The feed solution for the extraction experiments involving PIMs with D2EHPA as the extractant contained 22 mg L^{-1} Zn(II) (prepared from $ZnCl_2$), 1.0 M acetic acid/acetate buffer and 0.2 M KCl. KCl was used for maintaining a constant ionic strength. The pH was adjusted to 3.0 using a 1.0 M HCl solution. Sample volumes of 0.1 mL were withdrawn at predetermined periods of time and replaced with 0.1 mL of deionized water to maintain constant the feed solution volume (100 mL). For the extraction experiments involving PIMs with LIX84I as the extractant, a feed solution containing 65 mg L^{-1} Cu(II) was prepared by dissolving $CuSO_4 \cdot 5H_2O$ in 0.075 mol L^{-1} ammonium sulfate solution, where the pH was adjusted to 8.5 using a 1.0 M NaOH solution. The sampling procedure was similar to the one described for the extraction of Zn(II). All of the extraction experiments were carried out in triplicate. The samples withdrawn from the feed solutions were diluted in 10 mM HCl for the subsequent determination of Zn(II) or Cu(II) by atomic absorption spectrometry (AAS, Analyst 400, Perkin Elmer).

The membranes with TOA as the extractant were used to extract Cr(VI) from a feed solution containing 2.0 mM Cr(VI), which was prepared by dissolving $K_2Cr_2O_7$ in 0.1 M HCl solution.

2.5. Transport experiments

Transport experiments were carried out using a two-compartment glass transport cell [23]. Each compartment contained 100 mL of feed or receiving solution which were separated from each other by a PIM. The exposed membrane surface area to both solutions was 1.96×10^{-3} m^2 since the inner diameter of the glass compartment was 50 mm. Experiments were conducted at room temperature and solutions were stirred at 1000 rpm using glass paddle stirrers. Aliquots of 0.2 mL were withdrawn from each compartment at predetermined times for the determination of Cu(II) or Zn(II), and the volume was kept constant by replacing it with 0.2 mL of the corresponding original solutions. Three successive transport cycles (about 24 h each) were carried out using the same PIM to assess the stability of D2EHPA- and LIX84I-based PIMs for the transport of Cu(II) or Zn(II), respectively. For each cycle, the feed and receiving solutions were replaced with the corresponding fresh solutions.

3. Results and discussion

3.1. Study of different extractants and PIM optimization

SBS consists of a thermoplastic elastomer [24] and it has been reported that a film of SBS looks transparent despite exhibiting a microphase-separation [20]. However, to the best of our knowledge, the suitability of SBS as a base-polymer in PIMs has not been reported to date. Hence, with the aim of assessing the compatibility of SBS with a wide range of extractants commonly used in PIMs [5], different types of extractants were selected, namely, acidic and/or chelating extractants (i.e., LIX84I, D2EHPA and Cyanex 272), basic extractants (i.e., Aliquat 336 and TOA), and neutral or solvating extractants (i.e., TBP, Cyphos® IL 101 and Cyphos® IL 104).

Table 1 summarizes the different membrane compositions prepared with each of the extractants mentioned above, and the respective visual observations which supported the decision on whether a membrane was considered successful (i.e., homogenous, transparent and flexible). SBS-based PIMs with D2EHPA, LIX84I, TOA, or TBP as the extractants were considered as successful for extractant concentrations of up to 35, 30, 25, and 15 %, respectively. When increasing the concentrations of the extractants above these values, the membranes became too soft and mechanically unstable.

Table 1. Characteristics of SBS-based PIMs with different compositions.

Extractants	Concentration of extractant (%)						
	10	15	20	25	30	35	40
D2EHPA	+	+	+	+	+	+	~
LIX84I	+	+	+	+	+	~	~
Cyanex 272	Op	Op	Op	Oil	-	-	-
Aliquat 336	Op	Op	Op	Op	-	-	-
TOA	+	+	+	+	~	-	-
TBP	+	+	~	-	-	-	-
Cyphos® IL 101	Op	Op	Op	Op	Oil	-	-
Cyphos® IL 104	Op	Op	Op	-	Oil	-	-

"+" successful membrane; "~" membrane with poor mechanical stability; "*Op*" opaque membrane; "*Oil*" oily membrane; "-" membrane composition not tested.

When the extractants Cyanex 272, Aliquat 336, Cyphos® IL 101, and Cyphos® IL 104 were used to prepare SBS-based PIMs, only opaque membranes could be obtained for concentrations of up to either 20 or 25% of the extractants. In the case of membranes with 25% Cyanex 272 or 30% Cyphos® IL 101/Cyphos® IL 104 oily surfaces were observed suggesting exudation of the extractant onto the membrane surface. The addition of a modifier or a plasticizer (e.g., TDOL or NPOE (5%)) was also attempted in SBS-based PIMs containing 20% Aliquat 336, although no improvement was observed, and the resultant membranes were still opaque. Considering the molecular structures of these extractants (Supplementary Material, Figure S1) it was concluded that those composed of relatively long aliphatic chain(s), with the exception of the ionic liquids, produced successful SBS-based PIMs possibly due to the lack of polar interactions between the membrane components. It should be noted that even though PIMs containing the extractant TBP, having short aliphatic chains, were successful, only a very small amount of extractant could be included in these membranes. The SBS-based PIMs containing D2EHPA, LIX84I, or TOA were thus selected for further studies.

