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Technical Note

Investigating the effect of the hydrophilic property of NPE modifier on the kinetics and stability of the PIM containing D2EHPA in Uranium transferring

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Flux

Abstract

In the present work, the extraction and separation of uranium from acidic phosphoric solutions using a polymer inclusion membrane (PIM) containing di(2-ethylhexyl) phosphoric acid (D2EHPA) as the carrier and polyvinyl chloride (PVC) as the polymer were studied. Different nonylphenol ethoxylates (NPE) were introduced as modifiers used in PIMs. Physicochemical properties of the resulting membranes were analyzed and correlated with their structure. The infrared analysis revealed the presence of intermolecular interactions between the base polymer and NPE, sustaining their good compatibility. The cross-section SEM images showed a dense structure for all studied membranes. However, the surface structure and hydrophilic/hydrophobic balance of the PIMs strongly depend on the NPE. The contact angle measurements indicated that the addition of NPE to the PVC membrane decreases the contact angle, indicating improved membrane wettability. The results of transport measurements showed that PIMs containing NPE are more efficient for uranium extraction than those with only D2EHPA/PVC due to the plasticizing effect of the NPE. After investigating the best mathematical kinetics models for transport, the highest uranium transport flux ($0.81\times10-6$ $mol\cdot m^{-2}\cdot s^{-1}$) was measured for the PIM containing 5 wt% of NPE10. Moreover, the membrane with only 5 wt.% of NPE10 had improved reuse stability compared to the PVC-based membrane due to the hydration effect provided by the water molecules interacting with the polar hydroxyl groups of NPE.

1. INTRODUCTION

The separation of uranium from its ores has been studied in great detail, whereas the uranium concentrates for enrichment are commonly produced using solvent extraction and ion exchange techniques[1-3]. Liquid membranes can be a very suitable alternative for the liquid-liquid extraction system, which contains a large volume of volatile, flammable, and toxic substances. Studies on membrane separation of uranium have included systems based on bulk liquid membranes (BLM), emulsion liquid membranes (ELM), and supported liquid membranes (SLM). While the current techniques of separating uranium are considered cost-effective and relatively efficient, polymer inclusion membranes (PIMs) are increasingly gaining attention because they are mechanically strong, easy and safe to handle, and reasonably simple to fabricate. In PIM techniques, encapsulating the extractant within a polymer matrix eliminates the need for flammable and toxic solvents as diluents. This approach also minimizes extractant loss due to leakage into the source and/or receiving solutions, thereby reducing health and safety risks associated with the process, since many commercial extractants are toxic and/or corrosive compounds [4-6]. Some

studies have been conducted on the use of PIMs for uranium separation. St John et al. demonstrated the suitability of PIMs incorporating di(2-ethylhexyl) phosphoric acid (D2EHPA) to extract uranium (VI) from acidic sulfate solutions compared to other commercial extractants:

Alamine 336, di(2,4,4-trimethylpentyl) phosphinic acid (Cyanex272), Aliquat 336, and tri-n-butyl phosphate (TBP). (It is noted that Alamine 336 is a mixture of tri-alkyl amines, with the substituent chain length varying between 6 and 12 carbon atoms, and Aliquat 336 is a mixture of tri-alkyl methyl ammonium chloride salts produced from the methylation of Alamine 336, with the substituent alkyl chain length varying between 6 and 12 carbon atoms [7]). St John et al. optimized the main system parameters affecting the rate of transport (i.e., the composition of the membrane and the source and receiving solutions). An initial flux of uranium of 3.0×10^{-6} mol m^{-2} s^{-1} was recorded when using a PIM composed of 35% D2EHPA, 10% o-nitrophenyloctyl ether (NPOE), and 55 wt% poly(vinyl chloride) (PVC) from a source phase containing 0.1 mol L^{-1} H_2SO_4 to a receiving phase containing 6.0 mol L^{-1} H_2SO_4. In another study, a mathematical model for the extraction of uranium (VI) from sulfuric acid solutions into a PIM composed of D2EHPA and PVC has been developed. This model can be used for the optimization of this process using numerical simulation. In a recent study, transport of U(VI) through the PIM containing Alamine 336 and the plasticizer polyoxyethylene alkyl ether (POE) depended on the amounts of the extractant and plasticizer in the PIM composition, the sulfuric acid concentration in the feed phase, and the receiving phase concentration. In previous studies, different PIMs have been used for the extraction of uranium from ore leached with sulfuric acid media. However, the extraction of uranium through PIM in phosphoric acid media has not been reported yet in the literature. Girgin et al. employed industrial extractants, such as D2EHPA and tri-n-octyl phosphine oxide (TOPO), diluted in kerosene, to extract uranium from phosphoric acid using solvent extraction. They reported that the mechanism of uranium extraction in the presence of D2EHPA and TOPO in the organic phase differs from that of D2EHPA alone. Moreover, the acid concentration plays a crucial role in the extraction of U(VI); specifically, the critical acid concentration is 3.3 M, above which efficient extraction is not achieved. Additionally, when the volume ratio of H_3PO_4 to the organic phase exceeds 4, a straightforward extraction mechanism may no longer be applicable[8].

