Pervaporation of toluene and iso-octane through poly(vinyl alcohol)/graphene oxide nanoplate mixed matrix membranes: Comparison of crosslinked and noncrosslinked membranes

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ABSTRACT: Removal of aromatic compounds from fuel is an essential requirement in new environmental policies. In the present study, poly(vinyl alcohol)/graphene oxide (GO) mixed matrix membranes were prepared and applied to the separation of toluene from iso-octane by pervaporation, considering the similarity and interaction between graphene and aromatics. The effects of crosslinking and GO content on separation efficiency have been investigated in detail. Owing to the high affinity of GO with toluene through s and π bonds, the selectivity of the membranes was increased by incorporating a low amount of GO. The results also indicated that noncrosslinked membranes have higher selectivity and permeation flux due to higher crystallinity and also have lower mechanical properties. © 2017 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 2018, 135, 45853.

KEYWORDS: fullerenes; graphene; membranes; nanotubes

INTRODUCTION

According to new environmental requirements, light aromatic hydrocarbons should be reduced in motor gasoline; therefore, refineries need to employ new facilities to meet gasoline standards.1-3 Conventional processes such as distillation are inappropriate for the separation of aromatic hydrocarbons from aliphatic mixtures. The problem in this case arises from the fact that the system includes compounds with close boiling points and azeotropic compounds.4 Other industrial processes such as liquid–liquid extraction, extractive distillation, and azeotropic distillation are too complex and expensive and generally utilize contaminant solvents; this problem becomes more challenging when fuel with very low aromatic content is required.5

One of the potential candidates to be applied to industrial aromatic/aliphatic separation is pervaporation. This method is very efficient in terms of initial investment and energy consumption. In addition, since there is no need for solvents, pervaporation is an environmentally friendly process.6 Consequently, this method could be very effective in separating aromatic and aliphatic compounds in refineries and petrochemical plants.3,7

Pervaporation of organic–organic mixtures with satisfactory selectivity and permeability is still under investigation, and the separation performance of the membranes, in most cases, is below the standards expected by industries. Accordingly, more innovative solutions are required to meet industrial requirements.8

High permeability and selectivity as well as low swelling are the main characteristics of the membranes used for organic–organic separation. For this purpose, different physical and chemical approaches have been developed to modify the structure of the membranes. Introducing inorganic compounds into the polymer matrix, which can create charge-transfer complexes with aromatics, is one of the efficient approaches that can significantly improve the solubility and mechanical properties of the membranes.9,10 So far, several studies have focused on the separation of aromatic from nonaromatic mixtures using mixed matrix membranes. A number of important studies relating to hybrid membranes for the separation of aromatics from nonaromatic systems are presented in Table I.

Carbon materials are one of the most effective compounds to be employed in the separation of aromatics. These materials have a structure similar to the aromatics, and they can interact with aromatic compounds through s and π bonds. Graphene, which was developed in recent years, is a layer of carbon graphite with a hexagonal structure and is commonly produced by exfoliating graphite.20 For polymer composites, a functionalized form of graphene, graphene oxide (GO), is normally used because of its good compatibility with a polymer matrix
through its functional groups. The surface of GO can be treated to enhance compatibility with polymers or solvents. For instance, Xue et al. treated GO with tert-butyl isocyanate to improve its dispersibility in both water and organic solvents.

Considering the high specific surface area and aspect ratio of graphene (41,000), a large number of aromatic molecules could be adsorbed on GO, resulting in improved membrane performance for the separation of aromatics.

As indicated in Table I, PVA is the most common polymer utilized in the separation of aromatic compounds from nonaromatic ones. PVA is a hydrophilic membrane with a remarkable resistance to organic mixtures; as a consequence, swelling is not a challenge to PVA. Furthermore, PVA is permselective toward aromatics, with its polar structure.

The polymer chains in PVA are normally crosslinked using glutaraldehyde to protect the membranes against extra swelling, especially when they are employed for the separation of hydrophilic mixtures. Crosslinking materials are also added to PVA membranes to improve their mechanical properties. Nevertheless, crosslinking of PVA membranes may change the intrinsic characteristic of the membranes and have an influence on separation efficiency.

