



Research Paper

Feasibility of Polysulfone as Base Polymer in a Polymer Inclusion Membrane: Synthesis and Characterisation

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Highlights

- Polysulfone can be used as alternative base polymer in polymer inclusion membranes.
- PSF based PIM is permeable and can transport Cr (VI) at a flux of $2.17 \times 10^{-8} \text{ mol.m}^{-2}.\text{s}^{-1}$
- PSF based PIMs has a lower extraction efficiency compared to the PVC based PIMs
- PSF based PIMs is more stable under basic conditions

Abstract

Polysulfone was investigated as an alternative base-polymer for polymer inclusion membranes (PIM's) that could withstand harsh environmental conditions and have good transport efficiency of metal ions. PIM's were prepared using polysulfone as a base polymer and Aliquat 336 as a carrier in the absence of a plasticizer. Chromium (VI) was used as standard to study the extraction efficiency of the membranes. The optimal composition ratio for the membrane with the highest extraction efficiency during passive sampling of the chromium (VI) from solution was 40:60 (w/w) polysulfone: Aliquat 336. This membrane had a flux of $8.68 \times 10^{-7} \text{ mol.m}^{-2}.\text{s}^{-1}$ and had increased chemical stability over a range of pH 2 – 12 compared to poly(vinyl chloride) based membranes. The presence of functional groups on the polysulfone, Aliquat 336 and the synthesized polymer inclusion membrane were confirmed using Fourier Transformed Infrared Spectroscopy. The results showed that only physical interaction exists between the carrier and the polymer matrix. Scanning electron microscopy and atomic force microscopy indicated that the membrane surface was dense and the roughness increased with an increase in carrier concentration. The hydrophilicity of the membranes was studied using a drop shape analyser. The results revealed that an increase in carrier concentration increases the membrane's hydrophilicity. Thermal stability was investigated and the membranes were found to be stable up to 180 °C.

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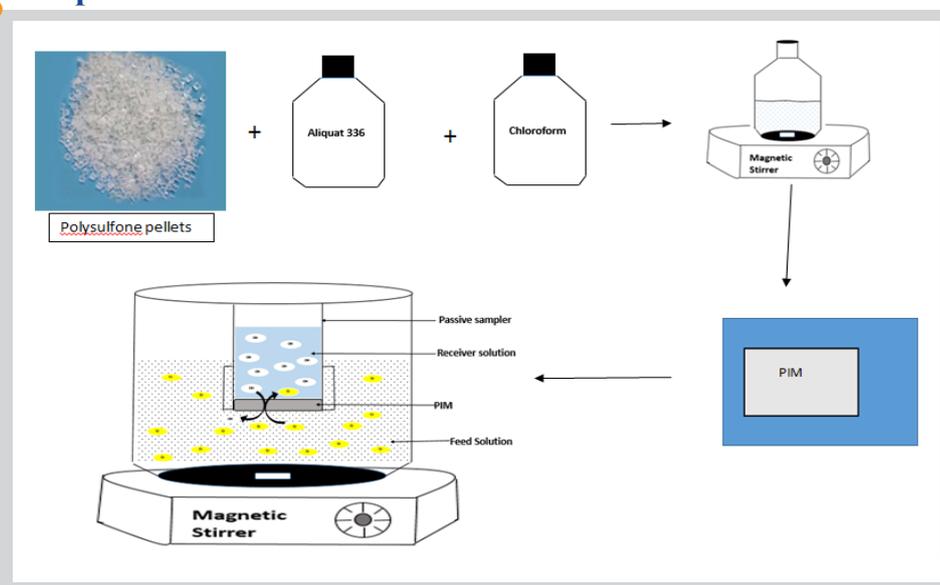
1. Introduction

Liquid membrane (LM) systems have become an attractive alternative separation method due to their relatively environmentally friendly properties compared to conventional methods [1,2]. A LM scheme consists of a liquid that is immiscible in both the source and the receiving phase which serves as a semipermeable barrier [3]. The common types of LMs are supported liquid membrane (SLM), emulsion liquid membrane (ELM), and bulk liquid membrane (BLM) [4]. Even though liquid membranes have attracted a lot of

attention in a number of membrane sectors such as the membrane filtration and electro-dialysis; they have limitations. These include the emulsion breakage for the ELM, the low interfacial surface areas and mass transfer in the BLM, and the poor stability in SLM [5].

The concept of liquid membranes that are polymer-based has been investigated for over 40 years and it has been identified as a potential replacement for the conventional solvent extraction [6]. These polymer-based

Graphical abstract



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membranes are now called the polymer inclusion membranes (PIMs) and they have demonstrated good stability and versatility relative to other known liquid membranes [6,7].

PIMs are a thin, stable and flexible form of liquid membranes [2,8]. They are prepared by dissolving a base polymer, a carrier, and a plasticizer in an appropriate solvent which is then evaporated. Each component of the membrane plays a vital role in ensuring good separation efficiency [9]. The base polymer holds the carrier and provides the membrane with physical strength [5,10]. The carrier acts as an ion exchanger or a complexing agent which binds with the target analyte and transports it across the PIM into a receiver solution [6,11]. The plasticizer softens the membrane, hence increasing its flexibility by decreasing its glass transition temperature [6]. Some ionic liquids like Aliquat 336 at room temperature can act as both a carrier and a plasticizer, in such cases it is not necessary to add a plasticizer [6, 12–14]. Since plasticizers are expensive, using these ionic liquids is a cost-effective approach. PIMs have been widely investigated for the extraction of a variety of both organic and inorganic compounds in the environment [1,11,22–25,13,15–21].