Although liquid-liquid solvent extraction is widely used in industry, this process is being applied with limitations due to the heavy usage of organic solvents and diluents. Khayambashi et al. investigated the parameters affecting uranium extraction from an aqueous phosphoric acid medium using a silica/polymer-based D2EHPA-TOPO adsorbent. Their results demonstrated that 95% uranium extraction was achieved after 10 minutes of contact time with the D2EHPA-TOPO/SiO_2-P adsorbent (mass ratio 3:1 w/w) from a 1 M phosphoric acid solution containing 165 ppm U(VI) at 25 °C. [9].

In the present study, the transport of uranium through the PIM containing D2EHPA from phosphoric acid media was investigated for the first time. One of the most frequently used plasticizers for polymer inclusion membranes in recent years is 2-NPOE, which is characterized by a high dielectric constant and low viscosity [10, 11]. When 2-NPOE is added to PIMs containing PVC, the plasticizer molecules can readily interact with the PVC chains, creating a solvent-like environment that facilitates the transport of metal–carrier ion complexes across the membrane [12]. Since plasticizers are generally expensive chemicals, the use of non-plasticized PIMs would lead to significant cost reduction in the separation process. It is worth pointing out that some carriers also have plasticizing abilities and can form flexible and stable membranes without the need to add any other component, as is the case with D2EHPA[13].

In this study, considering the plasticizing properties of D2EHPA, various types of nonylphenol ethoxylates (NPE) modifiers were investigated with respect to the change in the balance of their hydrophilic branches. The transport performance of the fabricated PIMs modified with different NPEs, as well as their stability, were investigated and compared with the performance of the PVC-based PIM. The correlation between the membrane structure and morphology was established, allowing a better understanding of the influence of the NPE modifier incorporation on the physical properties of the resulting PIMs. The optimum values for various parameters, such as stirring speed, acid concentration in the receiving phase, acid concentration in the feed phase, and concentration of the target element in the feed solution, were selected according to our previous study[14]. Four mathematical kinetics models for transport were investigated. Finally, the selectivity and stability of the prepared PIMs were also checked.

2. EXPERIMENTAL METHODS

2.1 Materials

Di(2-ethylhexyl) phosphoric acid (D2EHPA) (Sigma-Aldrich Co.), poly(vinyl chloride) with high molecular weight (domestic producer), tetrahydrofuran (THF) (Neutron Co.), and phosphoric acid (Dr. Mojalli Chemical Industries) were all used as received. Also, the uranium-containing solution was synthetically obtained by dissolving ammonium uranyl carbonate ($(NH_4)_4UO_2(CO_3)_3$) powder in dilute phosphoric acid according to the desired concentration. Three grades of nonylphenol ethoxylates (NPE) with different chain lengths of polar oxyethylene groups and an alkyl chain were prepared from Kimyagaran Emrooz Co. (Iran). Deionized water was utilized in all experiments for aqueous solutions. As shown in Figure 1, nonylphenol ethoxylate consists of a hydrophobic moiety (nonylphenol) and one or more ethylene oxide chains attached to it. The number of ethylene oxide chains attached to the nonylphenol determines the grade of the product. As the ethylene oxide moiety increases, the HLB (water solubility), density, and viscosity increase, as shown in Table 1[15].

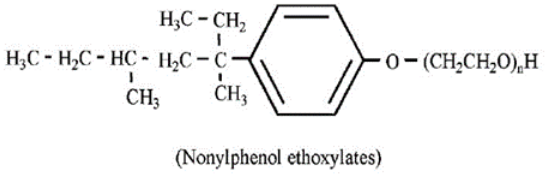

Fig. 1. Molecular structure of nonylphenol ethoxylate [15]

Table 1. Physicochemical Properties of Three Types of Nonylphenol Ethoxylates

Grades	Viscosity@25°C (c.st)	HLB	Hydroxyl Value(mgKOG/g)	Average Molecular Weight(g/mol)
NPE 20	ca. 110 at 50°C	16	48-54	1038-1168
NPE 10	230-260	13.3-14.0	85-89	630-660
NPE 6	210-240	10.8-11.3	115-120	467-488

2.2 Instrumentation

The Optima 7300 DV ICP-OES device manufactured by PerkinElmer was used to measure the quality of the samples with an accuracy of 0.1 ppm. Also, a scale made by AND Company was used with an accuracy of four decimal places to weigh the raw materials of the membrane, and a Digimatic Micrometer (Mitutoyo, MDH-25MC) was used for thickness measurement.

2.3 Membrane Preparation

Membranes were prepared by dissolving the extractant, modifier, and the base polymer (PVC) in THF. The mixture was magnetically stirred for 4 h at room temperature (24±1 °C) to form a homogenous solution. The solution was then poured into a Petri dish which was covered with filter paper to slow the evaporation of the solvent. The membrane solution was allowed to evaporate over 72 h and then was peeled from the Petri dish. For membrane thickness measurement, the corresponding value was calculated as the average of 5 spots along the membrane diameter. The average thickness of the membranes used in all experiments was 60 ± 5 μm.