In this work, GO nanoplates have been implemented into crosslinked and noncrosslinked PVA membranes for the separation of aromatic/aliphatic mixtures (toluene and iso-octane). The transfer coefficients of organic compounds into the membranes are investigated using an activity coefficient model. This is the first time that the effect of crosslinking of PVA on the pervaporation of organic mixtures has been studied. Moreover, GO is a relatively novel material, and PVA/GO has never been investigated in the form of a mixed matrix membrane. Our findings confirm the capability of GO for the adsorption and separation of aromatic compounds.

### EXPERIMENTAL

#### Materials

Poly(vinyl alcohol), toluene (methylbenzene) with >99% purity, and hydrochloric acid (38%) were supplied by Merck Millipore (Mumbai, India). Iso-octane (2,2,4-trimethylpentane) with >99% purity was purchased from SRL Chemical Co. (Mumbai, India). Glutaraldehyde (25 wt % in H2O) was provided by Sigma Aldrich Chemicals (Bangalore, India). Graphene oxide (>99% purity) was supplied by Payam Persian Ins. (Tehran, Iran).

#### Membrane Preparation

The procedure to prepare appropriate mixed matrix membranes was developed through trial and error. The membranes were finally prepared according to the following procedure.

First, PVA was dissolved in 30 cm³ of distilled water at 363 K, and mechanical stirring was continued for about 1 h to obtain a homogeneous solution. Afterward, the solution was cooled down to room temperature. GO was dispersed in 20 cm³ of water, using sonication for 30 min (ultrasonic homogenizer 400 w, 20 kHz, Topsonic, Tehran, Iran). Subsequently, the dispersed GO was added to the polymer solution and stirred for 30 min. To prepare crosslinked membranes, 0.8 cm³ of glutaraldehyde (as crosslinker) and 0.4 cm³ of 0.5 M HCl (as initiator) were added, and the solution was stirred for 30 min. The solution was finally cast on petri dishes and dried at room temperature for 4 days. The final thickness of the prepared membranes was 100 µm.

### Table I. Previous Works on Separation of Aromatic and Nonaromatic Compounds Using Hybrid Membranes

<table>
<thead>
<tr>
<th>Reference</th>
<th>System (binary liquid mixtures)</th>
<th>Matrix</th>
<th>Inorganic particles or nanoparticles</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>Benzene/cyclohexane</td>
<td>PVA</td>
<td>AgNO₃</td>
</tr>
<tr>
<td>12</td>
<td>Benzene/cyclohexane</td>
<td>Nylon 6</td>
<td>Carbon graphite</td>
</tr>
<tr>
<td>1</td>
<td>Benzene/cyclohexane</td>
<td>Nafion</td>
<td>AgNO</td>
</tr>
<tr>
<td>13</td>
<td>Benzene/cyclohexane</td>
<td>Neosepta</td>
<td>Cu(II)</td>
</tr>
<tr>
<td>14</td>
<td>Benzene/cyclohexane</td>
<td>PVA</td>
<td>Carbon molecular sieve</td>
</tr>
<tr>
<td>9</td>
<td>Benzene/cyclohexane</td>
<td>PVA and chitosan</td>
<td>Carbon graphite</td>
</tr>
<tr>
<td>15</td>
<td>Benzene/cyclohexane</td>
<td>PVA</td>
<td>β-CD-CNT</td>
</tr>
<tr>
<td>16</td>
<td>Benzene/cyclohexane</td>
<td>PVA</td>
<td>MWNT(CS)</td>
</tr>
<tr>
<td>17</td>
<td>Benzene/cyclohexane</td>
<td>PVC</td>
<td>Rh/H-zeolite</td>
</tr>
<tr>
<td>18</td>
<td>Toluene/heptane</td>
<td>PVA/ polyacrylonitrile (pore-filling)</td>
<td>GO</td>
</tr>
<tr>
<td>19</td>
<td>Benzene/cyclohexane</td>
<td>Chitosan</td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Formulations of Prepared Membranes