The base-polymers used for the preparation of PIMs are usually thermoplastic polymers with weak physical bonds holding the polymer chains together [8]. Their main role is to provide physical strength for the membrane. However, they are also responsible for ensuring the entrapment of the carrier and minimizing its loss to the surrounding solutions [12]. The most commonly used base-polymers in the synthesis of PIMs include poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) [10,26]. This is because PVC based PIMs exhibit very good physical strength and flexibility, and they also have high chemical resistance [8]. Furthermore, CTA based PIMs exhibit remarkable physical properties as a result of their crystalline structure, they are also easy to work with and readily available [8,16]. However they are less chemically resistant compared to the PVC based PIMs [8].

Despite the evidence of favourable qualities that PVC and CTA have as base-polymers for PIMs, they also have a number of drawbacks. When exposed to highly alkaline conditions PVC dehydrochlorinates [27,28] and in highly acidic and/or basic conditions CTA hydrolyses [16,17]. This has resulted in the limitations of their applications.

In this study, we explored an alternative base-polymer that could overcome these limitations, whilst maintaining good or improved transport efficiency. We investigated polysulfone as a potential base polymer as it is known for its hydrophobicity, toughness and stability at high temperatures. It has good chemical and physical strength, it maintains its properties over a wide range of pH and has exceptional oxidative resistance [29–31]. As such, polysulfone is widely used in various industries for different applications such as ultrafiltration membrane material for water treatment, biomedical applications and other industrial fields [32–35]. A passive sampling device was used to assess the transport efficiency of the membrane in synthetic aqueous samples containing Cr(VI) as a target analyte.

2. Methods and materials

2.1. Materials and methods

2.1.1. Reagents

Polysulfone pellets (Mw ~ 35000), poly(vinyl chloride) (Mw ~ 43000), tetrahydrofuran and Aliquat 336 were purchased from Sigma Aldrich (Johannesburg, South Africa). Chloroform and sodium hydroxide pellets were purchased from associated chemical enterprises (ACE) (Johannesburg, South Africa). Potassium chromate was purchased from May & Baker LTD (Dagenham, England).

2.1.2. Instrumentation

For casting of the membranes an Elcometer 3570 micrometric film applicator (Manchester, UK) was used. A Milli-Q-RO4 system (Millipore, Bedford, MA, USA) was used to purify deionised water. The pH of the solutions was measured using a Five easy FE20 pH metre purchased from Mettler Toledo (Johannesburg, South Africa). All metal ions were then analysed using an Agilent 7700 series ICP-MS (Kleve, Germany). Scanning electron microscopy (SEM) analysis was done to acquire information regarding membrane surface morphology. The images were recorded using a Carl Zeiss Sigma FESEM (Tokyo, Japan). Atomic force microscopy (AFM) analysis was carried out to investigate the roughness of the membrane surfaces. Images were obtained using a Veeco Di3100 AFM (Kleve, Germany). Fourier transformed infrared spectrometry (FTIR), IR spectra were recorded to determine the interactions between the polymer and the carrier in the PIM using a FT-IR Bruker Tensor 27 Spectrophotometer (Bruker,

Germany) in transmission mode, of the range of 400 to 4000 cm⁻¹. Contact angle analysis was also done using a Kruss Drop Shape Analyzer, DSA30 (GmbH, Germany) to determine hydrophilicity of the PIM, and how the change in carrier concentration affects it. Thermal stability studies were carried out using TA Q600 SDT- Simultaneous Differential Scanning Calorimeter/Thermogravimetric analyser (Trossingen, Germany).

2.1.3. Membrane synthesis

2.1.3.1. Polysulfone based PIM synthesis

Polysulfone (PSF), Aliquat 336 and 2-Nitrophenyl octyl ether (2-NPOE) were mixed at various weight percentages (Table 1). A mass of 1.00 g of the polysulfone, Aliquat 336 and 2-NPOE mixture was then dissolved in 10 mL of chloroform by stirring for 1 h. An automatic film applicator was then used to cast the solution on a glass plate at 50 µm thickness and it was left for 24 h to allow for complete evaporation of the solvent. The glass plate was then immersed in a water bath for the membrane to easily peel off. The membrane was air dried before analysis.

2.1.3.2. Poly(vinyl chloride) (PVC) based PIM synthesis

A solution containing the fixed masses of PVC and Aliquat 336 at varying ratios (Table 2) were dissolved in tetrahydrofuran (THF) for 3 h. A mass/volume ratio of 1.00 g of PVC and Aliquat 336 mixture and 10 mL of THF was used. The resulting dissolved solution was then casted on a glass plate at 50 µm thickness using an automatic film applicator. The casted solution was left to completely evaporate over 24 h. The glass plate was immersed in a water bath for the membrane to easily peel off. The membrane was then air dried before analysis.

2.1.4. Extraction studies

Preliminary membrane transport studies were conducted in the laboratory using a passive sampling device that was designed and assembled in the laboratory. The experimental conditions were adopted from Gherasim *et al.*, (2011). A feed/donor phase solution of 500 µg L⁻¹ Cr(VI) at pH 4 in a beaker containing 200 mL deionised water was prepared. The membrane based passive samplers contained a 5 mL receiver solution chamber where 0.05 M NaOH receiver solution was added and it was sealed with a round cut PIM with an area of 3.14 × 10⁻⁴ m². The passive sampler was then deployed into the feed solution. The extraction study was done over a period of 3 h. The receiver solution was then analysed using an ICP-MS. The experiment was done in triplicate. This procedure was repeated for all membranes studied.

To measure the membrane's extraction efficiency the flux was then calculated with the formula [36]:

$$J = \frac{V}{A} \times \frac{[\text{Concentration}]}{t} \quad (1)$$

where V is the Volume of feed, A= membrane surface area, [concentration] = concentration of the receiver solution, t = time of deployment, J = flux.