2.4.Membrane Characterizations

FTIR Attenuated Total Reflection (ATR) mode spectra were acquired using a PerkinElmer spectrometer. Measurements were taken in a wave number range from 500 to 4000 cm^{-1}. Field emission scanning electron microscopy (FE-SEM) images of the PIMs were obtained using a CIQTEK microscope. Atomic Force Microscopy (AFM) (Bruker's Dimension Icon) images were obtained in contact mode. The hydrophilic/hydrophobic nature of PIMs was analyzed through water contact angle measurements using the sessile drop method at room temperature (24 ± 1 °C). A water drop of ~25 μL was deposited on the membrane surface, and the contact angle between the water drop and the membrane surface was measured.

2.5 Transport Experiment

The experimental transport studies were carried out in a membrane cell consisting of two compartments of 300 mL capacity each (Fig. 2). The effective geometrical area of the PIM separating the two compartments joined by glass flanges was 9.62 cm^2. The feed and strip solutions were mechanically stirred at an optimum speed of 100 rpm at ambient temperature (24 ± 1 °C). The metal concentration was evaluated by sampling at different time intervals aliquots of 1 ml each from the feed and strip solutions and analyzed with a PerkinElmer ICP-OES. For the kinetics test, a phosphoric acid feed solution with a concentration of 0.5 M and a uranium concentration of 30 mg/L and a 50% concentrated phosphoric acid receiving solution free of any impurities were selected.

The percentage of uranium ions removed from the feed solution (i.e. the so-called removal factor) is determined according to [16] :

$$R\ (\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (1)$$

The percentage of uranium ions transported from the feed to strip solution (i.e. the recovery factor) is defined as follows:

$$\text{Recovery Factor } (\%) = \frac{C_s}{C_0} \times 100 \quad (2)$$

In the above relations, C_{0f}, C_f and C_s are respectively the initial concentration of uranium in the feed phase, the concentration of uranium in the feed phase at time t and the concentration of uranium in the receiving phase at time t.

The initial flux is obtained from equation (3)[17]:

$$J = Pf.\ Cf \quad (3)$$

In this relation, J is the flux, P_f is the diffusion coefficient and C_f is the metal ion concentration in the feed section. Alternatively, the initial flux (J) can be calculated by the following equation:

$$\text{Flux} = \frac{V \times C_s}{A \times t} \quad (4)$$

Also, V is the volume of the feed and A is the effective surface of the membrane (the surface in contact with the solution and the interface between the two solutions).

The flux can also be obtained by equation 5[18]:

$$J = -\left(\frac{1}{Q}\right).\frac{dV_f C_f}{dt} \quad (5)$$

In this relationship, V_f is the volume of the feed and Q is the surface area in contact with the membrane and the feed solution.

By combining relations 4 and 5, we will have:

$$\ln\frac{V_{f,0}\ C_{f,0}}{V_{f,t} C_{f,t}} = \frac{QP_f t}{V} \quad (6)$$

In this relation, $V_{f,0}$, $C_{f,0}$, Vf,t and $C_{f,t}$ are the volume and concentration of metal ions in the feed phase at the beginning of the experiment and time t, respectively. If the volume of the feed phase does not change much during the experiment and we ignore its changes, equation 6 will be as follows[19]:

$$\text{Ln}\left(\frac{C_{f,t}}{C_{f,0}}\right) = -\left(\frac{Q}{V_f}\right) P_f t \quad (7)$$

The Danesi model has been used to investigate kinetics. The Danesi equation follows the first order kinetics, whose general form is given in Equations 8 and 9 for adsorption and desorption, respectively[20-22]:

$$\frac{dc_f}{d_t} = -\ k_1 c_f \quad (8)$$

$$\frac{dc_s}{d_t} = \frac{v_f}{v_s} k_1 c_f \quad (9)$$

By obtaining the k_1 coefficient, the penetration coefficient (P_1) can be calculated from equation 10:

$$P_1 = k_1 \frac{v_f}{A} \quad (10)$$

With P_1, the maximum initial flux will also be obtained from equation 11:

$$J_m = -\frac{v_f}{A}\frac{dc_f}{dt} = P_1 c_{f,t=0} \quad (11)$$

In relation 11, J_m is equal to the maximum initial flux and A is equal to the surface area in contact between the feed and receiving phases, which will actually be the effective surface of the membrane.