<table>
<thead>
<tr>
<th>Sample code</th>
<th>GO Content (% of polymer)</th>
<th>Crosslinker, initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td>F-1</td>
<td>0</td>
<td>Glutaraldehyde, HCl</td>
</tr>
<tr>
<td>F-2</td>
<td>0.5%</td>
<td>Glutaraldehyde, HCl</td>
</tr>
<tr>
<td>F-3</td>
<td>1%</td>
<td>Glutaraldehyde, HCl</td>
</tr>
<tr>
<td>F-4</td>
<td>1.5%</td>
<td>Glutaraldehyde, HCl</td>
</tr>
<tr>
<td>F-5</td>
<td>2%</td>
<td>Glutaraldehyde, HCl</td>
</tr>
<tr>
<td>F-6</td>
<td>0</td>
<td>None</td>
</tr>
<tr>
<td>F-7</td>
<td>0.5%</td>
<td>None</td>
</tr>
<tr>
<td>F-8</td>
<td>1%</td>
<td>None</td>
</tr>
<tr>
<td>F-9</td>
<td>1.5%</td>
<td>None</td>
</tr>
<tr>
<td>F-10</td>
<td>2%</td>
<td>None</td>
</tr>
</tbody>
</table>
Membrane Characterization

Scanning Electron Microscopy. The morphology and dispersion of GO nanoplates and also the interface between polymer and nanoplates were investigated by field emission scanning electron microscopy (FE-SEM) using a Hitachi scanning electron microscope model S-4160 (Tokyo, Japan). For the FE-SEM analysis, the samples were gold-coated using a DSR1 device (Nano-Structured Coating Co., Tehran, Iran).

X-ray Diffraction. X-ray diffraction analysis (XRD) was applied to analyze the crystalline structure of the membranes with and without nanoplates. The exfoliation of GO sheets was also investigated via XRD. An X’Pert PRO MPD (PANalytical, Almelo, Netherlands) was employed for the XRD analysis. Additionally, X’Pert High Score Plus (V. 3) software was applied to process the data.

Degree of Swelling. To evaluate the amount of solvent adsorbed into the membranes and accordingly the interaction between membranes and the liquid solution, the degree of swelling (%DS) was calculated for the samples in different feed compositions. The swelling experiments were simultaneously performed on all samples at room temperature for 48 h. Subsequently, the degree of swelling was calculated as follows:

\[
\text{Degree of swelling (DS)} = \frac{W_s - W_d}{W_d} \tag{1}
\]

where \(W_s\) and \(W_d\) represent the weights of the swollen and dry membranes, respectively.

Tensile Testing. The mechanical properties of the membranes, tensile strength and elongation at break, were evaluated by tensile testing using a Hiwa 200 device (Hiwaco, Tehran, Iran).

Pervaporation Experiments

Pervaporation experiments were performed using a laboratory pervaporation setup. Figure 1 demonstrates the major parts of the laboratory setup, the details of the membrane module, and the cold trap. The effective area of the membrane module is 9 cm² equipped with a metal grid for mechanical support. A nitrogen flask containing a Friedrich condenser was employed as a cold trap. The pressure on the permeate side of the module was kept at 0.15 torr, using a vacuum pump. The time required to achieve steady-state conditions of pervaporation was considered to be 2 h, and the experiments were performed at a constant temperature of 330 K. The weight of permeate collected in the cold trap was measured with an electronic analytical balance and analyzed by a refractometer (E-line ATC, Bellingham + Stanley Ltd., Tunbridge Wells, United Kingdom) to determine the composition.

