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단 신

올레핀 촉진수송 분리막의 성능향상을 위한 Valine의 효과

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Effect of Valine on Facilitated Olefin Transport Membranes

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요 약: 은염이 함유된 고분자 전해질을 이용한 올리핀 촉진수송 분리막은 고체상에서 높은 올레핀/파라핀 분리 성능을 나타내었다. 본 연구에서는, 프로필렌/프로판 분리 선택도와 투과도의 성능을 향상시키기 위해 아미노산의 일종인 valine을 고분자 전해질막에 첨가하였다. FT-IR 분광학을 통해 valine의 양이온과 은염의 음이온이 상호작용을 하고, 그 결과 valine은 은이온의 활성도를 증가시킴을 알 수 있었다. 따라서 valine을 포함하고 있는 촉진수송 분리막은 valine이 없을 때보다 더 높은 선택도와 투과도를 나타내었다.

Abstract: A remarkable separation performance of olefin/paraffin mixtures has been observed through facilitated olefin transport membranes consisting of silver ions dissolved in polymer matrices. In this research, valine, an amino acid, was introduced in poly (2-ethyl-2-oxazoline) (POZ)/$AgBF_4$ membranes to increase the separation performance. FT-IR spectra show that the cationic sites ($-NH_3^+$) of valine interact with the counter anion of the silver salt, resulting in the enhanced activity of the silver ions and consequently improved separation performance. Therefore, the POZ/$AgBF_4$ membranes containing valines exhibit the higher permeance as well as the higher selectivity of propylene/propane than those without valine.

Keywords: *valine, amino acid, membrane, facilitated transport, silver salt, olefin*

1. Introduction

Olefin/paraffin separation, one of the most important processes in petrochemical industry has been typically performed by highly energy-intensive low-temperature distillation [1]. Among various alternative energy saving separation processes [2-4], the facilitated transport membranes based upon silver polymer electrolytes have attracted significant interest because of their remarkable separation performance for olefin/paraffin in the solid state [5-16]. For example, when silver salts such as $AgBF_4$ or $AgCF_3SO_3$ are dissolved in polymer matrices such as poly(ethylene oxide) (PEO), poly(2-ethyl-2-oxazoline) (POZ) or poly(N-vinyl pyrrolidone) (PVP), the silver ions are active as an olefin carrier, resulting in facilitated olefin transport.

To enhance the separation performance and the membrane stability for gaseous mixtures, the addition

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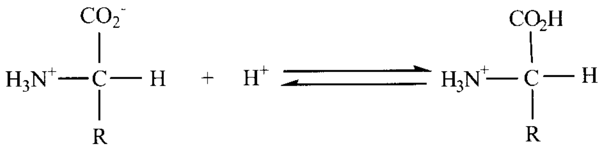


Scheme 1.

of a third component has been commonly employed [17,18]. The idea of using amino acids is based on the fact that they are quite reactive with chemical substances involving metal ions such as a silver ion [19]. In particular, valines containing NH_3^+ in acidic condition are expected to interact with counter anions of the silver salt, rendering the silver ion more active olefin carrier [20].

The complex formation of silver ion with olefin molecule is known to be quite sensitive to counter anions of silver salt [21-24]. Large and low electronegative anions such as BF_4^-, $CF_3SO_3^-$ and ClO_4^-, form silver salts with low lattice energy and they provide more free silver cation to act as an effective olefin carrier when dissolved in polymer matrices [24]. In contrast, small and highly electronegative anions such as F^-, Cl^- and NO_3^- form the salts with high lattice energy and hinder complexation of the silver ion with olefin molecule [24]. It is furthermore found that the silver polymer complex membranes with strong silver ion-polymer and weak silver ion-anion interactions exhibit more favorable silver ion complexation with olefin, resulting in higher olefin solubility and its permeation property [23]. Valine maintains its NH_3^+ cations in the presence of POZ/$AgBF_4$ solution in water because pH in its solution is in the range of 3-4, a relatively strong acidic range. Thus, the forward reaction of Scheme 1 would prodominantly occur both in the solution and in the membrane. Therefore, it is assumed that the positive charge of NH_3^+ may interact with the counter anion of silver salt in silver-polymer complexes. Thus, the interaction between silver ion and counter anion will be reduced upon the addition of valines, and consequently causes the silver ions to be more active for olefin coordination. Based on this concept, we introduced valines into POZ/$AgBF_4$ membrane system. Thus the effect of valines on the complexation behavior of the silver ions with propylene and the facilitated propylene transport through the membranes have been investigated in this study.