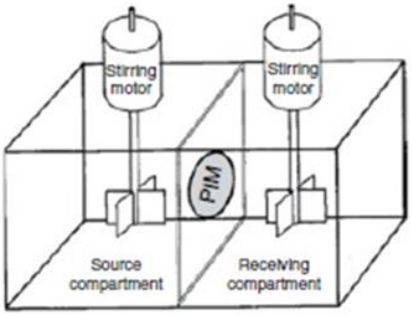

Fig. 2. Schematic of an extraction-rejection system with a polymer membrane[12]

3. RESULTS AND DISCUSSION

3.1 Membrane Extraction Of Uranium

The proposed mechanism of uranium extraction by D2EHPA is that the uranyl ion in phosphoric acid has different complexes. As Thamer suggested [23], in phosphoric acid with concentrations of 0.5 to 3 M, uranium can be present in the forms of $UO_2H_2PO_4^+$ and $UO_2(H_2PO_4)_2$. Therefore, in the feed phase, the uranium-phosphate complex can be separated as follows:

$UO_2H_2PO_4^+ \Leftrightarrow UO_2^{2+} + H_2PO_4^-$

$UO_2(H_2PO_4)_2 \Leftrightarrow UO_2^{2+} + 2H_2PO_4^-$

The D2EHPA extractant present inside the membrane, which is abbreviated as H_2R_2, can be separated as follows:

$H_2R_2 \Leftrightarrow HR_2^- + H^+$

Therefore, it can be predicted that the UO_2^{2+} ion will react with HR_2^- according to the following relationships:

$UO_2H_2PO_4^+ + 2\ H_2R_2 \Leftrightarrow UO_2(HR_2)_2 + H_3PO_4 + H^+$

$UO_2(H_2PO_4)_2 + 2H_2R_2 \Leftrightarrow UO_2(HR_2)_2 + 3H_3PO_4$

The $UO_2(HR_2)_2$ complex is formed at the interface of the membrane with the feed phase. Due to the difference in concentration between the two phases, this complex moves towards the interface between the membrane and the receiving phase, where it is decomposed due to the high concentration of acid and uranium enters the receiving phase in the form of a new complex. The proposed reactions for the transfer of uranium in the receiving phase are according to the following relationships:

$UO_2(HR_2)_2 + 2H_3PO_4 \Leftrightarrow UO_2(H_2PO_4)_2 + 2\ H_2R_2$

$UO_2(HR_2)_2 + 3H_3PO_4 \Leftrightarrow UO_2(H_2PO_4)_2.H_3PO_4 + 2H_2R_2$

In PIM, the polymer ensures the mechanical resistance of the membrane, the carrier is responsible for the complexation and the transport of the target metal ions. As is known, the transport rate through PIMs is affected by different parameters, such as the composition of the membrane (in terms of the concentration of the carrier, type and concentration of the plasticizer, and the kind of polymer matrix), and the properties of the feed and the receiving phases. In this study, we used three grades of NPEs for the preparation of PIM. It seems that the simultaneous hydrophilic and hydrophobic property of NPEs, which is related to the two alkyl and polyethoxy branches of this material, makes it highly attractive for use as a modifier in the composition of the membrane. In our previous study[14], the experimental design (Combined Design model) was used to evaluate the effects of D2EHPA and NPE content, acid concentration in the feed and receiving solution, uranium concentration, and stirring speed. The results showed that increasing the acid concentration in the feed phase and the receiving phase is inversely and directly proportional to efficiency, respectively. This behavior is caused by the difference in the concentration of H^+ ions in the feed phase compared to the receiving phase, so that the lower the concentration of this ion in the feed phase or the higher the concentration in the receiving solution, the faster the reaction and the higher the extraction efficiency in a certain time interval. Also, the results of increasing the uranium concentration in the feed phase from 30 mg/L to 90 mg/L, according to the results obtained, caused a slight decrease in the extraction efficiency. The reason for this decrease can be attributed to the saturation of the extracting ligands at the contact surface with the feed solution and also the decrease in the removal efficiency due to the influx of uranium-containing complexes towards the strip solution. This issue has been reported in similar studies on uranium and cobalt [24, 25]. The experimental design results showed that the highest uranium extraction was achieved at an acid concentration of 49 g/L in the feed solution and 667.5 g/L in the receiving solution, with an initial concentration of 30 ppm of uranium and a stirring speed of 100 rpm.

The concentration-time profile of uranium transport was studied over a period of 30 h under optimum conditions for each PIM in the aqueous feed, and strip phases is presented in Figure 3, and the values of the removal and recovery factor and the initial flux are gathered in Table 2. The kinetics of the transport process across PIMs can be described as a first-order reaction, which was confirmed by high values of the coefficient of determination (r^2) ≥ 0.96. As seen, U(VI) is transported into the strip phase with an increase in time, and there was almost 70% transport of U(VI) at 8 h of transport in the PVC-D2EHPA PIM. As seen in Figure 3, the incorporation of all of the modifiers improves the membrane permeability to uranium compared to the PVC-D2EHPA PIM. It can be seen that the increase occurs in the order NPE6 < NPE10 < NPE20. As seen, the addition of NPE6 into the membrane slightly improves the membrane performance compared to the corresponding PVC/D2EHPA PIM. It is interesting to note that all of the modifiers tested, except for NPE6, significantly improved the extraction as well as the flux of uranium when compared to a PVC-D2EHPA PIM. The initial flux for NPE20 and NPE10 are 70% and 65% higher than that of the PIM without a modifier. In addition, a removal factor > 95% and a recovery factor > 80% are obtained (Table 2). The viscosities of NPE6, NPE10, and NPE20 (210–240, 230–260, and ~110 c.st, respectively) are substantially higher than that of D2EHPA (~35 c.st) [26]. Although NPE6 has a lower viscosity, the influence on uranium transport performance is lower than that of other modifiers. This would suggest that the viscosity of the modifier is relatively unimportant in improving the flux through the membrane. Similarly, changes in molecular weight cannot fully explain the observed trends. It is known that a PIM exhibiting a hydrophilic character promotes the penetration of water and the hydration of the PIM, thereby facilitating the transport of target ions, while a hydrophobic character ensures good stability by delaying the leakage of the liquid phase (carrier and modifier) into the adjacent