2.1.5. Stability Studies

The chemical stability of both the PVC and PSF based PIMs was investigated in acidic and basic solutions using 1 M HNO₃ and 0.05 M NaOH respectively. The membranes were prepared and their initial mass was recorded. They were placed in the acidic and basic solutions and physically agitated for 24 h at 150 rpm. The membranes were left to dry for another 24 h and re-weighed. The average mass percentage lost was then calculated and reported.

3. Results and discussion

3.1. Synthesis of PIM

The optimum membrane composition was investigated by synthesizing six different PIMs. Their physical stability and extraction efficiencies were investigated and the membrane composition that produced the desired physical stability was used for further studies.

3.1.1. Physical stability

Physical stability is one of the most significant properties of any membrane, as it determines its applicability. A membrane lacking physical stability is not viable for application as it will not be able to function properly under environmental conditions of interest. It is therefore vital that the PIM

has good physical strength. The PIMs were considered physically stable when they could bend without tearing or visibly deforming.

PIMs of varied composition ratios (Table 1) were investigated to determine the optimum ratio where the carrier would plasticize the very rigid polysulfone, whilst maintaining its physical stability. It was observed that an increase in carrier concentration results in an increase in the membrane's flexibility. At low carrier concentrations (below 50%) the membranes were brittle and physically unstable. At higher concentrations (above 60%), the observed membranes became viscous, soft and physically unstable. It was therefore decided that PIM 1, PIM 2, PIM 5 and PIM 6 would be excluded from further studies. The control PIM (PIM 0), PIM 3 and PIM 4 presented the desired membrane properties in terms of flexibility and strength, they were therefore used in further studies.

Table 1
Composition and physical properties of various synthesised PIM membranes.

PIM	Polysulfone	Aliquat336	flexibility	Physical stability
PIM 0	100		flexible	✓
PIM 1	70	30	Brittle	×
PIM 2	60	40	Brittle	×
PIM 3	50	50	flexible	✓
PIM 4	40	60	flexible	✓
PIM 5	30	70	Soft	×
PIM 6	20	80	Soft	×

3.1.2. Extraction efficiency

Permeability of the membranes was investigated by monitoring their extraction capacity of Cr(VI). Preliminary extraction studies were done for PIM 3 (50% PSF: 50% Aliquat 336), and PIM 4 (40% PSF: 60% Aliquat 336) because they had the desired flexibility and physical stability. They were then compared to a control membrane composed of only PSF (PIM 0). In this study the extraction efficiencies of PIMs with carrier concentration above 60% and those below 50% were not investigated due to their lack of physical stability.

Results showed that on its own, PSF can transport the target analyte at a flux of $2.17 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$ demonstrating that PSF is permeable. This is in agreement with Casadellà, Schaeztle and Loos, (2016) where the control PIM was reported to allow ion transport at slow rates compared to carrier containing membrane, but contradicts the observation by Kebiche-Senhadjji et al., (2008) and Meng et al., (2017), where in the absence of carrier the membrane prohibits ion transfer from feed to receiver phase. Ladewig and Al-Shaeli, (2017) reported that permeability in solvent evaporation prepared (dense) membranes can only be observed when the polymer is a highly permeable or porous one such as silicon. PSF is known to be naturally hydrophobic and porous. Its porosity enables the membrane permeability in the absence of carrier. However, its hydrophobicity reduces its extraction efficiency. The hydrophobicity causes a repulsive response towards the feed solution. This limits the contact time the membrane surface has with the source solution and thus lowers permeability. This agrees with findings of O'Bryan et al., (2016) that membranes with high glass transition temperatures have higher ion-pair mass transfer diffusive resistance and thus poor permeability rate [10].

Figure 1 shows that when the carrier was introduced, an increase in extraction efficiency of the PIMs was observed. The carrier acts as a facilitator for ion-exchange between feed and receiver solution. Thus, the introduction of a carrier resulted in an increase in the membrane permeability. PIM 3 achieved a flux of $4.86 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$ which is two folds higher than that of PIM 0.

A further increase in the carrier concentration resulted in faster ion exchange. This is attributed to both the plasticizing nature of the carrier Aliquat 336 and its facilitation of ion-exchange. The higher the carrier concentration the more ions available to transport the analyte from the feed phase to the receiver phase. Higher carrier concentrations also increase the flexibility of the membrane, which is a consequence of a lower glass transition temperature. This means that the ion-pair mass transfer diffusive resistance decreases resulting in faster ion-exchange and thus better permeability rate.

The highest permeability was observed in PIM 4 with a flux of $8.68 \times 10^{-7} \text{ mol.m}^{-2}\text{s}^{-1}$. This makes PIM 4 (40% PSF: 60% Aliquat 336) the optimal composition weight ratio, with an extraction efficiency of 17 fold higher than PIM 3 and about 40 fold higher than that of PIM 0.

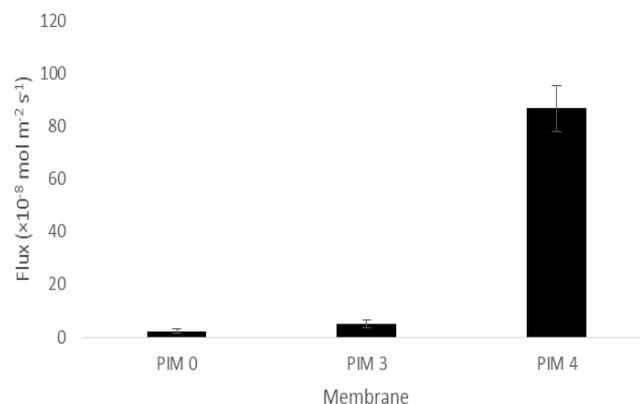


Fig. 1. Extraction efficiency of Cr (VI) by PIM with different carrier concentrations.

