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Effect of Salt on Facilitated Propylene Transport through Crosslinked PVA/Silver Salt Complex Membranes

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Abstract: Complex membranes consisting of silver salt ($AgBF_4$, $AgCF_3SO_3$, $AgSbF_6$, $AgNO_3$) and poly(vinyl alcohol) (PVA) or crosslinked PVA (CPVA) were prepared and tested for the separation of propylene/propane mixtures. For the tested membranes, the complex membranes containing $AgBF_4$ exhibited the highest separation properties, i.e., approximately 20 GPU (1 GPU=10^{-6} cm^3 (STP)/(cm^2 sec cmHg)) and 100 of selectivity at 0.2 of silver mole fraction. The CPVA membranes containing silver salt always showed higher selectivity than PVA membranes, presenting silver ions coordinated to -CHO are more effective than those to -OH groups. The threshold silver concentration of CPVA membranes was lower than that of PVA membranes, which might be due to stronger interaction of silver ions with -CHO than that with -OH. The composition at which the selectivity is the highest did not significantly depend on the crosslinking, but did on the kind of silver salt.

Keywords: *facilitated transport, olefin, polymer complex, PVA, silver ion*

1. Introduction

Olefins are an important feedstock with a wide range of uses, particularly in the production of polymers, acids, alcohols, esters, and ethers. The recovery of olefin from olefin/paraffin mixtures, i.e. ethylene from ethylene/ethane, propylene from propylene/propane, in petrochemical industry is of pivotal importance. Cryogenic distillation has usually been used in the production of usable olefins. However, this distillation process has the disadvantage that it requires high energy consumption and produces inevitably air pollution. Membrane separation technology has been proposed as an alternative to distillation because of its low cost and simple operation. However, the separation of olefin/paraffin mixtures using conventional polymeric membranes has not been effective because the physico-chemical properties of olefins and paraffins such as their molecular size and solubility are largely indistinguishable[1-3].

Facilitated olefin transport membranes have received much attention because of their excellent separation properties. Among various kinds of facilitated transport membranes[4-8], the polymer electrolyte membranes consisting of silver ions dissolved in a polymeric matrix have very recently been investigated because of their excellent separation performance in the solid state [9-26]. The propylene permeance through the poly (2-ethyl-2-oxazoline) (POZ)[11,12,15], poly(vinyl pyrrolidone) (PVP)[14,17,20] or poly(ethylene oxide) (PEO) [21-23] membranes containing $AgBF_4$ was as high as 40~50 GPU (1 GPU=10^{-6} cm^3 (STP)/(cm^2 sec cmHg)), while the propane permeance was extremely low as 0.003 GPU. Thus, the pure gas selectivity of propylene

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over propane was more than 10,000, but the mixed gas selectivity is approximately 50 due to plasticization of membranes[14,16]. The high separation performance is based on 1) extremely high loading of silver salts in the polymer matrix, which is possible by the coordinative interaction between silver ions and carbonyl oxygens of polymer matrices[25], and 2) a fast reversible reaction of silver ions with olefin[26].

Facilitated olefin transport membranes consisting of crosslinked poly(vinyl alcohol) PVA (CPVA) containing silver salts has been firstly reported by Ho and Dalrymple[27]. Bryant *et al.* also developed the CPVA/silver salt complex membranes for the separation of benzene/cyclohexane mixtures[28]. In these studies, however, facilitated olefin transport was observed only when the feed stream was saturated with water, but not in the dry state. This observation might be due to two factors[29]. First, the silver salt used in these studies was $AgNO_3$, which has a high lattice energy and hence is not readily dissolved in the highly entangled solid polymer matrix thus, the CPVA/$AgNO_3$ system do not provide effective olefin carrier in the solid state. Second, they used a high crosslinking temperature more than 70°C without a catalyst topromote the crosslinking of PVA. However, it has been found that the high-temperature heat treatment of polymer membranes containing silver salts acceleratesthe reduction of silver ions Ag(I) to metal Ag(0), which degrades the membrane performance significantly[19].