aqueous phases. Therefore, we suggest that the higher transport of uranium in these PIMs can be attributed to the high hydrophilicity character of the modifier. Table 2 summarizes the water contact angle measurements for different PIMs. The water contact angle obtained for the D2EHPA/PVC membrane was 40 ± 2, indicating the hydrophilic character of the neat PVC membrane. The addition of different modifiers into the PVC membrane results in a lower contact angle, demonstrating the improved wettability of the PIM surface. Therefore, it is proposed that NPEs, owing to their polar hydroxyl groups, enhance membrane hydration. This hydration induces a softening effect, which facilitates the transport of the uranium–D2EHPA complex and consequently increases the flux through the membrane. However, despite the highest flux in PVC/D2EHPA/NPE20, this PIM was not mechanically strong and had a very oily surface and was slightly opaque. Previous studies have also indicated that such surface characteristics can compromise membrane stability and promote the leaching of the extractant into the surrounding phases [15-17]. In contrast, the PVC/D2EHPA/NPE6 and PVC/D2EHPA/NPE10 PIMs had a transparent and non-oily surface. Therefore, the most compatible PIM was found to be those containing NPE10. Taking all this into account, one may conclude that the uranium transport is greatly improved and occurs more easily in the presence of all NPEs.

Table2. Performance of the fabricated PIMs along with their kinetic results

Membrane	Removal Factor (%)	Recovery Factor (%)	Initial Flux (mol.m^{-2}. s^{-1})	K(h^{-1})	R^2
55PVC/45D2EHPA	70.5	58.8	4.9×10^{-7}	0.045	0.99
56PVC/39D2EHPA/5NPE6	76.6	63.2	5.2×10^{-7}	0.048	0.99
56PVC/39D2EHPA/5NPE10	95.5	80.5	8.1×10^{-7}	0.074	0.97
56PVC/39D2EHPA/5NPE20	98.7	82	8.8×10^{-7}	0.081	0.96

Table3. Water contact angle, thickness, and appearance of the fabricated polymeric membranes

PIM composition			Contact Angle(degree)	Thickness(μm)	Appearance
PVC(%)	D2EHPA(%)	NPE(%)			
55	45	0	40±2	100±5	Flexible, Transparent
56	39	5(NPE6)	29±3	100±5	Flexible, Transparent
56	39	5(NPE10)	15±1	100±5	Flexible, Transparent
56	39	5(NPE20)	10±4	100±5	Flexible, Oily surface

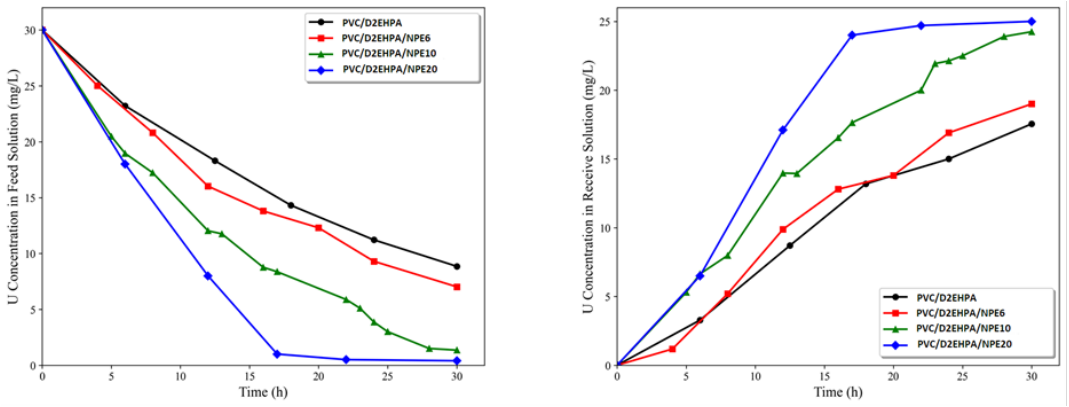

Fig. 3. Time-course analysis of uranium concentration in the feed phase for different PIMs

St. John et al. reported that the addition of various commercial plasticizers, dioctyl phthalate (DOP), dioctyl sebacate (DOS), and o-nitrophenyloctyl ether (NPOE), into PVC/D2EHPA PIM only slightly improved the transport of uranium (VI) from sulfate solutions. After the addition of NPOE into the PIM, the initial flux value for the PVC/D2EHPA PIM increased from 1.85 to 3.04. In some cases, with tris(2-ethylhexyl) phosphate (TEHP), a decrease was observed, which does not justify the use of these expensive plasticizers for the production of PVC/D2EHPA PIM [19]. In contrast, this result indicates a 65% increase in the initial flux through the addition of NPE10 to the PIM.

