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Evaluation of Various Structures for PVP Facilitated Transport Membranes Containing Silver Salts and Its Effect on Ethylene-Ethane Separation Process

Majid Esmaeili[1] and Sima Attar Nosrati[2]

1. Chemical, Polymeric and Petrochemical Technology Development Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

2. Young Researchers and Elite Club, Central Tehran Branch, Islamic Azad University, Tehran, Iran

esmaeilim@ripi.ir

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Introduction

In recent years, the membrane technology for C_2H_4/C_2H_6 or C_3H_6/C_3H_8 separation has received considerable attention due to its advantages such as simplicity and in spite of its operational problem such as lack of high selectivity and durability of separation potency [1-4]. In the best type of these membranes, which is known as solid state facilitated transport membranes, silver cations stabilize among polymer network after formation of dative bonds with electron donor groups of polymer chains such as carbonyl oxygen. By now, different silver salts such as AgBF4, $AgNO_3$, and $AgCF_3SO_3$ with different separation potency have been applied as carrier provider for olefin separation [4]. Stabilized silver (I) or other metal ions react with olefin molecules through π-bonding mechanism [5]. Moreover, unsaturated compounds, such as ethylene or propylene molecules, have capability of donating a pair of electrons and forming a coordinative bond with the metal ions such as Ag^+ or Ag^{+2}.

Therefore, transient complexes are created among silver ions and olefin molecules, which cause to separation of unsaturated hydrocarbons from feed gas. In this research, two types of these salts, $AgBF_4$ and $AgNO_3$ have been selected and incorporated separately into the PVP active layer of PES/PVP composite membranes for evaluation of various structural and performance changes between these membranes.

Experimental Procedure

Materials and membrane fabrication

The PES (Molecular weight=58000 Da), PVP (Molecular weight=360000 Da), poly dimetyl siloxane (PDMS or Silgard), dimethyl acetamide (DMAc), N-hexane, silver nitrate ($AgNO_3$, CAS No.: 7761-88-8), and Silver tetrafluroborate ($AgBF_4$) were purchased from BASF (Germany), Fluka (Netherland), Dow Corning Corporation (USA), Merck chemical and Sigma-Aldrich companies respectively. In addition, C_2H_4 and C_2H_6 as feed gases were obtained from Air Product Company. PES was dried further in a vacuum oven at 40 °C for 24 hours before being used. Other materials were utilized as they were received.

The PES support membranes (20 wt.%) were synthesized in accordance with phase inversion method described at our previous study [7]. Also, PVP active layer (15 wt.%) containing various molar ratio between Silver and carbonyl groups ([Ag]:[CO]=0.1:8, 1:4, and 1:1) were created according to our previous work [4]. The prepared membrane was analyzed through characterization methods such as SEM, FTIR-ATR and gas permeation tests.

Results and Discussion

Carbonyl groups strength

Formation of dative bond between carbonyl groups and silver cations (released from silver salts in the polymer solution) feeble the carbonyl bond (C=O) strength. Therefore, the maximum infra-red beam absorbance will be occurred at lower wavenumber or lower frequencies. This issue is illustrated in Fig. 1 where the wave number for minimum transmittance (maximum absorbance) of carbonyl groups attached to silver cations released from $AgBF_4$ is lower than the other case ($AgNO_3$). On the other hand, $AgBF_4$ salt has distributed more homogenously among the polymer matrix and causes to adjoin more and effectively with carbonyl sites. In this way, lower free surface will be appeared under carbonyl bonds at FTIR-ATR spectra as indicated in Fig. 1.