RESULTS AND DISCUSSION

XRD

The results of the XRD analysis are provided in Figure 2. As demonstrated, the trends of diffraction index in pristine PVA, crosslinked PVA, and PVA with GO nanoplates are relatively similar. For the samples F-1, F-3, F-6, and F-8, the peaks of the diffraction index are observed at 2\(\theta\) = 19.51, 2\(\theta\) = 19.48, 2\(\theta\) = 19.49, and 2\(\theta\) = 19.6, respectively. These variations show the alteration of the average intersegment spacing of the polymer chains. The calculation of crystallinity from the diffraction index illustrates that incorporation of GO in PVA has no considerable impact on the crystallinity of either crosslinked and noncrosslinked membranes. The crystallinities of the samples F-1, F-3, F-6, and F-8 were found to be 51.16%, 52.30%, 73.04%, and 72.21%, respectively. This also indicates that crosslinked membranes have lower crystallinity than noncrosslinked membranes. This may attributed to the fact that the rate of the crosslinking reaction with the current amount of initiators and consequently immobilization of polymer chains is higher than the rate of crystallization.
In the literature, it has been investigated that when sonication of GO leads to achieving monolayer GO sheets, the diffraction peak of GO will not be observed. The lack of the GO peak in both crosslinked and noncrosslinked membranes indicates the high exfoliation efficiency of nanoplates and the presence of monolayer sheets. Similarly, for carbon nanotubes (CNT), Ge et al. reported that the presence of nanoparticles has no considerable effect on crystallinity, and the XRD pattern of the polymer shows no change with the content of CNT.

**FE-SEM**

Figure 3 shows the FE-SEM results for the samples. As indicated, functional groups in GO provide compatibility between polymer matrix and nanoplates, so no considerable agglomeration or interface defect is observed in the samples. Nonselective voids as a consequence of poor polymer–nanoparticle interaction leads to reduced selectivity of the membrane. The functional groups in GO allow suspension of nanosheets in a polar solvent during membrane preparation. Consequently, there is

![Figure 3. FE-SEM images of the samples.](image-url)
an acceptable dispersion of nanosheets in the polymer matrix. The sizes of GO nanoplates are normally in the range of 100 to 500 nm. Moreover, there is no considerable difference between the SEM images of crosslinked and noncrosslinked membranes.

Swelling Test
The results of the swelling experiments are illustrated in Figure 4. It is clear that the presence of GO in the PVA matrix leads to increasing swelling of the membranes. This is due to the high affinity of toluene and GO nanoplates and the creation of $s$ and $\pi$ bonds.\(^\text{18}\) Increasing swelling in solutions with higher amounts of toluene validates the affinity between GO and toluene. The differences between swelling of crosslinked and noncrosslinked membranes are also notable. Because the polymer chains in crosslinked membranes are more immobilized and controlled over swelling, the DS values in noncrosslinked PVA are higher than those of crosslinked PVA. In noncrosslinked membranes, the movement of polymer chains is unlimited, leading to higher plasticization of the polymer. By incorporation of 2 wt % GO, the swelling is enhanced up to 16.7% in the solution with 30 vol % of toluene.

Tensile Testing
The tensile strength of the samples could show the effect of GO nanoplates and also crosslinking on the mechanical properties of the membranes (Figure 5). The results generally show that the mechanical properties of noncrosslinked membranes are intensely affected by GO nanoplates, while GO has no significant impact on the mechanical characteristics of crosslinked membranes. As can be seen in Figure 5, the presence of GO increases the tensile strength of the membranes; the enhancement of tensile strength is remarkable in the noncrosslinked membrane. The crosslinked membranes have higher strength and are little affected by GO. The enhancement of strength confirms a high interaction between GO and the polymer because low interfacial properties would lead to reduced mechanical properties. These results are the complete opposite of the results obtained by adding rigid nanoparticles such as zeolites, which cause reduced tensile strength owing to rigidification of the polymer.\(^\text{27}\)

The maximum tensile strengths were found to be 105.2 Mpa and 102.6 Mpa for crosslinked and noncrosslinked samples, respectively. The results for elongation at break (Figure 6) indicate that the elongation of pristine noncrosslinked PVA is higher than that of crosslinked PVA and decreases with the content of GO. Nevertheless, the elongation of crosslinked membranes does not change significantly with the content of GO.

Pervaporation Results
The separation performance of the mixed matrix membranes was evaluated by separation factor or selectivity, as follows:

$$\alpha = \frac{y_{p,i}/y_{p,j}}{x_{i}/x_{j}}$$

(2)

In eq. (2), $y_{p,i}$ and $x_{i}$ represent the weight fractions of toluene (as the preferential permeate) and $y_{p,j}$ and $x_{j}$ represent the weight fractions of iso-octane (as the secondary permeate) in the permeate and feed, respectively.\(^\text{12,29}\)
The permeation flux was also calculated experimentally by the following equation:

\[ J = \frac{W}{At} \]  

where \( W \) is the weight (10\(^{-3}\) kg) of the permeate phase, \( t \) is the time (s) of pervaporation, and \( A \) is the effective area (10\(^{-4}\) m\(^2\)) of the membrane.