As shown in Table 4, the permeability of the PVC/D2EHPA/NPE10 PIM is at a desirable level compared to similar PIMs in uranium extraction. It is important to note that the feed and receiving solutions used for other membranes were

generally sulfuric acid, but working in phosphoric acid has some challenges. D2EHPA, which is a weak acid, can be protonated in the presence of phosphoric acid. This proton production can lead to the formation of a water-friendly environment in the membrane, potentially changing its permeability and selectivity for ions. The reaction can be considered as the following relationship:

$D2EHPA+H_3PO_4 \rightarrow D2EHPA\ H^+ + H_2PO_4^-$

This reaction may not only affect the ion transport properties but also lead to the dissolution of D2EHPA from the membrane network into the solution, reducing its concentration and effectiveness as a carrier[27].

Table4. Comparison of the membrane permeability fabricated in this study with those reported in similar studies

Membrane composition (%w/w)	Permeability [$m.s^{-1}$]	References
PVC =56 / NPE10= 5 / D2EHPA=39	6.43×10^{-6}	Present Research
PVC= 55 / D2EHPA=45	6.96×10^{-6}	[19]
TBP=75 / PVC= 25	2.4×10^{-6}	[28]
CTA=40 / NPOE= 42 / TOPO= 18	2.15×10^{-6}	[24]
CTA= 38 / TBP= 62	4.76×10^{-6}	[25]
PVC= 36.78 / POE= 23.22 / Alamine336= 40	6.74×10^{-6}	[29]

3.2 Membrane stability

One of the key factors determining the suitability of PIMs for industrial separation processes is their stability and, consequently, their reusability[30]. Accordingly, considerable efforts have been made by several researchers to enhance the stability of PIMs[31-33]. Given that NPE10 was observed to be the best modifier for the transport of the uranyl-D2EHPA complex across the D2EHPA/PVC PIM, the stability of the D2EHPA/PVC/NPE10 and D2EHPA/PVC membranes was investigated. Figure 4 shows the results of 6 cycles (30 h for each cycle) of extraction using PIMs. As seen, the percentage of uranium extraction decreases by about 20% after three cycles of D2EHPA/PVC/NPE10 PIM use. The value of percentage of uranium extraction is equal to 86% and 72.6, respectively, in the first cycle. After the third cycle, the percentage of uranium extraction is equal to 70% and then the value is almost constant until the sixth cycle. The decrease in stability of the membrane may be caused by the partitioning of the D2EHPA carrier as well as NPE10 between the membrane and the aqueous solution. In contrast, the percentage of uranium extraction value in the D2EHPA/PVC PIM continuously decreased from 77% for the first cycle to 53% in the sixth cycle.

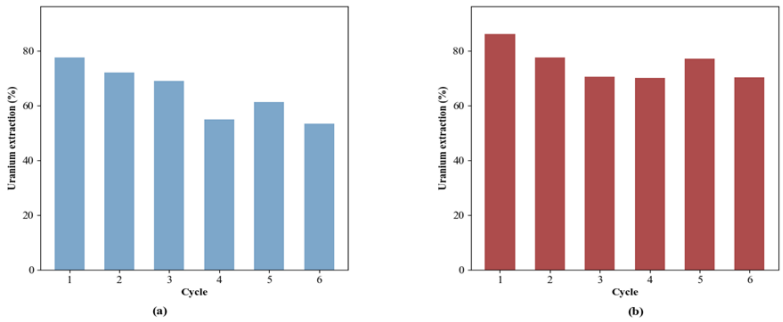

Fig. 4. Percentage of uranium extraction in seven 30 hours consecutive cycles for : (a) PVC/D2EHPA, and (b) PVC/D2EHPA/NPE10 PIMS.

The question is whether the reason for such a difference in the transport behavior and stability of the PIMs studied results from differences in their morphology and structure. Therefore, the microstructure of the membranes containing NPE6 and NPE10, which determines the distribution of a carrier in the polymer matrix and ultimately affects the efficiency of ion transport, was characterized by different techniques: AFM, FE-SEM, and FTIR measurements.

4. CHARACTERISTIC OF MEMBRANE SURFACE AND STRUCTURE

FT-IR spectroscopy provides information about the interaction/complexation between various constituents in the PIM. In the FT-IR spectrum of the PVC/D2EHPA PIM (Fig. 5), peaks at 695 and 865 cm^{-1} are assigned to the stretching mode of C-Cl. In addition, the stretching vibrations of the CH_2 group have been reported at 2922 cm^{-1} and 2961 cm^{-1}. The vibrations of the -CH_2 group are observed as (scissor-like in-plane bending vibrations) at 1426 cm^{-1}, while twisting vibrations of the C-H group at 1380 cm^{-1} are attributed to the polyvinyl chloride (PVC) matrix [34-36]. Additionally, a peak at 1021 cm^{-1} corresponds to the P–O–C and P–O–H functional groups, and the band at 1231 cm^{-1} is assigned to the P=O functional group, indicating the presence of D2EHPA within the membrane structure. The

