(PVC / ABS) and Nanocomposite (CAU-10-H) Composite Membrane for Separation of C₂H₆ from CH₄

Ehsan Kianfar¹, ²
¹ Department of Chemical Engineering, Arak Branch, Islamic Azad University, Arak, Iran
² Young Researchers and Elite Club, Gachsaran Branch, Islamic Azad University, Gachsaran, Iran
E-mail: e- kianfar94@iau-arak.ac.ir, ehsan_kianfar2010@yahoo.com

Abstract: In the research, composite membrane derived from Acrylonitrile butadiene styrene (ABS), Polyvinyl chloride (PVC) were prepared with 30wt.% In next step, adding 0.125, 0.250, 0.50wt.% of nanocomposite (CAU-10-H) in Acrylonitrile butadiene styrene (ABS), Polyvinyl chloride (PVC) was obtained. All of the polymeric and nanocomposite membranes were fabricated by the solvent foundry method use a dimethylacetamide solvent. The performance of prepared membranes was calculated for methane and ethane at the feed pressure of 2.5, 3.0, and 3.5 bar at a temperature of 35°C. Results showed that in most cases, increasing the percentage of Acrylonitrile butadiene styrene (ABS), Polyvinyl chloride (PVC). the permeability of CH₄ and C₂H₆ increased.

Keywords: nanocomposite membranes, gas separation performance, iso-phthalic acid / aluminum nitrate nanocomposite, PVC / ABS, dimethylacetamide (DMA)

1. Introduction

Natural gas has diverse compositions according to different petroleum resources. Methane is the main compound of natural gas since it forms about least 50% of gas wholly. Also, it consists of some contents of C₃H₆, C₄H₁₀ and heavier hydrocarbons [1]. Natural gas may be either sour or sweet. The sour gas refers to a gas containing such impurities as H₂S or CO₂. Due to destructive effects including severe wear on transmission pipes and process equipment, all mentioned impurities are refined while production. In addition to mentioned impurities, there are also some neutral gases (mostly nitrogen) in natural gas. Although the presence of nitrogen in natural gas provides no wearing effect on gas transmission and process equipment, it is necessary to be separated from natural gas in production place due to such effects as increased transportation and maintenance costs, decreased the thermal value and environmental issues. Following CH₄, C₂H₆ is the second constituent of natural gas [2-3]. The difference between natural gases obtained from diverse fields is originated from their ethane content from 1 to 6wt%. In the past, ethane and greater hydrocarbons were not typically separated from natural gas and they were burned along with CH₄ as fuel [4-7]. However, this gas- which is so invaluable- is currently extracted through establishing an ethane extraction complex and from natural gas, having a high value for export and providing petrochemical feeds [8-10]. The membrane systems are of the best, the most suitable and the most inexpensive separation processes with a high efficiency, which can be a suitable alternative for such complicated and costly operations as absorption, distillation [11-15]. Currently, membrane-based separation processes are being replaced by old separation processes such as surface adsorption, centrifuges, etc., on an industrial scale [16-19]. Petroleum, gas, and petrochemical industries are of those great industries which are being studied and replaced accordingly [20-22]. Although ceramics have been increasingly paid into attention as a membrane due to their considerable chemical and thermal strength, such membranes will not be suitable for separation of the mixtures with the components having similar molecular size since their selectivity is conducted the based on a difference of molecular size [23-25]. Additionally, lots of separation processes are conducted in medium operational processes- i.e. under 200°C- covering plenty of problems. The capacity of inorganic nanoparticles such as SiO₂, Al₂O₃, Fe₂O₃, ZrO₂ and TiO₂ inside the polymeric membranes were recognized as a method to improve membranes separation performance [26-30]. Among the mentioned nanoparticles, TiO₂ is more welcomed due to suitable physical and chemical properties and accessibility as well as potential anti-deposition capabilities [31-34]. The nanoparticles SiO₂ can be linked to one another and embedded in polymeric membranes by mixing them into membranes.
or depositing them on the membrane surface. 3, 4. Isophthalic acid (PIA) has three major uses:

- PET (PolyEthylene Terephthalate) copolymer, which is used in bottle resins and to a much lesser extent, for fibers. PIA (Purified Isophthalic Acid) reduces the crystallinity of PET, which serves to improve clarity and increase the productivity of bottle-making.