Figure 7 shows the separation factors of the mixed matrix membranes with different feed compositions (10 vol %, 20 vol %, and 30 vol % of toluene in the feed). As predicted, the high affinity of GO and aromatics has a remarkable impact on increasing the selectivity of PVA membranes.

The increase of selectivity as a result of interactions of nanoparticles with one component has been investigated in both gas and liquid media. For instance, the incorporation of TiO\(_2\) enhanced the hydrophilicity of membranes and increased the affinity to polar solvents such as ethanol.

In noncrosslinked membranes, the selectivity is enhanced to 11.05 by adding 0.5 wt % GO, which was the maximum value of selectivity obtained. In higher loadings of GO, the selectivity is somewhat lower than the maximum value, for the following reasons. Due to the strong interaction between GO and toluene, a large number of toluene molecules are adsorbed on GO and restricted from diffusing through the membranes. Moreover, the integrity of the membranes and also the compatibility of GO with the polymer matrix decrease in higher loadings of GO. Similarly, Ge et al. revealed that with a high content of carbon nanotubes, the agglomeration of nanoparticles caused blocking of the membrane and reduced both permeability and selectivity.

As indicated, the selectivities of noncrosslinked membranes are higher than that of the crosslinked ones. This shows that crystalline parts of the membrane have more of a contribution to separation and act as a filter to pass smaller molecules.

Normalized permeation flux values of the membranes are presented in Figure 8. As shown, the incorporation of GO nanoplates reduces the permeation flux of the membranes. This is mainly because nanoplates act as barriers and block some of the free passes of the membrane. Higher amounts of nanoplates result in a lower free volume in the membranes. The reduction of permeation flux could also be attributed to the high interaction between GO and toluene. As mentioned, the GO nanoplates adsorb and immobilize toluene molecules. Consequently, in high loadings of GO, higher amounts of toluene are adsorbed, and the permeation flux decreases. Blocking of the free volume of the membranes is due to the morphology of nanosheets, whereas nanoparticles normally increase the void concentration of the membranes by three mechanisms: (1) compression of the polymer chain, (2) weak interaction between nanoparticles and the polymer, and (3) the porous structure of inorganic nanoparticle such as zeolites. The voids act as a channel to transport molecules and increase permeability. Nevertheless, agglomerations of nanoparticles at high loadings may reduce the void fraction of the membrane. In the literature, different nanoparticles such as carbon nanotubes, zeolites, silica, alumina, Magnesium Oxide, and TiO\(_2\) and SiO\(_2\) are investigated that increase the permeability of the membranes. According to the size of the channels or the interaction between nanoparticles and feed, channeling of the membrane normally leads to decreased selectivity. Meanwhile, the enhancement of selectivity occurs due to the interaction of polymer or nanoparticle with one component.

The permeation flux of noncrosslinked membranes is higher than that of noncrosslinked ones. In swelled noncrosslinked

![Figure 7](wileyonlinelibrary.com)  
**Figure 7.** Separation factors of (a) crosslinked and (b) noncrosslinked membranes with different GO contents. [Color figure can be viewed at wileyonlinelibrary.com]

![Figure 8](wileyonlinelibrary.com)  
**Figure 8.** Normalized permeation flux of (a) crosslinked and (b) noncrosslinked membranes. [Color figure can be viewed at wileyonlinelibrary.com]
membranes with higher free area between amorphous chains, greater amounts of solvent could pass through the membranes. It has been revealed by Wijenayake et al.\textsuperscript{27} that crosslinking of the membranes can compress the polymer chains and reduce the permeation flux.