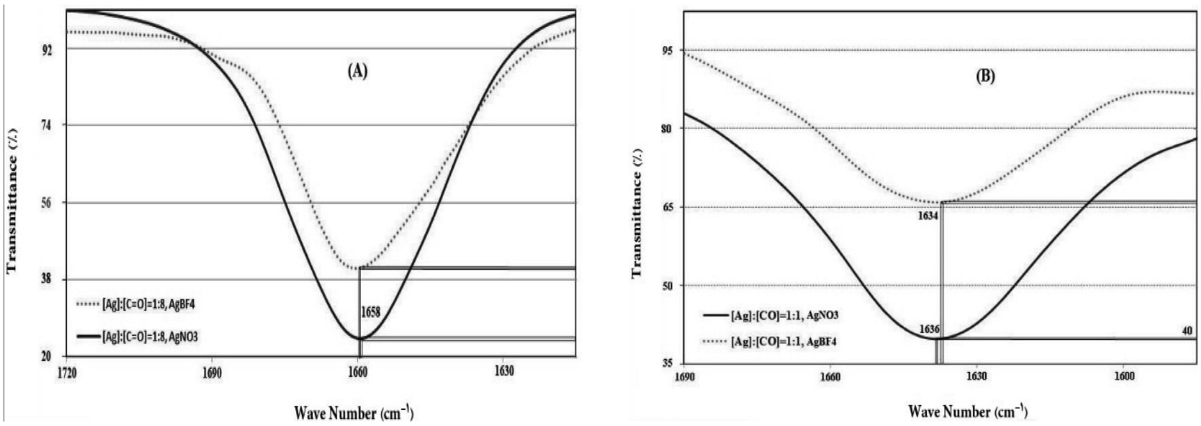


Figure 1: FTIR-ATR analysis from the PVP active layer focused on carbonyl bond at different salts concentrations (a) ([Ag]:[CO]=1:8) (b) ([Ag]:[CO]=1:1).

Surface and cross section structure

Fig. 2 exhibits the cross section and surface view of the PES/PVP composite membranes. A support layer of around 65 µm (PES) with spongy bottom section and tear-like structure above it is detectable in Fig 2 (a) which can assure users for mechanical strength of the composite membranes. Coating the surface of PES/PVP composite membranes, containing silver salts, diminishes the surface roughness of the membranes therefore, more smother surface will be distinguished by SEM apparatus that is visible in Fig. 2 (b and c).

Gas permeation tests

The results of gas permeation experiments are very important in any studies related to the membrane issues that can approve or reject all of the characterization tests. In this study, ideal and real gas tests have been conducted through our pre-defined set-up [6] which related results are showed in Fig. 3.

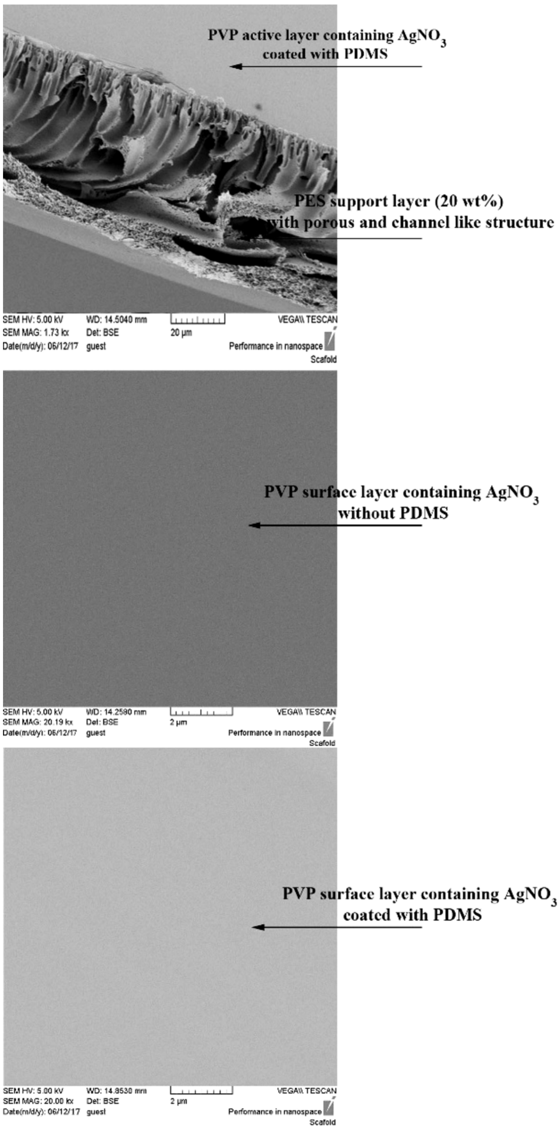
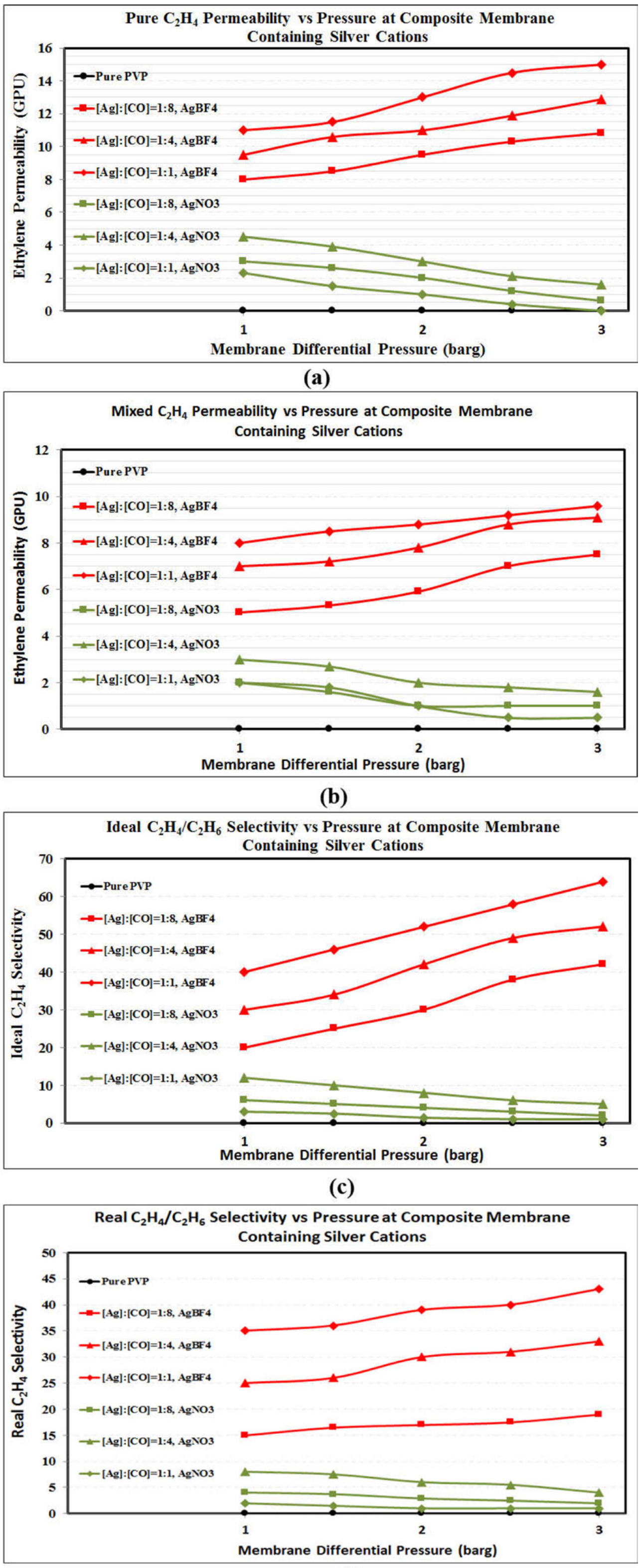