According to Table 1, when the TBP concentration was higher than 15% the membranes became too soft and mechanically unstable for further use. This concentration of extractant is lower than the commonly reported carrier percolation threshold concentration (i.e., the minimum concentration of extractant required for continuous transport across a PIM, which is usually approximately 20%) [4]. Therefore, the SBS-based membranes with TBP as the extractant were not studied further.

It was of interest to check if polystyrene and polybutadiene, which are the monomers of SBS, could form successful PIMs with D2EHPA, LIX84I, or TOA. Hence, PIMs composed of 30% D2EHPA, LIX84I or 25% TOA were prepared using either polystyrene or polybutadiene as the base-polymer. Polybutadiene is supplied as a liquid and, as a result, an oily mixture was obtained after casting, and no membranes were formed. The D2EHPA- and TOA-based PIMs with polystyrene as the base-polymer were white in color, opaque and very brittle, and thus were not considered as suitable for further studies. Membranes composed of LIX84I and polystyrene could be formed, although these were slightly rigid and opaque, and were also considered as not suitable for further studies. These observations emphasize the suitability of SBS as a base-polymer because it combines the advantageous properties (i.e., mechanical strength and flexibility) of its both homopolymers.

3.2. Extraction experiments with successful SBS-based PIMs

The performance of the SBS-based PIMs considered as successful in the previous section was investigated in regards to their ability to extract metal ions. Zn(II) and Cu(II) were chosen as model target metal ions for the membranes containing D2EHPA or LIX84I as extractants, respectively. Figure 2 shows the extraction curves for the D2EHPA-based PIMs with different concentrations of extractant, where the feed solution contained 22 mg L^{-1} Zn(II) at pH 3.0. As expected, the results indicated that both the extraction capacity (i.e., the amount of extracted metal ion) and the rate of extraction, increased with increasing the D2EHPA concentration in the membrane. The equilibrium in all three cases was reached in less than 5 h.

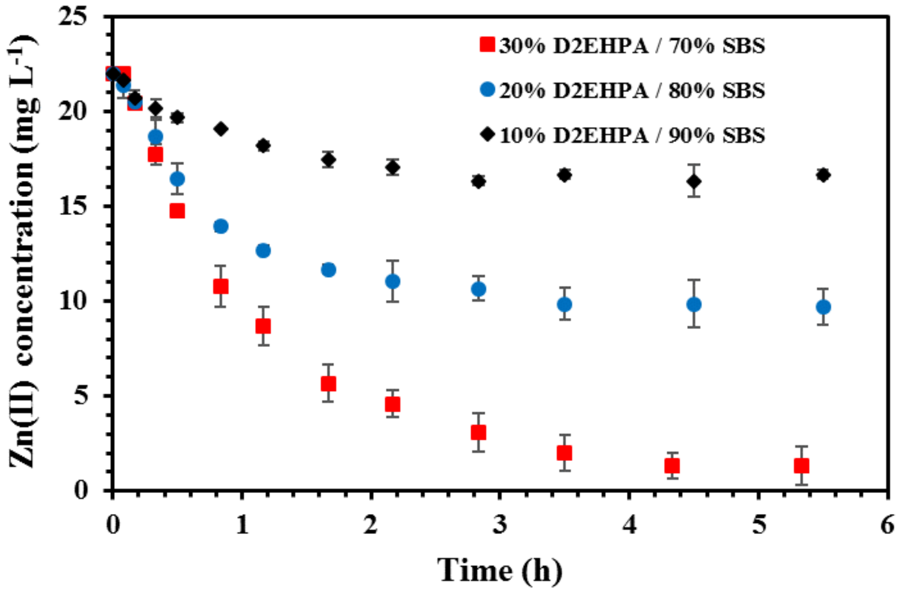

Figure 2. Effect of the concentration of D2EHPA in the SBS-based PIM on the extraction of Zn(II). Feed solution, 100 mL of 22.0 mg L^{-1} Zn(II) in 1.0 M acetic acid/sodium acetate buffer (pH 3.0) and 0.2 M KCl; membrane mass, 116±10 mg; membrane diameter, 45 mm; membrane thickness, 67.0±1.1 µm (10% D2EHPA/90% SBS), 58.4±2.1 µm (20% D2EHPA/80% SBS) and 48.0±2.3 µm (30% D2EHPA/70% SBS). Error bars are ± standard deviation (SD) based on 3 replicate experiments.

Figure 3 illustrates the effect of the LIX84I concentration on the extraction of Cu(II) using PIMs containing SBS as the base-polymer. A similar tendency as the one described for D2EHPA-based PIMs was observed, i.e., both the extraction capacity and the extraction rate increased as the LIX84I concentration in the membranes increased. It was also observed that the transparent SBS/LIX84I membranes changed color from colorless to light green within 10 min of contact with the feed solution, which was consistent with the sharp decrease of the Cu(II) concentration in the feed solution during the initial stages of the extraction experiments. Equilibrium was reached in less than 8 h for the LIX84I-based PIMs.

In order to assess if the base-polymer has the ability to adsorb any of the metals mentioned above, membranes containing only SBS were prepared and exposed to the same feed solutions containing Zn(II) or Cu(II). No significant difference was observed when comparing the concentration of Zn(II) and Cu(II) in the feed solutions before and after 6 or 8 h of contact with the SBS membrane, respectively, thus proving that the extraction of these metals only occurs in the presence of the corresponding extractant.