3.2. Stability studies

A PIM needs to have both physical and chemical stability. Chemical stability is dictated by its ability to effectively entrap carrier into its polymer matrix with minimum leaching to its surrounding solutions during application. Its behaviour in different environmental conditions is an important parameter to consider when choosing the PIM parameters for an application due to the different physical and chemical properties each component is associated with. The stability of a PIM on certain environmental conditions can therefore be quantified by monitoring its weight loss when exposed to that condition.

The stability of the PSF based PIM at optimum composition ratio of 40% PSF and 60% Aliquat 336 and different membrane thicknesses was investigated. This was done in both acidic (1 M HNO_3) and basic conditions (0.05 M NaOH). This was done by measuring the weight of the membranes before and after they were immersed in the 0.05 M NaOH and 1 M HNO_3 solutions. The average mass percentage lost after exposure are presented in Figure 2.

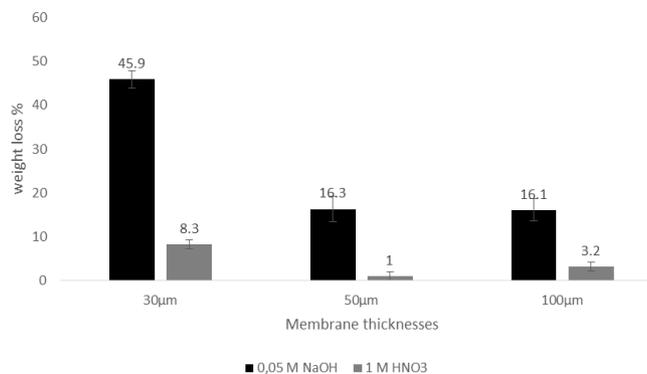


Fig. 2. Chemical stability of PIMs at different membrane thicknesses in acidic and basic conditions.

It was observed that all the membranes at different thicknesses were more stable in the acidic conditions compared to the basic conditions. This could be attributed to the positive charge of the carrier Aliquat 336 which enable an interaction between the highly concentrated hydroxide (OH^-) anions from the NaOH and thus that activity exposes the carrier which then results in it leaching out of the membrane. In the acidic solution there is a high presence

of hydronium cations (H_3O^+) and since Aliquat 336 is also cationic there will be very minimal interaction and thus the higher stability of the PIM.

At 30 μm membrane thickness the PIMs were at their most unstable, losing an average of 45.9% of their original mass in the basic solution and an average of 8.3% in the acidic solution. This could be due to the membrane being too thin, leaving very little room for the carrier to travel which then maximizes the interaction between the carrier and the surrounding solutions. This makes the membrane more prone to leaching and therefore the loss of its physical stability. There was an increase in the membrane stability with an increase in thickness. This observation is in agreement with the results obtained by Schow (1996) [15]. Between the membrane thickness of 50 μm and 100 μm , no significant difference was observed in their stability. They both lost respectively 16.3% and 16.1% on the basic solution and 1% and 3.2% in the acidic solution. This is however significantly lower than the results obtained for the PIMs of 30 μm thickness. Thus the thicker the membrane, the higher the stability.

3.3. Characterization

3.3.1. FTIR

The FTIR absorption spectra of PSF, Aliquat 336 and that of the PIM were recorded to determine the method of interaction between the polymer and the carrier in the PIM. The main PSF functional groups were observed on the PIM IR spectra as shown in Figure 2. The sulfone group $\text{S}=\text{O}$ symmetric stretch was observed at 1148.70 cm^{-1} , followed by the $\text{C}-\text{O}$ stretch at 1238.24 cm^{-1} , then the $-\text{CSO}_2\text{C}-$ at 1322.28 cm^{-1} and lastly the aromatic ring stretch at 1584.30 cm^{-1} . The presence of Aliquat 336 functional groups was also observed at 1467.31 cm^{-1} due to the $-\text{N}-\text{CH}_3$ and at 2955.48 cm^{-1} and 2854.69 cm^{-1} due to CH stretch.

The presence of the functional groups of both compounds in the IR spectra confirmed that the PIM is composed of both PSF and Aliquat 336. This also suggests that during membrane synthesis only physical interactions occurred between the two components. It can, therefore, be concluded that the membrane's physical stability is solely dependent on the weak physical interactions and thus, the polymer chains act as a support for the carrier's liquid domains.

3.3.2. Surface characteristics

To identify the surface morphology of the membranes, SEM and AFM analysis was done for flexible PIMs (PIM 0, PIM 3 and PIM 4). All three membranes were dense; thus no pores were observed (Figure 4). This is in agreement with Ladewig and Al-Shaeli [40], where it was reported that the membrane morphology is highly dependent on the method of preparation and dense membranes are to be observed when the solvent evaporation method is used. The control membrane (PIM 0) had a featureless, smoother surface relative to the other PIMs. It had an average roughness value of 3.75 nm. In contrast both PIM 3 and PIM 4 displayed randomly distributed small drops of the carrier Aliquat 336 on the membrane surface. The surface of the optimum PIM (PIM 4) also contained small precipitates distributed all over its surface. These precipitates created roughness of the surface, resulting in a bigger surface area and thus promoting better extraction of the analyte $\text{Cr}(\text{VI})$. An average roughness of 9.23 and 31.90 nm was observed for PIM 3 and PIM 4, respectively.

3.3.3. Contact angle

Hydrophilicity of the membrane surface at different carrier (Aliquat 336) concentrations was investigated by measuring their contact angle. When a membrane is too hydrophobic it is prone to low extraction efficiencies and biofouling; when it is too hydrophilic it will dissolve in water, leaching out the carrier. Therefore, the PIM must be hydrophobic enough for the carrier to not leach out and hydrophilic enough to maximize contact time between membrane surface and feed solution.