In our study, a simplified Rautenbach et al.\textsuperscript{39} model is employed to describe the permeation flux. The model is based on solution-diffusion theory and uses the fugacity of feed and permeate to define the driving force of pervaporation, as follows:\textsuperscript{40}

\[
J_i = \frac{D_i}{\gamma_i} \left( f_i - f_0 \right)
\]

(4)

where \( f_i \) and \( f_0 \) are the fugacity of component \( i \) in the feed and permeate, respectively; \( p_i^0 \) is the saturated vapor pressure of component \( i \); \( D_i \) is the transport coefficient of component \( i \); and \( \gamma_i \) is the geometric mean of activity coefficients at the feed (\( \gamma_{i,f} \)) and permeate (\( \gamma_{i,p} \)) sides. Note that \( \gamma_i \) is calculated as follows:\textsuperscript{40}

\[
\gamma_i = \sqrt[2]{\gamma_{i,f} \gamma_{i,p}}
\]

(5)

Considering a very low pressure at the permeate side, the fugacity of component \( i \) can be calculated as follows:

\[
f_i \approx p_i = \gamma_i P
\]

(6)

where \( p_i \) represents the partial pressure of component \( i \), and \( P \) is the pressure of the permeate side. Furthermore, non-random two-liquid (NRTL) model and Antoine equations were employed to calculate the activity coefficients and saturated vapor pressure, respectively. Parameters of NRTL equations and Antoine constants were derived from the database of the ChemCad (Houston, TX) 6.3.1 software (see the Appendix). The parameters are presented in Tables III and IV.

The transport coefficients were calculated using eqs. (3–5) and experimental data. For each formulation (different mass contents of GO in PVA), the transport coefficient was calculated using the mean square error of the results obtained from various feed compositions. The dependence of transport coefficients on mass content of GO in the membranes is illustrated in Figure 9. As indicated, the permeation flux of toluene is higher than that of iso-octane; this is mainly attributed to the size of toluene molecules and also the interaction between toluene and GO. Because GO nanoplates block the free volume of the membranes, increasing the mass content of GO leads to a reduced transport coefficient for the membranes. The effect of GO nanoplates on the transport coefficient of iso-octane is lower than that of toluene. Furthermore, transport coefficients of non-crosslinked membranes are higher than those of the crosslinked ones, and GO nanoplates have more impact on crosslinked membranes.

Table III. Antoine Constants for Toluene and Iso-octane from ChemCad Database

<table>
<thead>
<tr>
<th>Constant</th>
<th>Toluene</th>
<th>Iso-octane</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>76.945</td>
<td>120.81</td>
</tr>
<tr>
<td>B</td>
<td>-6279.8</td>
<td>-7550</td>
</tr>
<tr>
<td>C</td>
<td>-8.179</td>
<td>-16.111</td>
</tr>
<tr>
<td>D</td>
<td>5.3017 \times 10^{-6}</td>
<td>0.017099</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Table IV. NRTL Parameters for Toluene and Iso-octane from ChemCad Database

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>B_{ij}</td>
<td>233.852</td>
</tr>
<tr>
<td>B_{ji}</td>
<td>-91.4152</td>
</tr>
<tr>
<td>\alpha_{ij}</td>
<td>0.3011</td>
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<tr>
<td>A_{ij}</td>
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<tr>
<td>A_{ji}</td>
<td>0</td>
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<td>C_{ij}</td>
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<td>D_{ij}</td>
<td>0</td>
</tr>
<tr>
<td>D_{ji}</td>
<td>0</td>
</tr>
</tbody>
</table>

\( i \), Toluene; \( j \), iso-octane.

Figure 9. Transport coefficient of the membranes. [Color figure can be viewed at wileyonlinelibrary.com]

Figure 10. Permeance of (a) toluene and (b) iso-octane through crosslinked membranes. [Color figure can be viewed at wileyonlinelibrary.com]
Permeance of the membranes could be used to determine the inherent membrane permeability by excluding the influence of operating conditions. The permeance is calculated from the normalizing permeation flux of the components by the driving force of pervaporation according to the following equation:

\[
\text{Permeance} = \frac{P_i}{T} = \frac{J_i}{(P_i x_i y_i - y_i P)}
\]  

(7)