The results obtained for the SBS-based PIMs containing D2EHPA or LIX84I as the extractants suggest that these membranes exhibit excellent extraction performance even in the absence of a plasticizer. However, a comparison with other base-polymers is important to assess the true feasibility of using SBS as an alternative base-polymer in PIMs. Section 3.3 describes the performance of SBS-based PIMs and PIMs containing common base-polymers under the same conditions.

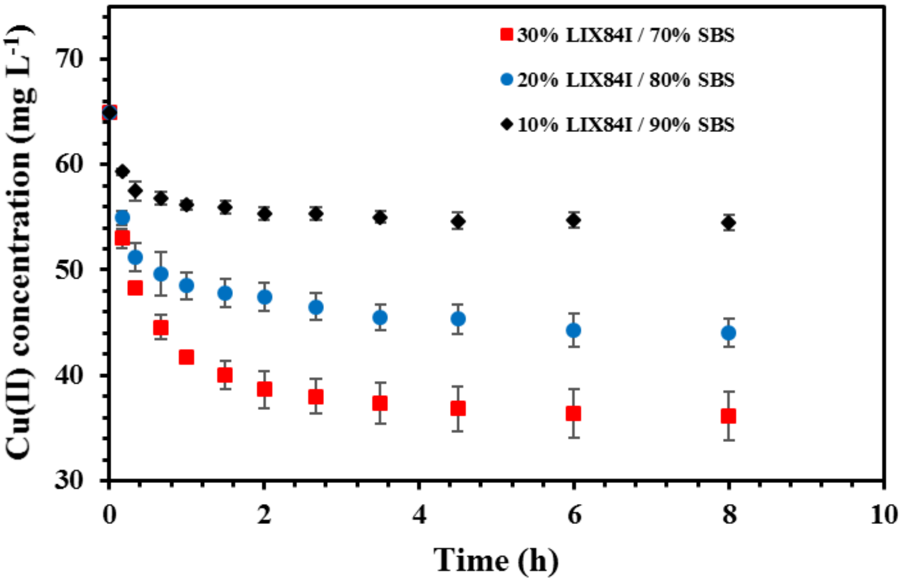

Figure 3. Transient concentrations of Cu(II) in the feed solution in extraction experiments involving SBS-based PIMs with different concentrations of LIX84I. Feed solution, 100 mL of 65 mg L^{-1} Cu(II) and 0.075 mol L^{-1} ammonium sulfate solution at pH 8.5; membrane mass, 113±8 mg; membrane diameter, 45 mm; membrane thickness, 68.5±4.5 µm (10% LIX84I/90% SBS), 65.1±9.6 µm (20% LIX84I/80% SBS) and 58.5±6.6 µm (30% LIX84I/70% SBS). Error bars are ± SD based on 3 replicate experiments.

The performance of the SBS-based PIMs containing TOA was tested for the extraction of Cr(VI), following the procedure described by Kozlowski [25]. However, within 30 min of extraction orange colored oily droplets started to form on the surface of the membranes, which became bigger after approximately 2 h of extraction, irrespective of the TOA concentration in the membrane. The orange droplets were formed most likely by the leaching of the ion-pair consisting of the chromate anion and the protonated TOA cation (i.e., $(TOAH)HCrO_4$ [25]). This result suggests that protonated TOA is not compatible with the SBS polymer matrix, thus resulting in leaching of the extracted species ion-pair onto the membrane surface. Therefore, TOA-based PIMs were not evaluated further.

3.3. Comparison of SBS-based PIMs with PIMs incorporating common base-polymers

The results presented above for SBS-based membranes containing D2EHPA and LIX84I were viewed as promising, although a comparison with PIMs composed of commonly used based-polymers was considered essential for assessing the true feasibility of SBS as an alternative base-polymer. Figure 4 shows a comparison between D2EHPA-based PIMs containing PVC [22] with those containing SBS for the extraction of Zn(II) under the same experimental conditions.

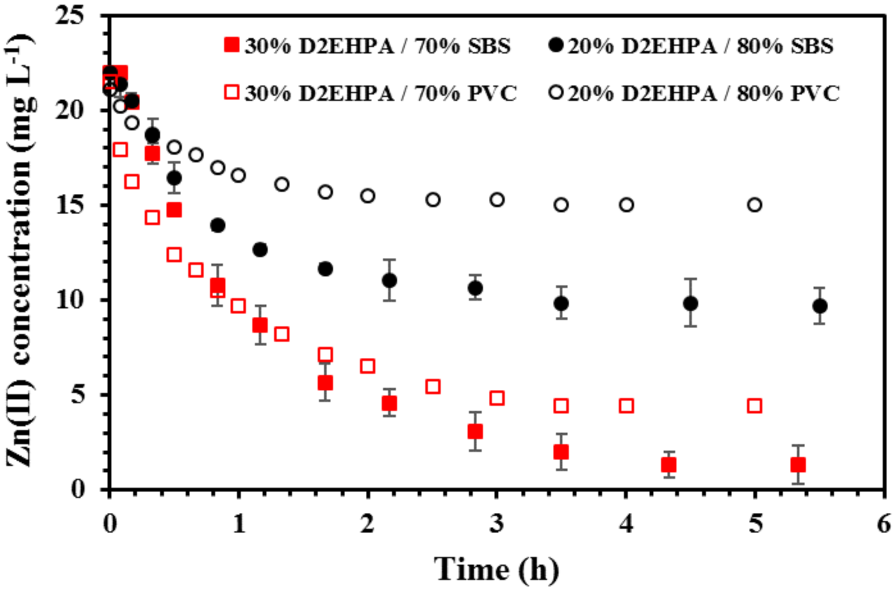

Figure 4. Transient concentrations of Zn(II) in the feed solution in extraction experiments involving D2EHPA-based PIMs containing PVC [22] or SBS as the base-polymer. PVC-based PIM mass and average thickness, 114±2 mg and 71 μm [22]. Remaining experimental conditions as in Figure 2.