2. Experimental

Polymer electrolyte solution was prepared by dissolving $AgBF_4$ and valine in water solution containing 20 wt% of POZ. The molar ratio of the carbonyl oxygen of POZ to silver ion was fixed at 1 (i.e., [C=O]:[Ag^+]=1:1) and various mole ratios of valine were added. The solution was coated onto a polysulfone microporous membrane support (Seahan Industies Inc., Seoul, Korea) using an RK Control Coater. After evaporation of the solvent in a convection oven at room temperature for two hours under nitrogen, the membrane was completely dried in a vacuum oven for two days at room temperature. The thickness of the top polymer electrolyte layer was ca. 1 μm as determined by scanning electron microscopy. Gas flow rates were measured by a bubble flow meter to obtain gas permeance. The unit of the gas permeance is GPU, where 1 GPU = $1\times10^{-6} cm^3(STP)/(cm^2 sec\ cmHg)$. The mixed gas (50 : 50 vol % of a propylene/propane mixture) separation properties of the membranes were evaluated using gas chromatography (Hewlett-Packard G1530AMA) equipped with a TCD and a unibead 2S 60/80 packed column.

3. Results and Discussion

Separation experiments of propylene/propane mixtures were conducted to evaluate the effect of valine on the separation performance of POZ/$AgBF_4$ membranes. In previous study, the separation performance of POZ/$AgBF_4$ membrane showed the selectivity of 45 and the permeance of 12 GPU [5]. When the valine is added into the POZ/$AgBF_4$ membrane, the selectivity of propylene/propane and the mixed gas permeance are increased up to 54.3 and 15.6 GPU. The molar ratio of valine to the silver ion for the best separation perfor-

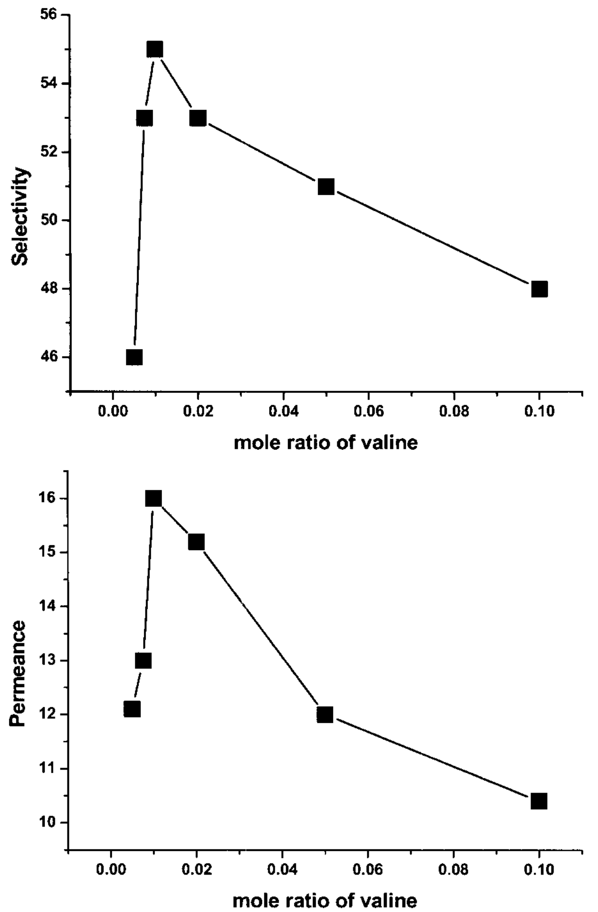
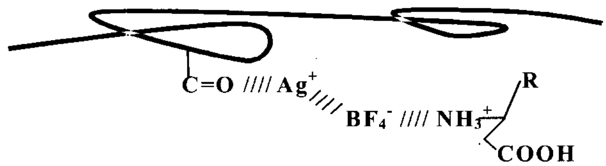