stretching vibration mode of alkyl groups was observed at 2930 cm^{-1}, while the $-CH_2$ deformation modes were observed at 1462 and 1375 cm-1[37, 38]. Notably, there is an overlap of characteristic peaks from both PVC and D2EHPA around the 2930 cm^{-1} region. For the PVC/D2EHPA/NPE10 and PVC/D2EHPA/NPE6 PIMs, the absorption peak at 3495 cm^{-1} is attributed to O-H group vibrations [39, 40]. In addition, the band at 1021 cm^{-1}, attributed to the P–OH and P–O–C groups of D2EHPA, was shifted to a higher wavenumber and overlapped with the peak at 1030 cm^{-1}. The latter band, assigned to C–O–C vibrations [41, 42], corresponds to the modifier, indicating its incorporation into the membrane structure. Finally, in the PVC/D2EHPA/NPE6 membrane, the peak at 1668 cm^{-1} was broadened and overlapped with the peak at 1773 cm^{-1}, indicating the presence of hydrogen bonding between D2EHPA and NPE6. These observations confirm that only weak physical interactions are involved.

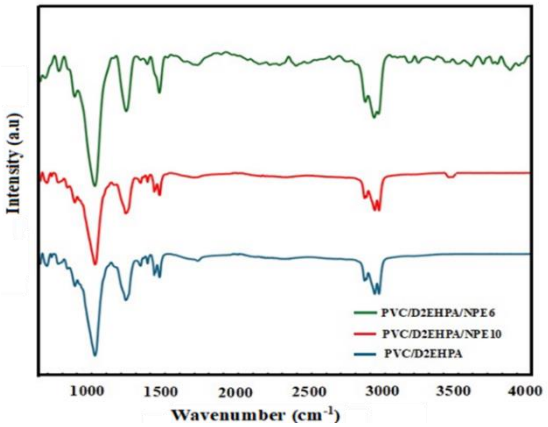

Fig. 5. FTIR spectrum of the PIMS

Figure 6 shows the membrane topography at a scale of 5 µm/div. The root-mean-square roughness (RMS) and average roughness (Ra) values for all membrane types are presented in Table 5. The AFM image of the PVC-D2EHPA PIM reveals a smooth surface with only minor surface defects, such as small, isolated cavities or nodules. In contrast, the AFM images of the PVC/D2EHPA/NPE10 and PVC/D2EHPA/NPE6 PIMs display surface morphologies characterized by rougher areas. This is attributed to the different rates of solvent evaporation. Additionally, D2EHPA may act as a plasticizer, with its molecules preferentially migrating to the membrane surface, thereby increasing roughness. Similar findings have been reported in previous studies [43, 44]. It is noteworthy that PIMs containing NPE6 and NPE10 exhibit a wider height distribution, indicating a non-homogeneous surface. This surface heterogeneity may facilitate the effective transport of metal ions across the membranes. The increase in roughness observed in PIMs after the addition of modifiers can be attributed to the enhanced migration of both D2EHPA and the modifiers toward the membrane surface. It has been reported that rougher PIM surfaces enhance the effective contact area with both the feed and receiving solutions, thereby facilitating ion transport across the membrane[45, 46]. Although the surface roughness of the PVC/D2EHPA/NPE6 PIM is greater than that of the PVC/D2EHPA/NPE10 PIM, the two membranes differ significantly in terms of microstructure and hydrophilicity. These differences ultimately lead to variations in uranium flux (see Fig. 3).

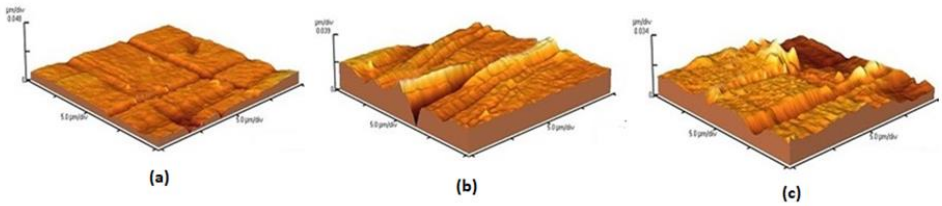

Fig. 6. AFM image of PVC/D2EHPA(a), PVC/D2EHPA/NPE10(b) and PVC/D2EHPA/NPE6(c) PIMs

Table 5. Mean roughness values for membranes

Membrane composition (%w/w)	R_a (nm)	RMS (nm)
55 PVC⁄45 D2EHPA	2.05	5.01
PVC 56/D2EHPA 39/NPE 10 5	4.21	6.86
PVC 56/D2EHPA 39/NPE6 5	6.12	8.1

The surface of the PVC/D2EHPA PIM appears smooth and relatively uniform. Spherically shaped droplets with uniform distribution are observed, indicating that D2EHPA is well-dispersed within the polymer matrix (Fig. 7a). The cross-sectional view of this PIM reveals a relatively layered and compact structure with no visible porosity. After the addition of NPE10, both the size and number of D2EHPA domains increased. The droplets appear more irregular and tend to coalesce in the presence of NPE10. The cross-sectional image of

the PVC/D2EHPA/NPE10 PIM reveals a dense and relatively uniform morphology (Fig. 7d). It is suggested that the addition of NPE-10 enhances the mobility of D2EHPA, leading to the formation of larger and more non-uniform domains. In the PVC/D2EHPA/NPE6 PIM, the dispersion of D2EHPA droplets appears relatively more uniform compared to the membrane containing NPE-10. The cross-sectional image shows a layered and compact structure (Fig. 7f).