PVC-based PIMs with 20 and 30% D2EHPA extracted 28.6 and 79.4% of Zn(II), respectively, while membranes with similar composition but containing SBS as the base-polymer extracted 56.1 and 93.9%, respectively. Even though, SBS-based PIMs extracted at a slightly lower rate than their PVC counterparts, these results clearly showed that SBS-based PIMs were superior in terms of the amount of Zn(II) extracted.

An attempt was made to compare the SBS-based PIM containing 30% LIX84I as the extractant with 30% LIX84I-based membranes using PVC, CTA or PVDF-HFP as the base-polymer, however, as reported by Wang et al. [19] the non-SBS PIMs were very rigid and did not extract Cu(II). Extraction of Cu(II) could only be achieved when NPOE was included in the PIM composition. Hence, the comparison was performed with the PIMs containing 20 or 25% NPOE as plasticizer. The corresponding results are shown in Figure 5, and it can be observed that the extraction rate of the SBS-based PIM is similar to those of its CTA and PVDF-HFP counterparts and is much higher than that of the PVC-based membrane. Moreover, the SBS-based PIM exhibited higher extraction capacity than the other PIMs studied. After 8 h of extraction, 44.4% of Cu(II) was extracted using the SBS-based membrane, while the PVC-, CTA- and PVDF-HFP-based PIMs containing NPOE extracted 17.7, 34.7 and 34.6% of Cu(II), respectively. These results not only illustrate the better performance of the PIM composed of 30% LIX84I and 70% SBS in comparison with 30% LIX84I PIMs containing other common base-polymers, but also highlight the fact that since there is no need of the expensive plasticizer NPOE, further significant improvement in the cost-effectiveness of Cu(II) extraction can be achieved in addition to using the inexpensive SBS as the base-polymer. The estimated cost of the SBS-based PIMs containing LIX84I, based on Sigma-Aldrich and Up-Fluorochem prices, is 25 US\$ m^{-2}, which is 3 to 4 times lower than the costs of PIMs containing other base-polymers and NPOE.

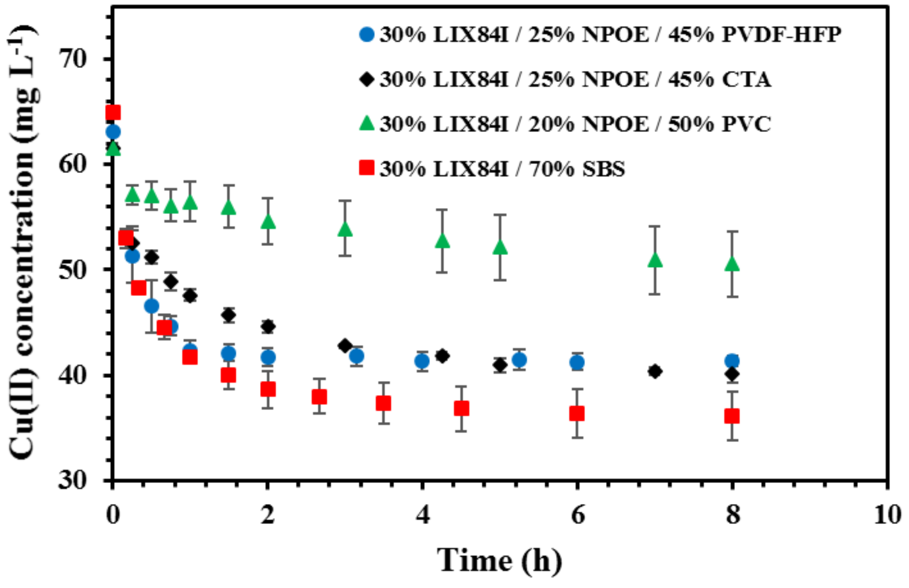

Figure 5. Transient concentration of Cu(II) in the feed solution during extraction experiments involving LIX84I-based PIMs containing PVC, CTA, PVDF-HFP [19] or SBS as the base-polymer. All membranes contained NPOE as plasticizer, except for the SBS-based PIMs. PVDF-HFP-based PIM mass and average thickness, 95 ± 4 mg and 90 μm. Remaining experimental conditions as in Figure 3.

3.4. Stability studies

D2EHPA- and LIX84I-based PIMs containing SBS as the base-polymer were also studied in terms of their stability by performing three successive transport experiments in each case. Figure 6 shows the results for the 3 consecutive Zn(II) transport experiments across the same PIM composed of 30% D2EHPA and 70% SBS. It can be observed that 100% of the Zn(II) was transported across the membrane within 7 h in the first transport experiment. However, the transport rate in the second experiment decreased significantly followed by a further decrease in the third experiment. These results suggest that the membrane had limited stability due to the leaching of the extractant from the membrane into the adjacent aqueous phases. However, due to the lower cost of the SBS-based PIM in comparison with its PVC-based counterpart (12 vs 16 US$ m^{-2}, based on Sigma-Aldrich prices) and the excellent transport performance of this membrane, it could be economically justified to use it for a single run.