Fig. 1. Effect of valine on the mixed gas permeance and the selectivity of propylene/propane for 1 : 1 POZ/$AgBF_4$.

mance was 0.01 as seen in Fig. 1. This would be attributable to the miscibility limitation between the components. The enhancement of facilitated propylene transport could be explained by the increased activity of the silver ion with propylene due to the addition of valine in POZ/$AgBF_4$ system. This is attributable to the weakened interaction between Ag+ and counter anion of BF_4^-, caused by the electrostatic interaction between the positively charged NH_3^+ of valine and BF_4^- as schematically depicted in Scheme 2 [23].

The electrostatic interaction between NH_3^+ and BF_4^- was investigated using FT-IR spectroscopy. FT-IR spectra for pure POZ and 1 : 1 POZ/$AgBF_4$ complex with and without valine are given in Fig. 2. Upon incorporation of $AgBF_4$ into POZ, the C=O stretching band shifted from 1641 cm^{-1} to a lower wavenumber at



Scheme 2.

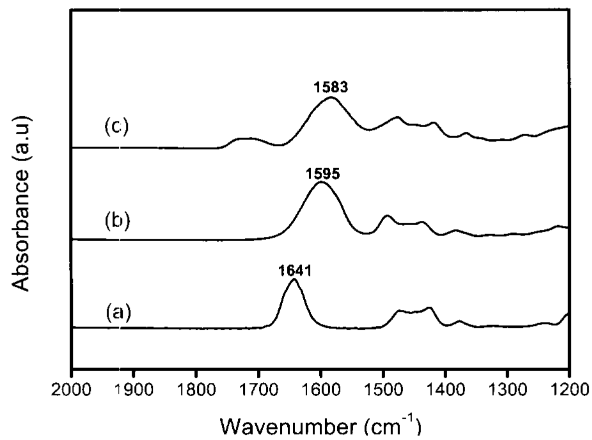


Fig. 2. FT-IR spectra of (a) pure POZ, (b) POZ/$AgBF_4$ and (c) 1 : 1 : 0.01 POZ/$AgBF_4$/valine complexes.

1595 cm^{-1}, which is presumably due to the loosened C=O double bond strength by the coordinative interaction between the silver cation and carbonyl oxygen of POZ. When a small amount of valine was added to the POZ/$AgBF_4$ complex, the position of the C=O stretching band was further changed from 1595 to 1583 cm^{-1}, demonstrating the increased interaction between the C=O of POZ and the silver ion. This result implies that the BF_4^- anion is pulled out, to some extent, from the silver ion by the positive charge of the protonated valine and thereby the interaction between the silver cation and the counter BF_4^- anion becomes weak. Judging from the peak of COOH observed through FT-IR as shown in Figure 2(c), it is thought that an inverse reaction of Scheme 1 does not happen after water is removed.

4. Colclusion

The introduction of valine into POZ/$AgBF_4$ complex membranes caused the enhanced separation performance of propylene/propane mixtures. The permeance is increased from 12.5 to 16.0 GPU and the selectivity is increased from 45.2 to 55.2. The increased activity of silver ion as olefin carrier is believed to be obtained by the diminished interaction of silver cations with counter anions owing to the electrostatic interaction of BF_4^- with NH_3^+ of valine.

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