Figure 2: SEM images from (a) cross section of PVP/$AgNO_3$ composite membrane (b) Surface layer without PDMS coating (c) Surface layer with PDMS coating.



(a)

(b)

(c)

(d)

Figure 3: The gas permeation performance of composite membrane at pure and mixed gas conditions (a & b)_permeability (c & d) selectivity.

When ethylene carrier sites distribute more homogeneously among polymer matrix, they can play their role, as the ethylene transporter, as well as possible. According to the results of FTIR analysis and also on behalf of the theory of Lewis acids and bases, $AgBF_4$ distributes more effectively than $AgNO_3$ and its cations and anions detach more easily when dissolve in the polymeric solution; therefore, it is expected to transfer ethylene molecules better than $AgNO_3$. Fig. 3 approves this idea and shows that ethylene permeation rated, at both cases of mixed and ideal ones, is higher when $AgBF_4$ has been incorporated as the carrier provider than $AgNO_3$. The differential pressure of the operation has positive effect on the ethylene permeation when the correct carrier is used in the membrane structure.

C_2H_4/C_2H_6 selectivity, as another main performance parameter, reveals the same trend vs pressure variations for both two salts. Moreover, the selectivity is higher when $AgBF_4$ is used as the carrier. By enhancing the feed pressure, silver cation sites, released from $AgNO_3$ salt, saturates with ethylene molecules due to the weak hopping mechanisms (attach, transfer, detach) that leads to diminish the permeation rate of C_2H_4 and therefore its selectivity.

Conclusions

This study reveals and compares the structural and performance change in PES/PVP facilitated transport membrane incorporated with $AgBF_4$ and $AgNO_3$. Moreover, characterization and gas permeation tests declared that $AgBF_4$ salt dissolves better in the PVP polymer matrix and more ethylene permeation rate, and C_2H_4/C_2H_6 selectivity obtains when $AgBF_4$ is selected as the carrier provider.

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