Figure 4 shows the average contact angle values for the different PIMs. PIM 0 had the highest value of 90.76° , suggesting that polysulfone is hydrophobic in nature. When carrier was introduced a decrease in contact angle was observed, meaning hydrophilicity increases with an increase in carrier concentration. This resulted in an increased in contact time between the PIM and the feed solution and thus increasing extraction efficiency. PIM 3 and PIM 4 had average contact angle of 48.75° and 34.00° respectively. This decrease in contact angle is in agreement with the extraction results. PIM 4 had the lowest contact angle meaning it has the highest contact time and thus the largest extraction capacity.

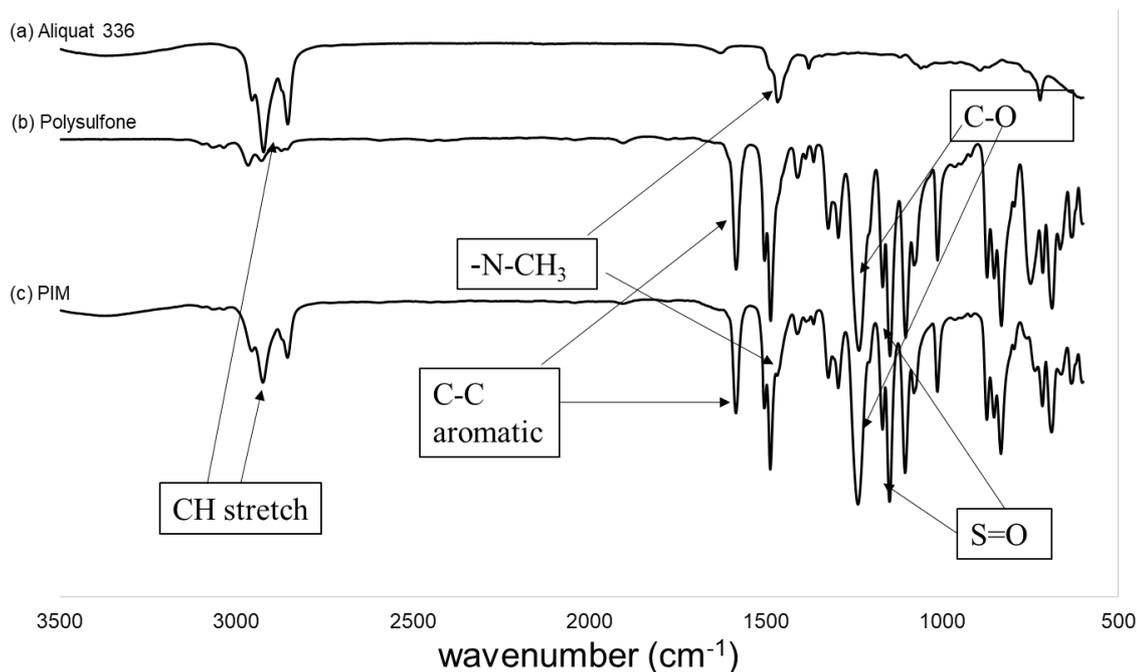


Fig. 3. FTIR spectra of (a) Aliquat 336 (b) Polysulfone (c) PIM.