- Unsaturated polyester resins, where the addition of PIA improves thermal resistance and mechanical performance, as well as resistance to chemicals and water.

- Polyester / alkyd surface coating resins, where PIA increases resistance to water, overall durability and weather ability.

Nitrates are excellent precursors for the production of ultra-high purity compounds and certain catalysts and nanoscale (nanoparticles and Nanopowders) materials. Aluminum Nitrate is generally immediately available in most volumes. High purity, submicron, and Nanopowder forms may be considered. We also produce Aluminum Nitrate Solution. American Elements produces to many standard grades when applicable, including Mil Spec (military grade); ACS, Reagent and Technical Grade; Food, Agricultural and Pharmaceutical Grade; Optical Grade, USP and EP / BP (European Pharmacopoeia / British Pharmacopoeia) and follows applicable ASTM testing standards.

In the present study, by adding nanocomposite (CAU-10-H) to the alloy membrane Polyvinyl chloride / acrylonitrile butadiene styrene and fabricating a mixed membrane structure, we tried to enhance the efficiency of this membrane for separation of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} gases.

2. Experiment

2.1 Gas permeability experiment

In this system, after placing the membrane in the permeability cell, the whole system is under vacuum for half an hour. The upstream part of the gas cell is placed under pressure. By passing the gas through the membrane pressure changes over time will be recorded by the computer. After a period of trial, the tank pressure changes to a steady state and becomes linear. By measuring the slope of the changes and using the equation (1), the permeability of the membrane will be calculated in terms of Barrer.

Figure 1 shows a Schematic of the gas-permeation setup. The pure gas permeability for Mixed Matrix membranes using the equation (1-2) for CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} at 35°C 1-2:

$$P = \frac{273.15 \times 10^{10} vl}{760AT ((p_0 \times 76)/14.7)} \left( \frac{dp}{dt} \right)$$

(1)

$$1\text{Barrer} = \frac{10^{-10} \text{cm}^3 (\text{STP}) - \text{cm}}{\text{cm}^2 \text{s} \cdot \text{cmHg}}$$

(2)

Where P is the gas permeability in Barrer (1 Barrer = $1 \times 10^{-10}$ cm$^3$(STP) cm / cm$^2$ s cmHg), v refers the volume of the downstream chamber (cm$^3$), l stands the membrane thickness (cm), A is effective area of the membrane (cm$^2$), and T is the operating temperature (K). The ideal selectivity for C\textsubscript{2}H\textsubscript{6} / CH\textsubscript{4} was determined by dividing the CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} permeability as Eq. (3) 1-2:

$$\alpha_{AB} = \frac{P_A}{P_B}$$

(3)
2.2 Preparation of nanocomposite membranes

The lining method has been used to make nanocomposite membrane. For this purpose, first, the iso-phthalic acid / aluminum nitrate nanocomposite in dimethylacetamide solvent were added to the solvent in different weight percentages of the total weight of the polymer and were stirred well at room temperature for 1h until the homogenous solution of nanoparticle-solvent was obtained. Table 1 shows Physical properties of iso-phthalic acid / aluminum nitrate nanocomposite nanoparticles.

| Table 1. Physical properties of iso-phthalic acid / aluminum nitrate nanocomposite nanoparticles |
|-------------------------------------------------|------------------------------------------------------------------|
| Typical properties                              | iso-phthalic acid / aluminum nitrate nanocomposite               |
| Specific surface area (BET)                     | 190 m$^2$/g                                                       |
| Particle size                                    | 5-10 nm                                                          |
| Density                                         | 3.26 g/mL                                                        |
| Color                                           | White                                                            |
| Purity (based on metal)                         | > 99.9%                                                          |