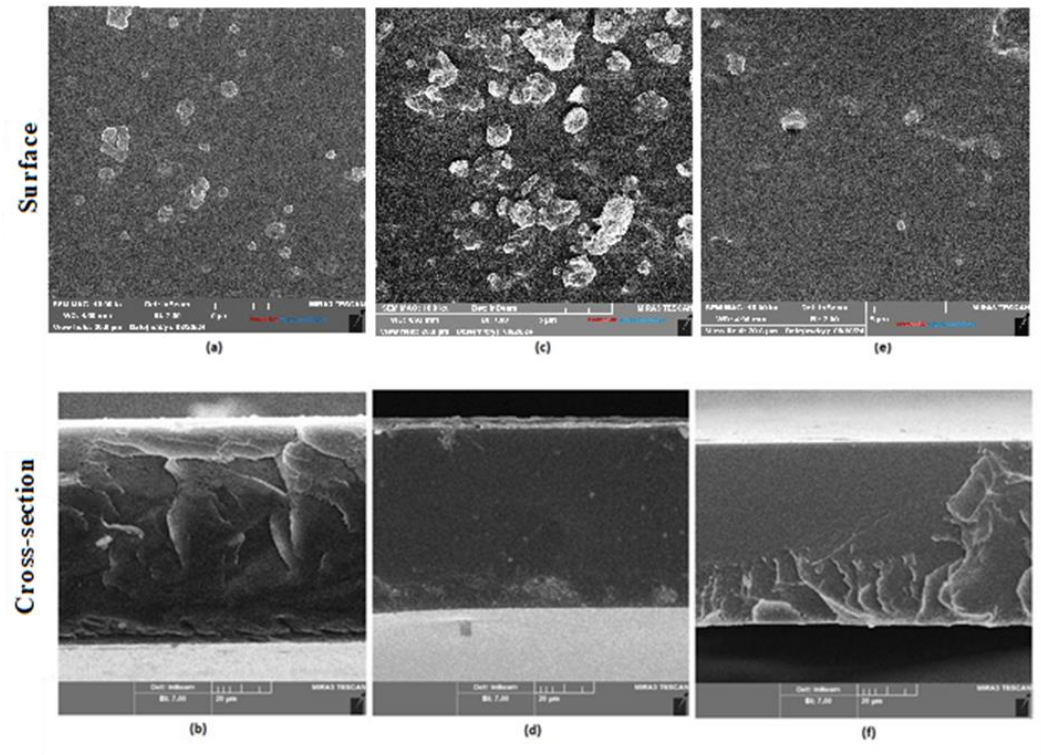

Fig. 7. SEM images of surface and cross-section of (a&b) PVC/D2EHPA, (c&d) PVC/D2EHPA/NPE10, and (e&f) PVC/D2EHPA/NPE6 PIMS.

5. CONCLUSION

The PIMs based on PVC were fabricated using D2EHPA as an extractant for uranium transport from acidic phosphoric solutions. Different Nonylphenol ethoxylates (NPEs) were introduced as alternatives to conventional modifiers used in PIMs. The resulting PIMs were characterized using various techniques to provide information on their physicochemical properties. FTIR analysis indicated that all modifiers were incorporated into the membrane via weak hydrogen bonding and van der Waals interactions, without any chemical bonding. Cross-sectional images of the PIMs showed uniform surface areas that appeared dense and without apparent porosity.The results obtained in this study indicate that the presence of polar hydroxyl groups in NPEs affects membrane wettability and, consequently, the transport properties of the PIMs. It was found that the PVC/D2EHPA/NPE10 membrane achieved an initial uranium flux of 8.1×10^{-7} $mol \cdot m^{-2} \cdot s^{-1}$, representing a 65% increase over the unmodified PVC-based PIM under optimal conditions (feed: 49 $g \cdot L^{-1}$ H_3PO_4; strip: 667.5 $g \cdot L^{-1}$ H_3PO_4; 30 ppm U(VI); 100 rpm; 24 ± 1 °C). The removal factor exceeded 95%, and the recovery factor surpassed 80%, highlighting the markedly enhanced transport performance. Long-term stability tests over six 30-hour cycles demonstrated that the PVC/D2EHPA/NPE10 PIM retained over 70% of its initial extraction efficiency, whereas the unmodified membrane declined to 53% under the same conditions. This improved durability can be attributed to the water-plasticizing effect of NPE10. Thus, NPE10 can effectively replace conventional liquid plasticizers while simultaneously improving uranium transport performance.

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