High performance CPVA membranes containing silver salts in the solid state has been recently developed by both employing $AgSbF_6$ with a low lattice energy and room temperature crosslinking with the use of HCl catalyst[29]. As a result, the mixed gas permeance and the selectivity of propylene over propane through CPVA/$AgSbF_6$ complexes were increased from 0.1 to 4.1 GPU (1 GPU = 1×10^{-6} cm^3 (STP)/cm^2 sec cmHg) and from 1 to 125, respectively, at a silver mole fraction of 0.2, compared to pristine CPVA membranes. In this study, the effect of silver salt on the separation performances of both gas permeance and selectivity was investigated in detail.

2. Experimental

Poly(vinyl alcohol) (PVA) (99 +% hydrolyzed, M_w = 85,000~146,000), glutaraldehyde (GA, 50% in water) and the silver salts of silver tetrafluoroborate ($AgBF_4$, 98%), silver trifluoromethanesulfonate ($AgCF_3SO_3$, >99%), silver hexafluoroantimonate ($AgSbF_6$, 98%) and silver nitrate ($AgNO_3$, >99%) were purchased from Aldrich Chemical Co. and were used without further purification.

PVA solutions were prepared by dissolving 10 wt% PVA in deionized water with stirring at 70~80°C and then cooling the solutions to room temperature. After complete dissolution, HCl (0.15 wt% of the total PVA solution) and GA were successively added to the solutions as a catalyst and crosslinking agent, respectively. The concentration of GA was fixed to maintain [OH]:[GA] at 4:1. The appropriate amounts of silver salts were added to each solution, depending on the required mole fraction of silver salt. The polymer solutions were coated onto microporous polysulfone substrates (Seahan Industries Inc., Seoul, Korea) using an RK Control Coater (Model 101, Control Coater RK Print-Coat Instruments LTD, UK). After the evaporation of the solvent in a convection oven at room temperature under nitrogen, the membranes were dried completely in a vacuum oven for two days at room temperature. Gas permeation experiments were carried out using the constant pressure/variable volume method. The mixed gas (a 50:50 vol% propylene/propane mixture) separation performance of the membranes was evaluated by a gas chromatograph (Hewlett Packard G1530A, MA) equipped with a TCD detector. The stage cut (θ), which is the ratio of the permeate to the feed flow rates, was always less than 2%. The unit of gas permeance was GPU, where 1 GPU = 1×10^{-6} cm^3 (STP)/cm^2 s cm Hg.

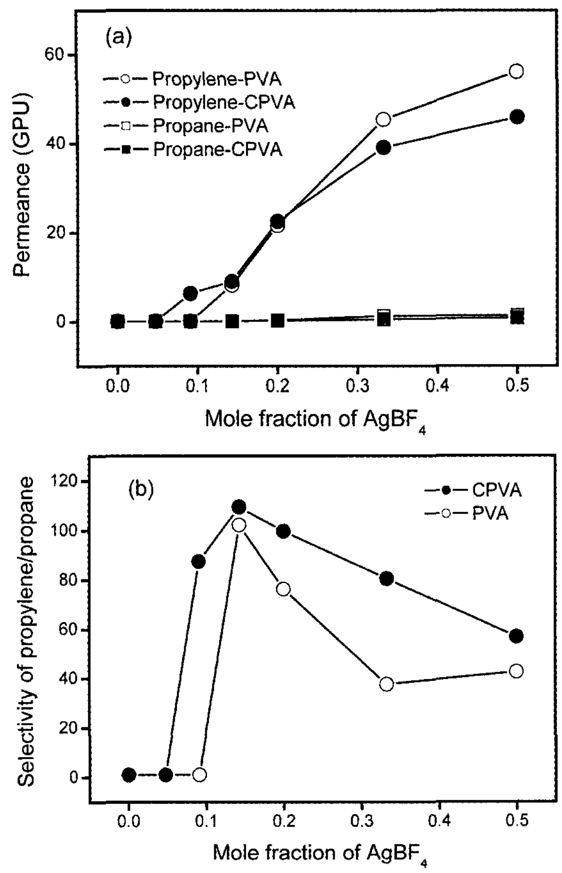

Fig. 1. The separation properties of PVA and CPVA/ $AgBF_4$ complex membranes as a function of silver mole fraction; (a) the permeances of propylene and propane and (b) the selectivity of propylene over propane.