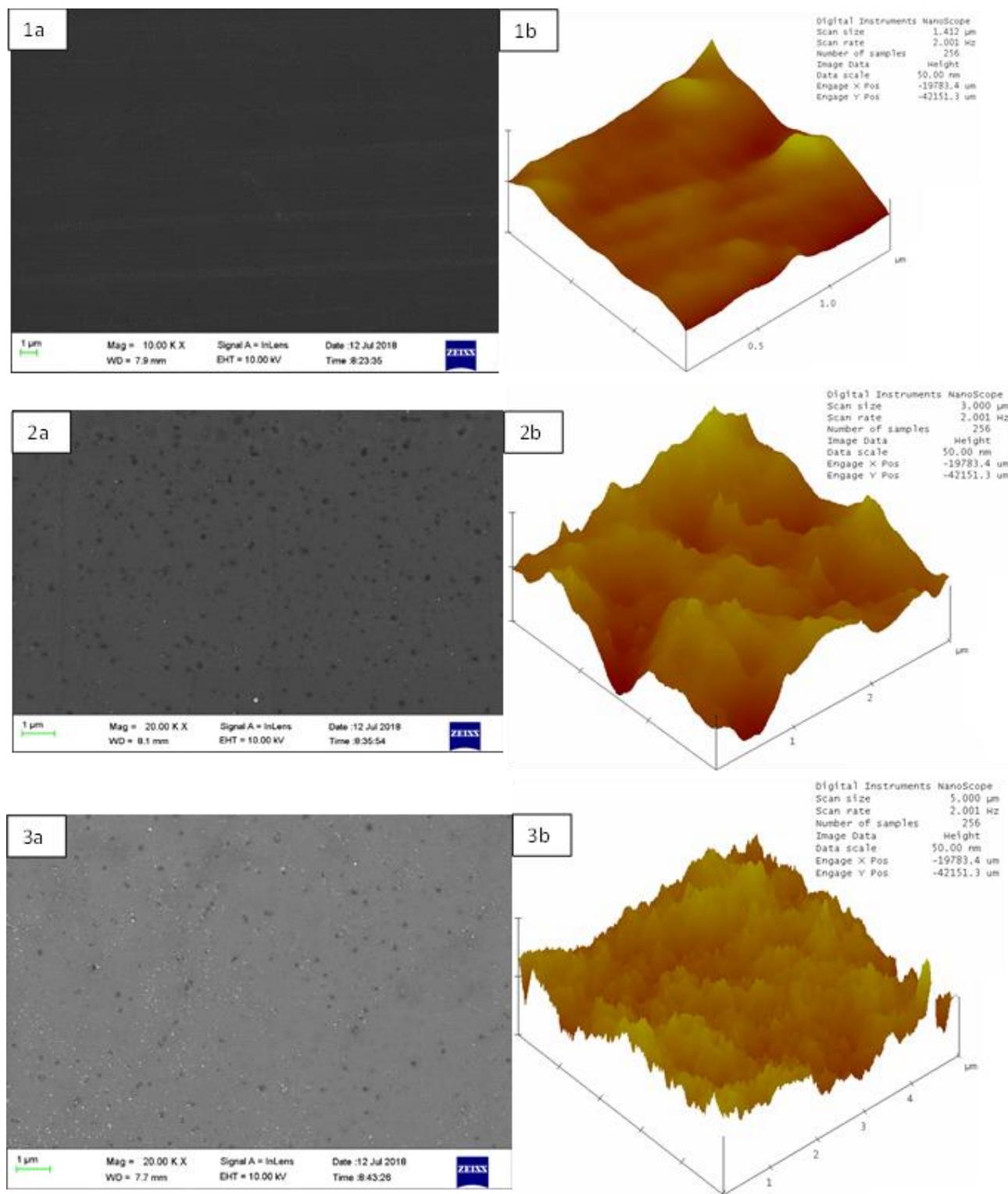


Fig. 4. 1-PIM 0, 2-PIM 3, and 3-PIM 4. (a) SEM images and (b) AFM images.

3.3.4. Thermal stability

TGA analysis was done to investigate the thermal stability of the control membrane (PIM 0), PIM 3 and PIM 4. This was done by observing the weight loss of polysulfone and the PIMs at different carrier concentrations as the temperature increases. The thermogram curves are shown in Figure 6.

Polysulfone is thermally stable up to 500 °C where its thermal degradation occurs, losing about 64% of its original weight. PIM 3 and PIM 4 have the same degradation pattern. A minor mass loss was observed before

100 °C, this was attributable to the evaporation of the solvent and moisture that remained in the membrane matrix during synthesis. They are both stable until the temperature of about 180 °C where they start degrading, losing the carrier. This indicates that the PIMs are stable at standard operating temperatures (≤ 45 °C). PIM 4 has higher carrier concentration, hence the larger weight loss. It can be observed that the polysulfone degrades at the same temperature for all 3 membranes. This means that the polymer matrix is not chemically disturbed by the presence of carrier in the membrane.

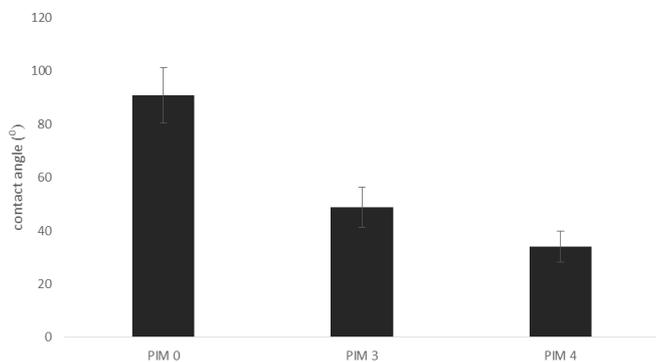


Fig. 5. Water contact angle of PIM with different carrier concentrations.

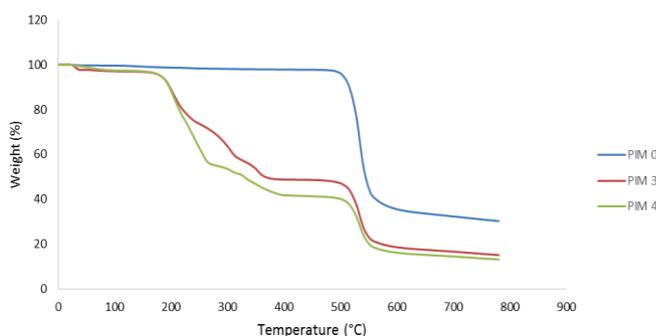


Fig. 6. Thermograms of PIM 0, PIM 3 and PIM 4.

3.4. Comparison studies

Poly(vinyl chloride) (PVC) is one of the most commonly used base polymers for preparation of PIMs. However, its instability under basic conditions brought about the need to explore other base polymers that will overcome such limitations. Polysulfone (PSF) was then investigated. A comparison study was conducted between the PSF based PIMs and the PVC based PIMs. This was done to determine if PSF can outperform PVC as a base polymer.

3.4.1. Physical stability and permeability

The optimum membrane composition of PVC based PIMs was investigated. The physical stability and permeability of the PIMs was then compared with those obtained for polysulfone based PIM. The stability results of the PVC based PIMs is detailed in Table 2.

Physical stability of the PVC based PIMs was observed between 20% and 40% carrier concentration. Below 20% the control PIM, PIM 7 (100% PVC) was stiff and brittle. When carrier concentration was increased above 40% the membranes lost their physical stability and became soft and sticky. This could be attributed to the saturation of the base polymer with the carrier therefore at higher concentration of the carrier, over plasticization occurs thus making the polymer physically unstable. The PSF based PIMs only lost their physical stability at carrier concentrations above 60%, they were physically stable between 50% and 60% carrier concentration. The PVC requires less carrier concentration than the PSF to reach oversaturation of the polymer matrix and thus producing a physically unstable membrane. This is due to the difference in glass transition temperature (T_g), PSF has a T_g value of 185°C and PVC has a T_g of about 80°C. This means that PSF has stronger intermolecular forces relative to PVC, therefore it will require much higher carrier concentrations to overcome its very rigid nature.