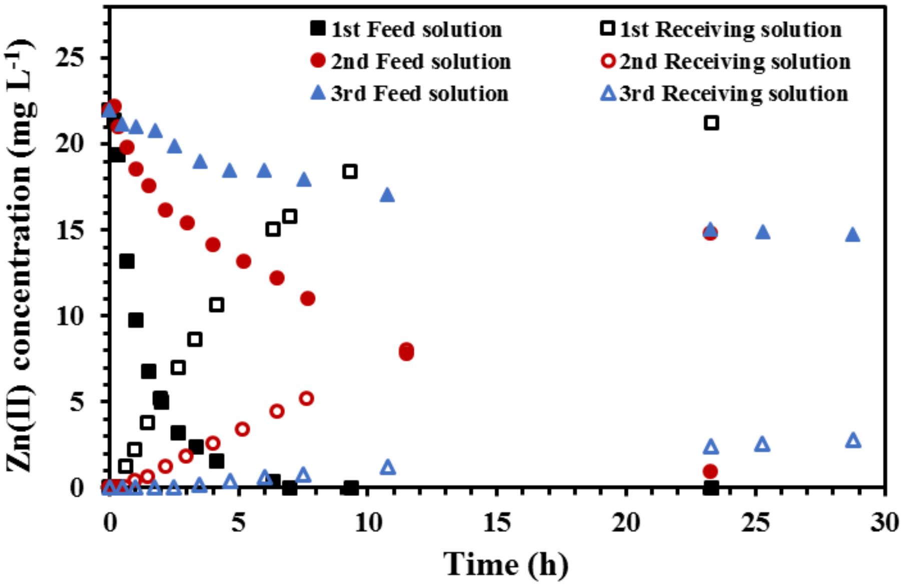

Figure 6. Transient Zn(II) concentrations in the feed and receiving solutions in 3 consecutive transport experiments involving a PIM containing 30% D2EHPA and 70% SBS. Feed solution, 100 mL of 22 mg L^{-1} Zn(II) in 1.0 M acetic acid/acetate buffer and 0.2 M KCl at pH 3.0; receiving solution, 100 mL of 1.0 M HCl; membrane thickness, 48.0±2.3 μm.

The results obtained for the PIM composed of 30% LIX84I and 70% SBS in 3 successive Cu(II) transport experiments (~24 h each) are shown in Figure 7. In the first experiment, the transport of Cu(II) across the PIM was completed within ~7 h, which was slightly slower in comparison with the PVDF-HFP-based PIM reported by Wang et al. [19]. For the second and third experiments, 100%

Cu(II) transport was also achieved, although in both cases it took approximately 12 h instead of 7 h as in the first experiment. The slower transport might be related to a small loss of LIX84I extractant from the PIM due to leaching. However, it is interesting to notice that the second and the third experiments are characterized by very similar transport rates. This finding suggests that the LIX84I-based membrane can be reused at least up to three times with complete transport of Cu(II) in less than 12 h.

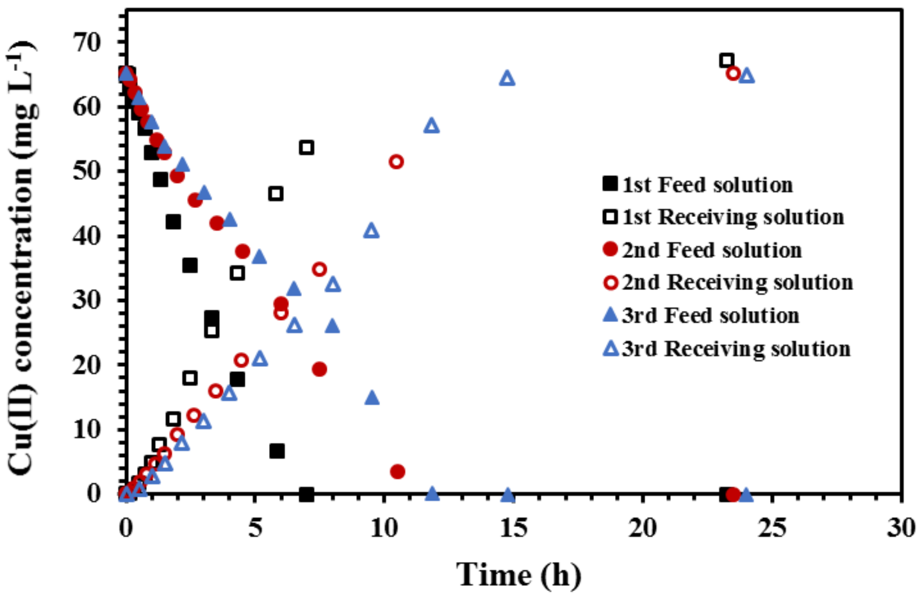

Figure 7. Transient Cu(II) concentrations in the feed and receiving solutions in 3 consecutive transport experiments involving a PIM containing 30% LIX84I and 70% SBS. Feed solution, 100 mL of 65 mg L^{-1} Cu(II) and 0.075 mol L^{-1} ammonium sulfate solution at pH 8.5; receiving solution, 100 mL of 1.0 M H_2SO_4; membrane thickness, 53.8±2.1 µm.