Permeances of the membranes are presented in Figures 10 and 11. It is illustrated that with increasing GO content, the permeance of both toluene and iso-octane decreases. As shown, the permeance of the organic compounds by including noncrosslinked membranes is higher than that of the crosslinked ones. Moreover, the permeance of toluene is much greater than that of iso-octane. The effect of increasing GO on reducing permeance is negligible for iso-octane when more than 0.5% GO is added to the polymer matrix. Furthermore, the influence of feed composition on the permeance of iso-octane is not considerable. By neglecting the effect of feed composition, it is obvious that the permeance of toluene is higher in solutions with lower contents of toluene. The reason may be associated with the strong interaction between toluene and GO; when a feed solution with a higher amount of toluene is used, a greater amount of toluene is adsorbed on GO nanoplates and restricted from transferring.

**CONCLUSIONS**

The similarity between the structures of GO and aromatic compounds can be used for the separation of aromatic from aliphatic mixtures using a pervaporation technique. The functional groups in GO create good compatibility between hydrophilic polymer and nanoplates. Although a crosslinking reaction is normally used to increase the mechanical properties of the membrane, the separation performance of the membranes is impacted by crosslinking. The crosslinking reaction leads to reduced crystallinity of the membranes, while GO has no significant impact on the crystallinity of either crosslinked and noncrosslinked membranes. Owing to the creation of \( s \) and \( \pi \) bonds between toluene and GO, swelling of the membranes increases with increasing GO in the membranes. The swelling in noncrosslinked membranes is higher than that of the crosslinked ones due to the greater movement of polymer chains. It was found that GO has a notable impact on the selectivity of PVA membranes: the incorporation of 0.5 wt % of GO improves the selectivity by about four times. The selectivity of noncrosslinked membranes is higher than that of the crosslinked ones, which shows the crystalline parts of the membranes make a greater contribution in separation and act as a filter. GO blocks the free volume of PVA and therefore reduces the permeation flux of PVA membranes. In contrast to most nanoparticles increasing the permeability, GO nanosheets reduce the permeation flux. Moreover, noncrosslinked membranes have a greater permeation flux in regard to the higher swelling. Consequently, noncrosslinked membranes are more effective in terms of both selectivity and permeation flux. The results of tensile testing indicate that the main drawback of noncrosslinked membranes is poor mechanical properties, though this could be overlooked with a proper design of module and mechanical support.

**APPENDIX**

The activity coefficients of a liquid mixture are defined from the NRTL model as follows (from ChemCad instructions):

\[
\ln \gamma_i = \frac{\sum_i^N \frac{\tau_{ij} G_{ij} x_i}{G_{ij} x_i} + \sum_j^N \frac{\sum_i^N \frac{G_{ij} x_i}{G_{ij} x_i} \left( \sum_j^N \frac{G_{ij} x_j}{G_{ij} x_j} \right) \tau_{ij} - \sum_j^N \frac{\sum_i^N G_{ij} x_i}{G_{ij} x_i} \tau_{ij} G_{ij} x_i}{\sum_j^N \frac{\sum_i^N G_{ij} x_i}{G_{ij} x_i} \tau_{ij} G_{ij} x_i}}}{\frac{\sum_i^N \frac{\tau_{ij} G_{ij} x_i}{G_{ij} x_i} + \sum_j^N \frac{\sum_i^N \frac{G_{ij} x_i}{G_{ij} x_i} \left( \sum_j^N \frac{G_{ij} x_j}{G_{ij} x_j} \right) \tau_{ij} - \sum_j^N \frac{\sum_i^N G_{ij} x_i}{G_{ij} x_i} \tau_{ij} G_{ij} x_i}{\sum_j^N \frac{\sum_i^N G_{ij} x_i}{G_{ij} x_i} \tau_{ij} G_{ij} x_i}}}
\]  

(A.1)

\[
\tau_{ij} = \frac{B_{ij}}{T} + C_{ij} \ln (T) + D_{ij} T
\]  

(A.2)

\[
G_{ij} = \exp (-\alpha_{ij} \tau_{ij})
\]  

(A.3)

\[
\alpha_{ij} = \alpha_{ji}
\]  

(A.4)

\( T = \) Temperature in Kelvin

**REFERENCES**

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