3. Results and discussion

3.1 Membranes characterization

3.1.1 XRD analysis

Figure 2 shows the XRD of nanocomposite (CAU-10-H). Peaks in the range of 10-50 2θ reflect the crystal structure of (CAU-10-H). According to the XRD pattern database for nanocomposite (CAU-10-H), sharp peaks at 18, 20, 22, 23, 24, 25, 27 2θ and 30 are the most predominant peaks for calcined (CAU-10-H) [29].
3.1.2 FTIR analysis

The FTIR spectra of control and various loading of nanocomposite (CAU-10-H) membrane are shown in Figure 3. High-intensity bands at 699 and 718 cm\(^{-1}\), attributed to C-H out-of-plane vibrations of the aromatic ring. The top spectrum taken from the edge of the sample shows a broad carbonyl band at 1724.4 cm\(^{-1}\) and broadband for the hydroxyl group and FTIR spectra ABS 600 cm\(^{-1}\) to 1300 cm\(^{-1}\). As discussed, the absorbance bands in virgin ABS corresponding to the trans C = C unsaturation (vinyl) at 966.92 cm\(^{-1}\) and 1500-1550 cm\(^{-1}\) and the 1,2 butadiene terminal vinyl C-H band being 911.43 cm\(^{-1}\), decrease considerably for the aged ABS specimen [29].

![Figure 3. FTIR spectra of the Nano, (a) (Nano) (b) (PVC / ABS-%0.125 (Nano) (c) (PVC / ABS-%0.250 (Nano) (d) (PVC / ABS-%0.50 (Nano)](image-url)
3.1.3 SEM, EDX, TEM analysis

Figure 4 shows SEM images of (CAU-10-H), PVC/ABS-%0.125(Nano) and PVC/ABS-%0.250(Nano), PVC/ABS-
%0.50(Nano) samples after calcination. The SEM images of calcined samples confirm that the particles are spherical. After
impregnation, on the significant change was observed in the crystal morphology of nanocomposite (CAU-10-H). The TEM
images of the nanocomposite (CAU-10-H) shown in Figure 5 further confirmed that the microspheres are formed as a
homogeneous aggregation of nanocomposite (CAU-10-H) crystallites.

![Figure 4. FESEM images of (a) (Nano) (b) (PVC/ABS-%0.125 (Nano) (c) (PVC/ABS-%0.250 (Nano) (d) (PVC/ABS-%0.50 (Nano)](image)
4. Results nanocomposite (CAU-10-H) at different pressures

Results (CAU-10-H) Obtained from PVC and (ABS) + (CAU-10-H) with loading percentage Nanocomposite (CAU-10-H) shown in Tables 2-4 and Figures 6-8. Methane and ethane permeability increases by increasing the percentage of Nanocomposite (CAU-10-H) from 0.125 to 0.250wt.% in PVC and (ABS) precursor (Figures 6-8). This increase is due to increased permeability of Nanocomposite (CAU-10-H) in the polymer network and lack of compatibility of Nanocomposite with the polymer caused changes in the intensity of polymer chains and cause the interface between organic polymers and Nanocomposite. Increasing nanoparticle to polymer cause to increase porosity in the membrane. These pores are suitable places for interaction between gases and provide polymer network which helps to increase the influence and gas solubility, and permeability thereby increases. This may denote the dominant contribution of molecular sieving mechanism compared to others that usually complicated in gas molecules transport in nanocomposite membranes in comparison with the polymeric membrane. The selectivity changes of C$_2$H$_6$ / CH$_4$ by pressure are depicted in Figure 9. As it can be seen, the selectivity of C$_2$H$_6$ / CH$_4$ will experience an increasing trend with increased pressure and nanoparticle contents of Isa-phthalic acid /Aluminum Nitrate.