The rate of permeation of the physically stable PVC based PIMs was investigated by determining their flux of Cr(VI). The preliminary study was done for PIM 8 (80% PVC: 20% Aliquat 336), PIM 9 (70% PVC: 30% Aliquat 336) and PIM 10 (60% PVC: 40% Aliquat 336) and then compared to the flux of the physically stable PSF based PIMs, PIM 0 (100% PSF), PIM 3 (50% PSF: 50% Aliquat 336) and PIM 4 (40% PSF: 60% Aliquat 336).

In the PVC based PIMs, PIM 8 with 20% carrier concentration showed

the lowest flux. When carrier concentration was increased to 30%, an increase in the flux was also observed. The highest permeability was observed at PIM 10 where an average flux of $305 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$ over the 3 h period hereby making the 60% PVC and 40% Aliquat 336 the optimal compositional ratio for the extraction. Similar to the PSF based PIMs an increase in permeability of the PIMs was observed with an increase in carrier concentration.

Table 2

Effect of varying PVC and Aliquat 336 concentration on flexibility and stability.

PIM	PVC	Aliquat 336	Flexibility	Physical stability
PIM 7	100	0	Stiff	×
PIM 8	80	20	flexible	✓
PIM 9	70	30	flexible	✓
PIM 10	60	40	flexible	✓
PIM 11	50	50	soft	×
PIM 12	40	60	Soft	×

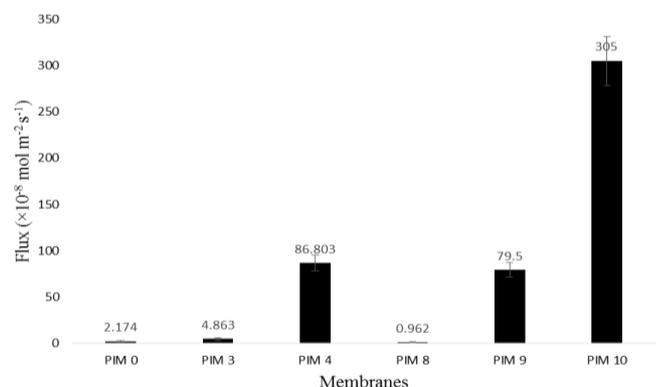


Fig. 7. Extraction efficiency of Cr(VI) by PSF and PVC based PIMs at different carrier concentrations

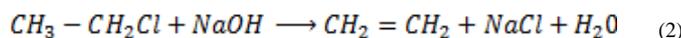
The PSF control PIM, PIM 0 had the lowest transport efficiency in the PSF based PIMs, exhibiting an average flux of $2.174 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$. This was however twice that of PVC base PIM, PIM 8 with a value of $0.962 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$ meaning the PSF control PIM performs better than PVC based PIMs in transporting Cr across the membrane when the carrier concentration was $\leq 20\%$ Aliquat. The optimum compositional ratio for the PSF membrane was found to be PIM 4 with a carrier concentration of 60% and a flux of $86.80 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$, these was significantly lower when compared to that of PVC based PIM optimum (PIM 10), with an average flux of $305 \times 10^{-8} \text{ mol.m}^{-2}\text{s}^{-1}$.

The optimum PVC based PIM had a flux more than threefold higher than that of the optimum PSF based PIM, even though the PSF PIM had a higher carrier concentration. This could be attributed to their wettability. Wettability refers to the propensity of a liquid to spread across a solid and this process can be measured in terms of contact angle where such wetting can be total, partial and non-wetting [41]. The lower the contact angle means higher hydrophilicity and thus proper interaction between the aqueous liquid and the membrane surface. This agrees with the contact angle values obtained for the PSF based PIMs (Figure 5) where the optimum PIM had the highest hydrophilicity at a contact angle value of 34° . Although actual values of the contact angle of PVC varies across different solutions, reports have shown that PVC has a lower water contact angle than PSF [42]. In a study Vázquez et al., (2014) demonstrated that the of Aliquat 336 results in an increase in hydrophilicity of a membrane surface. When 9% of Aliquat 336 was added the PIM's surfaced went from hydrophobic with a value of 86° to hydrophilic at 28° contact angle. This is evidence that PVC is more hydrophilic even at low carrier concentration values and thus the higher permeability compared to PSF based PIM even though it had lower carrier concentration.

3.4.1.2. Stability studies

The behaviour of a PIM in different environmental conditions is an important parameter to consider when choosing a PIM for an application due to the different physical and chemical properties associated with the PIMs components. The chemical stability of PVC based PIMs and PSF based PIMs was investigated. The thickness of both PIMs was kept at 50 μm . It was observed that both PVC and PSF are highly in acidic conditions with the PSF based PIM losing 1% of its original mass and the PVC based losing 1.8%. However, under basic conditions both PIMs are less stable than they are in the acidic conditions. The PSF based PIM is more chemically stable in basic conditions than the PVC based PIM. IT lost about 16% of its original mass, whilst the PVC based PIM lost more than 30% of its original mass. The instability of the PVC in basic conditions is due to a dehalogenation reaction occurring within the polymer matrix. Since PVC is a chloroethene organochloride, there is a tendency for the poly(chloroethene) to undergo dehydrochlorination with a base in the presence of a quaternary ammonium (Aliquat 336) [27, 43].

The general mechanism for dehydrohalogenation is shown in Eqn 2. This reaction is initiated by the hydroxide ions binding to the hydrogen atoms of the β -carbon and stripping it away from its original binding site in the carbon atom. The reaction then propagates with the spontaneous release of the chloride ion to form a stable ethane complex. As a consequence, the membrane degrades and loses its physical stability.



The result of the dehydrogenation reaction will yield NaCl and H_2O .