3.5. Characterization of SBS-based PIMs

PIMs containing SBS as the base-polymer were characterized by CA, FTIR, AFM, and DSC. To assess their hydrophilicity, contact angle measurements were performed. Figure 8 shows the water contact angles as a function of the concentration of extractant (i.e., D2EHPA, LIX84I) added to the membrane. The pure polymer membrane, prepared under identical conditions as those used for the PIM preparation (i.e., solvent casting), showed a CA of 92.8±0.9°, which was consistent with that of the SBS film reported by Ke et al. [26]. A CA greater than 90° suggested that the pure SBS membrane had a hydrophobic surface. However, the inclusion of the extractants D2EHPA or LIX84I in the SBS polymeric structure in concentrations up to 20% reduced the CA value to about 65° in both cases, reaching a plateau after that. This suggested that the surface of the SBS-based PIMs became more hydrophilic as more D2EHPA or LIX84I was added to the base-polymer.

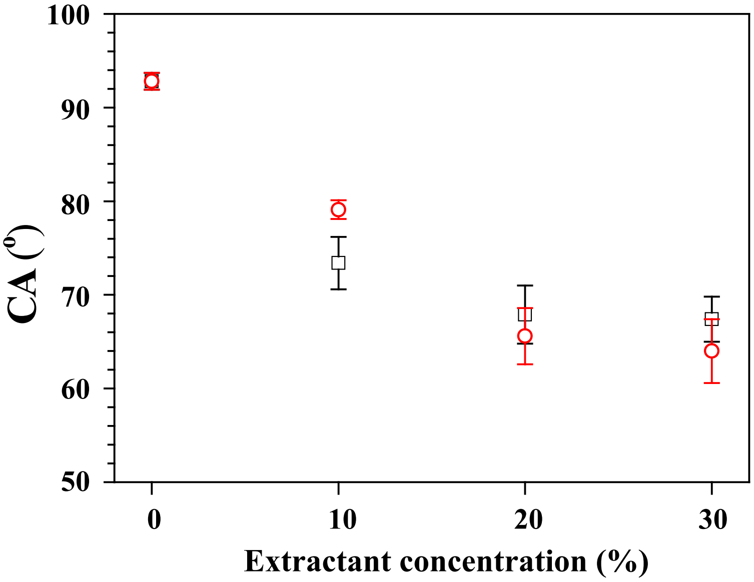

Figure 8. Contact angle (CA) of an SBS membrane and SBS-based PIMs containing different concentrations of D2EHPA (☐) or LIX84I (○) as the extractant. Error bars are ± SD based on 5 replicate experiments.

The FTIR spectra (Supplementary Material, Figure S2) obtained for the D2EHPA- and LIX84I-based PIMs showed profiles similar to those of the corresponding pure extractants, thus suggesting the lack of strong chemical interactions between the base-polymer and the extractants.

The surface morphology of the PIMs studied was investigated by AFM. As expected, the side of the PIMs in contact with the PTFE sheet during membrane casting was found to be smoother than the side in contact with air, as illustrated with the images of a pure SBS PIM and an SBS-based PIM containing 10% LIX84I (Figure 9). The surfaces of the pure SBS membrane exhibited higher roughness compared to those of the PIM containing 10% LIX84I which was consistent with the presence of a microphase-separated microstructure resulting from the phase separation of the incompatible blocks of polystyrene and polybutadiene of the triblock co-polymer used (Figure 1) [24]. As expected, this roughness decreased upon the addition of extractant which might have acted as a plasticizer.