Table 2. Permeability and selectivity of PVC and (ABS) + nanocomposite (CAU-10-H) membrane at a pressure of 2.5 bar

<table>
<thead>
<tr>
<th>Polymer-nanoparticle</th>
<th>$P_{C_2H_6}$ (barrer)</th>
<th>$P_{CH_4}$ (barrer)</th>
<th>$\alpha$ C$_2$H$_6$ / CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC / ABS (30Wt%)</td>
<td>0.66</td>
<td>0.36</td>
<td>1.83</td>
</tr>
<tr>
<td>PVC / ABS-%0.125 (Nano)</td>
<td>1.25</td>
<td>0.63</td>
<td>1.98</td>
</tr>
<tr>
<td>PVC / ABS-%0.250 (Nano)</td>
<td>1.50</td>
<td>0.70</td>
<td>2.14</td>
</tr>
<tr>
<td>PVC / ABS-%0.50 (Nano)</td>
<td>1.65</td>
<td>0.72</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Table 3. Permeability and selectivity of PVC and (ABS) + nanocomposite (CAU-10-H) membrane at a pressure of 3 bar

<table>
<thead>
<tr>
<th>Polymer-nanoparticle</th>
<th>$P_{C_2H_6}$ (barrer)</th>
<th>$P_{CH_4}$ (barrer)</th>
<th>$\alpha$ C$_2$H$_6$ / CH$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC / ABS (30Wt %)</td>
<td>0.80</td>
<td>0.40</td>
<td>2.02</td>
</tr>
<tr>
<td>PVC / ABS-%0.125 (Nano)</td>
<td>1.35</td>
<td>0.65</td>
<td>2.07</td>
</tr>
<tr>
<td>PVC / ABS-%0.250 (Nano)</td>
<td>1.60</td>
<td>0.71</td>
<td>2.25</td>
</tr>
<tr>
<td>PVC / ABS-%0.50 (Nano)</td>
<td>1.70</td>
<td>0.73</td>
<td>2.32</td>
</tr>
</tbody>
</table>
Table 4. Permeability and selectivity of PVC and (ABS) + nanocomposite (CAU-10-H) membrane at a pressure of 3.5 bar

<table>
<thead>
<tr>
<th>Polymer-nanoparticle</th>
<th>( P_{C_2H_6} ) (barrer)</th>
<th>( P_{CH_4} ) (barrer)</th>
<th>( \alpha_{C_2H_6/CH_4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC / ABS (30Wt %)</td>
<td>0.85</td>
<td>0.41</td>
<td>2.07</td>
</tr>
<tr>
<td>PVC / ABS-%0.125 (Nano)</td>
<td>1.55</td>
<td>0.70</td>
<td>2.21</td>
</tr>
<tr>
<td>PVC / ABS-%0.250 (Nano)</td>
<td>1.75</td>
<td>0.75</td>
<td>2.33</td>
</tr>
<tr>
<td>PVC / ABS-%0.50 (Nano)</td>
<td>2.3</td>
<td>0.80</td>
<td>2.87</td>
</tr>
</tbody>
</table>

Figure 6. Permeability of PVC and (ABS) a) \( C_2H_6 \) and b) \( CH_4 \)
Figure 7. PVC and (ABS) + nanocomposite (CAU-10-H) (a) $C_2H_6$ and (b) $CH_4$

Figure 8. selectivity of PVC and (ABS) ($C_2H_6/CH_4$)

Selectivity ($C_2H_6/CH_4$)

Pressure, bar

2 2.5 3 3.5 4

PVC/ABS-NANO(0.125Wt%)
PVC/ABS-NANO(0.250Wt%)
PVC/ABS-NANO(0.50Wt%)

Permeability of $C_2H_6$, barrer

Permeability of $CH_4$, barrer

2 2.5 3 3.5 4

PVC/ABS-NANO(0.125Wt%)
PVC/ABS-NANO(0.250Wt%)
PVC/ABS-NANO(0.50Wt%)
5. Conclusion
Based on these experiments, the main results are summarized as below:
1. Permeability increases significantly for membranes containing PVC / ABS.
2. Membranes containing carbon or porous organic polymer nanoparticles are more stable.
3. These membranes show increased PVC / ABS selectivity.
4. Permeability of each studied gas is enhanced with the increased pressure of input feed and nanoparticles.
5. Selectivity of $\text{CH}_4 / \text{C}_2\text{H}_6$ follows an increase with the increased pressure.

6. Compliance with ethical standards
Funding: There is no funding to report for this submission.
Conflict of interest: the authors declare that they have no conflict of interest

References