The instability of the PVC in the NaOH was also observed by the change in coloration of the PVC membrane from transparent to black. The PSF based membrane is seen to be considerably stable in the basic condition, unlike PVC. The better stability observed is a result of the absent of halogens in its molecular structure which are responsible for dehydrohalogenations in PVC, PSF is rather composed of aromatic groups and sulfonyl groups which are not decomposed by bases. The chemical and physical stability of PSF can also be attributed to the aromaticity existing within the polymers and also due to the positioning of the groups holding the aromatic compounds in para positions [44]. This base stability of PSF gives it an edge in applications or environmental conditions that requires basic conditions.

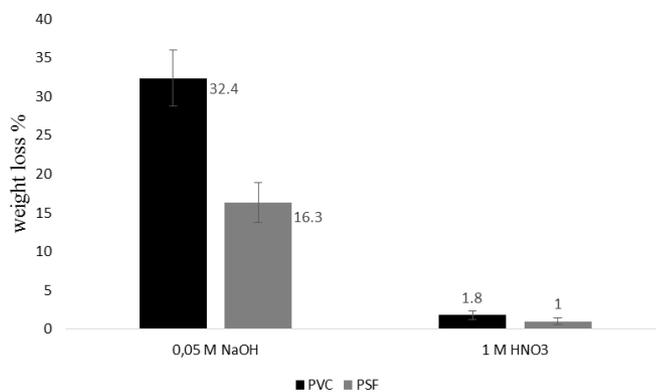


Fig. 8. Chemical stability of PIMs composed of different base polymers in acidic and basic conditions

4. Conclusions

In this work, novel polysulfone based PIMs were successfully synthesized using the solvent evaporation technique. The PIMs did not contain plasticizer; Aliquat 336 acted as both carrier and plasticizer. The optimum PSF based PIM (PIM 4) was found to be chemically stable in both acidic and basic mediums as well as temperatures as high as 180 $^{\circ}\text{C}$. This indicated that the PSF-PIMs are applicable at a wider range of environmental conditions. The thickness of the PIM played a significant role in its stability with a thickness of 50 μm and above found to produce chemically stable membranes. PSF based PIMs had a significantly lower extraction efficiency for Cr (VI) when compared to the PVC based PIMs. However, they had the advantage of overcoming the stability issues associated with PVC based PIMs under basic conditions. The characterization results confirmed that the PIMs were dense, hydrophilic and rough on the surface with only physical interactions existing between the carrier and the polymer matrix. The results obtained in this study indicate that polysulfone can effectively be used as a base polymer for PIMs and the absence of plasticizer makes the polysulfone based PIM more cost effective to synthesise.

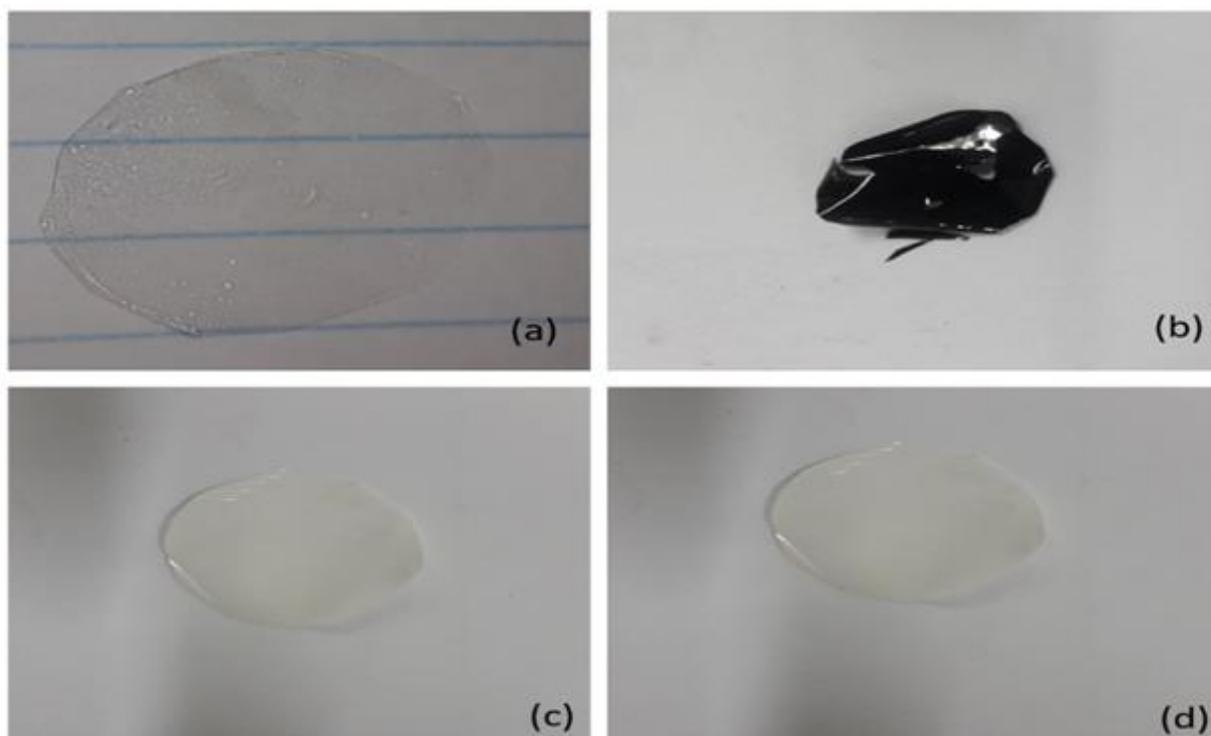


Fig. 9. (a) image of PVC before base stability experiment, (b) image of PVC after base stability experiment, (c) image of PSF before base stability experiment, (d) image of PSF after base stability experiment

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