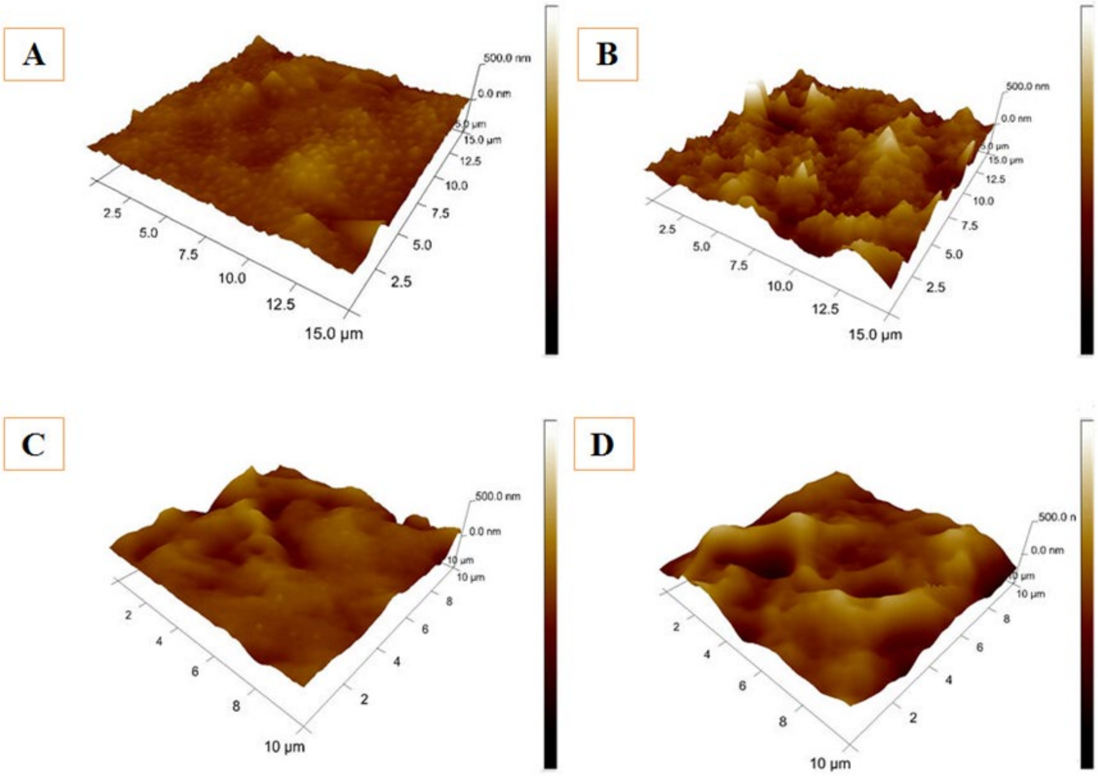

Figure 9. 3D AFM images of the surface of PIMs (*10 x 10 µm*) containing only SBS (A and B) and 90% SBS and 10% LIX84I (C and D). Images A and C show PIM surfaces in contact with the PTFE sheet during membrane casting, and images B and D show the surfaces exposed to air of the same PIMs.

This plasticization effect of both LIX84I and D2EHPA leading to a reduction in the PIM phase separation mentioned above, and consequently in the PIM surface roughness, increased with increasing extractant concentration as shown in Figure 10. These results are consistent with the reduction of the PIM contact angles at higher extractant concentrations (Figure 8).

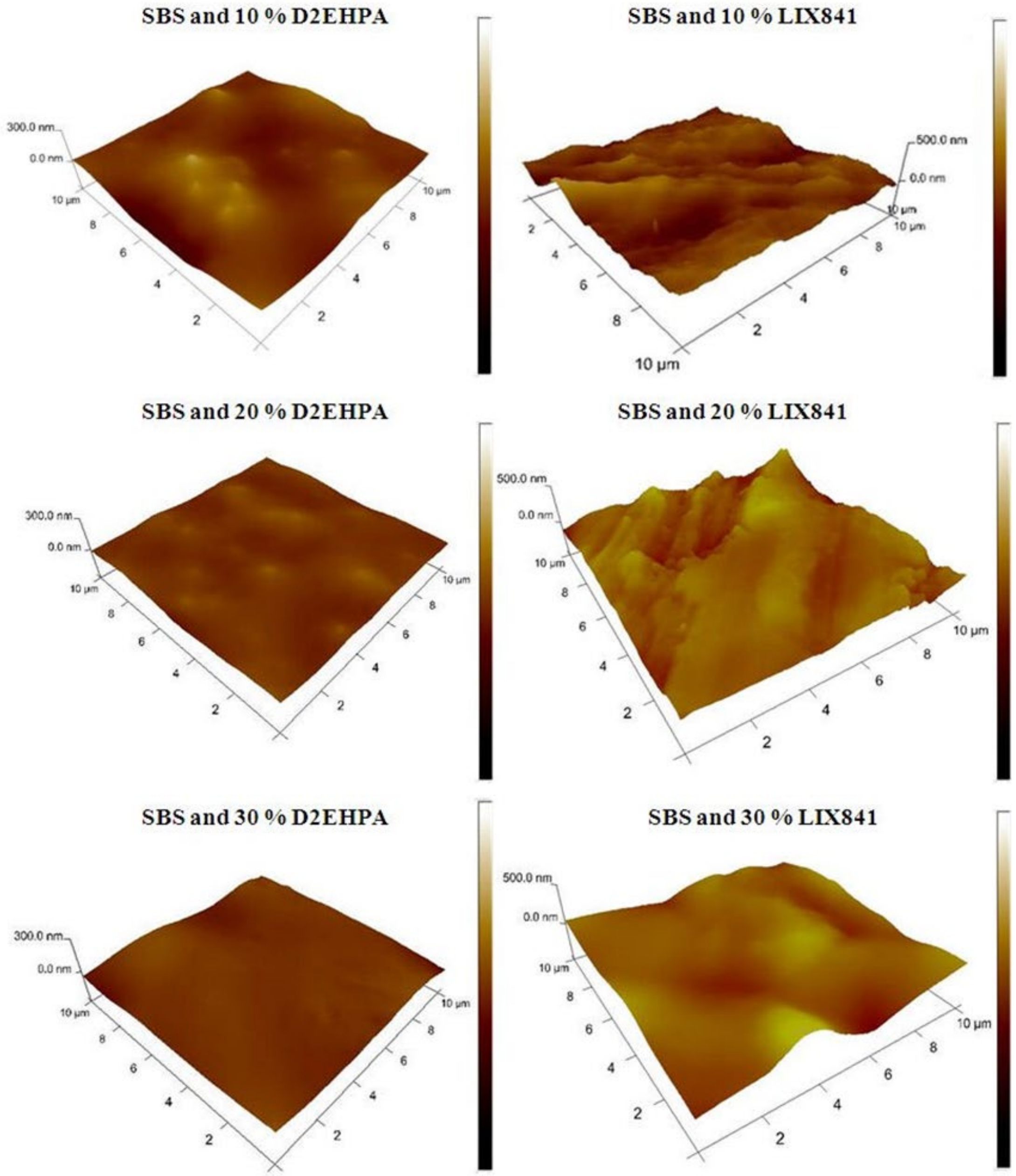

Figure 10. 3D AFM images of membrane surfaces (*10 x 10 µm*) exposed to air during the casting of SBS-based PIMs containing 10, 20 or 30% D2EHPA or LIX84I.

Figure 11 shows the DSC thermograms of an SBS membrane in the presence or absence of extractant. Each curve exhibits an endothermic stage, which normally indicates the glass transition of the polymer [27]. The glass transition temperature (T_g) of the pure SBS membrane was estimated to be 70 ºC, which could be attributed to the glass transition of the polystyrene (PS) block in the triblock co-polymer of SBS [21]. The T_g values for the SBS-based PIMs containing 30% D2EHPA or LIX84I PIMs were found to be 67 ºC and 61 ºC, respectively. The obvious lowering of the T_g value meant that the PS block became more flexible in the membranes, which could be the result of the plasticizing effect of the extractants. Moreover, the fact that there was only one T_g transition suggested that the blend between SBS and each extractant was homogenous [28]. The greater reduction in the T_g value for the LIX84I-based PIM could be attributed to the presence of 15.3% of a diluent in this membrane (LIX84I is supplied with 49% purity in a high flash point hydrocarbon) [29], which most likely acted as a plasticizer allowing the polymer chains of SBS to move more freely than those in D2EHPA-based PIMs.

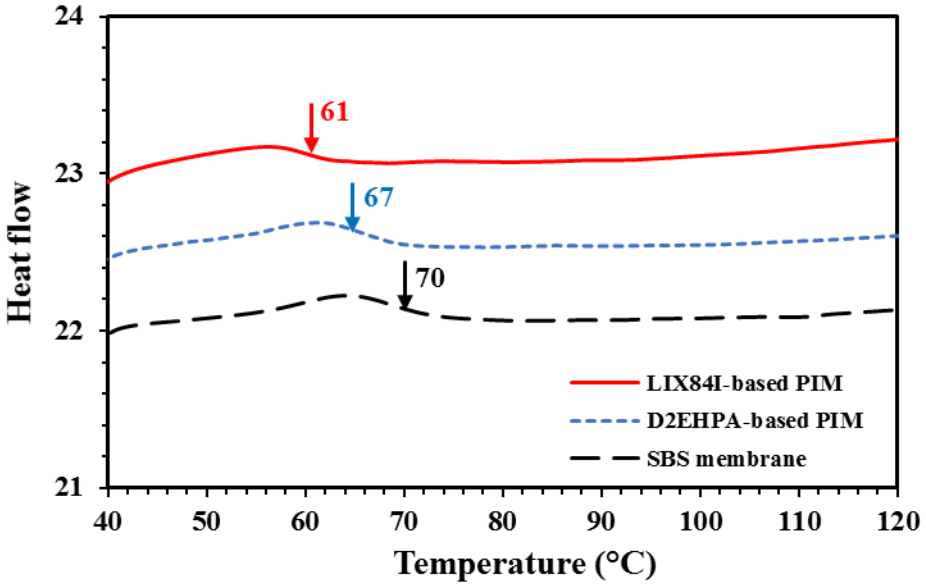

Figure 11. DSC thermograms of the SBS membrane and SBS-based PIMs containing 30% D2EHPA or 30% LIX84I as the extractant.

4. Conclusions

The triblock co-polymer SBS was used as a base-polymer in the preparation of PIMs for the first time. Commonly used extractants in PIMs were selected to assess their compatibility with SBS, and those with relatively long aliphatic chain(s) and low polarity due to the lack of strong acidic groups such as LIX84I and D2EHPA exhibited good compatibility with the non-polar SBS unlike more polar extractants such as the ionic liquids Aliquat 336, Cyphos® IL 101 and Cyphos® IL 104. PIMs containing D2EHPA or LIX84I as the extractant and SBS as the base-polymer were used in the extraction of Zn(II) or Cu(II), respectively, and both exhibited better extraction performance than their PVC or PVDF-HFP counterparts. Stability studies showed that the D2EHPA-based membrane could only be used once, although the LIX84I-based PIM could be reused at least up to 3 times with only a small decrease in the transport rate after the first experiment. Two possible ways of improving the stability of SBS-based PIMs could involve the incorporation of either a cross-linking polymer to the membrane skeleton in order to create a semi-interpenetrating polymer network able to reduce the loss of extractant, or of a long alkyl chain modifier, like 1-tetradecanol, known to have very low water solubility. Surface morphology analysis suggested that the surface of the SBS-based PIMs became smoother and more hydrophilic as the amount of extractant in the membrane increased.

In summary, SBS was found to be an attractive alternative to common base-polymer such as CTA, PVC and PVDF-HFP because of its low cost *(*68 US$ vs 253/154/426 US$ per kg, respectively, based on Sigma-Aldrich prices except for the price of CTA purchased from Fisher Scientific) and ability to form PIMs with some frequently used extractants such as D2EHPA and LIX84I. The SBS-based PIMs exhibited extraction performance superior to that of PIMs incorporating common base-polymers. Moreover, SBS is a thermoplastic elastomer and addition of plasticizers is unnecessary, thus further reducing the cost of SBS-based PIMs.

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COMPETING INTERESTS

The authors declare no competing interests.

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