3. Results and Discussion

The separation performances of both the permeances and selectivity of propylene/propane mixtures have been evaluated for the CPVA and PVA membranes with silver salt. Fig. 1 shows (a) the permeances of propylene and propane, and (b) the selectivity of propylene/propane through PVA and CPVA membranes containing $AgBF_4$. The permeances of propylene were always much higher than those of propane irrespective of crosslinking, resulting in remarkably higher separation performance for propylene/propane mixtures. Pristine PVA and CPVA membranes exhibited very low permeances, i.e. less than 0.01 GPU, together with the selectivity as low as unity. Upon the incorporation of $AgBF_4$, the permeances of propylene gradually started to increase from 0.09 of silver mole fraction and 0.14 for CPVA and PVA membranes, respectively. This is a very intriguing result in the point that CPVA membranes exhibited lower threshold silver concentration than PVA membranes.

Previously, we investigated the dependence of threshold silver concentration on the polymer matrix in facilitated olefin transport through polymer/silver salt complex membranes[16]. The effect was assessed for complexes of silver salts with polymeric ligands containing three different carbonyl groups, i.e., amide, ketone and ester groups. It wasfound that the threshold concentration of silver salt for facilitated olefin transport depends on the polymeric ligand, and has the following order: amide > ketone > ester. This dependence of the threshold concentration on the polymeric ligand was explained in terms of the differences between the comparative strengths of the interactions of silver ions with the different carbonyl oxygens, and that of silver ions with olefin molecules. It was therefore concluded that when the former interaction is stronger than the latter, the threshold concentration for facilitated olefin transport is high, and when the former interaction is weaker than the latter, the threshold concentration for facilitated olefin transport is low.

Silver ions mostly coordinate to hydroxyl oxygens in the PVA complex membranes whereas they do to both hydroxyl and aldehyde oxygens in the CPVA membranes. According to our previous work[30], the interaction of silver ions with aldehyde oxygens was marginally stronger than that with hydroxyl oxygens. Therefore, the lower threshold silver concentration for CPVA/$AgBF_4$ membranes than PVA/$AgBF_4$ may be attributed to the difference of these interactions and coordination structures.

The permeance of propylene through PVA/$AgBF_4$ membrane was slightly higher than that through CPVA/ $AgBF_4$, which can be explained by the structural compactness of polymeric chains due to crosslinking reaction. However, their difference was not greatly prominent, which might come from the use of the most active silver salt as olefin carrier, i.e. $AgBF_4$. On the other hand, the permeances of propane were as low as 0.01 GPU, irrespective of the concentration of silver salt and the crosslinking reaction.

A linear increase of propylene permeances with an increase of the concentration of silver salt above threshold concentration was observed for both PVA and CPVA membranes. Concentration fluctuation theory predicts an almost linear relationship between the permeability through a facilitated transport membrane and the carrier concentration[31]:

$$\frac{\overline{P_f}}{\overline{P}} = 1 + \left(\frac{p_d}{p_0}\right)\sqrt{n^2\left\{\frac{2\pi k_2 L^2 C_B^0}{\overline{P}}\,\frac{\ln(1+Kp_0)}{p_0}\right\}^2}$$

where $\overline{P_f}$ and $\overline{P}$ are the permeabilities of the facilitated transport membrane and membrane matrix, respectively p_0 and p_d are the applied pressure and pressure fluctuation due to the reversible reaction, respectively $n = N_A C_B^0(\pi r_s^2 L)$, where L is the membrane thickness, r_s is the permeant radius, and C_B^0 is the carrier concentration and k_2 and K are the backward reaction rate constant and the equilibrium constant of the solute-carrier reaction, respectively. Therefore, the linear dependence between the propylene permeance and the silver concentration evident in the experimental results is consistent with the concentration fluctuation theory.

Maximum selectivities were observed at around 0.14 of silver mole fraction for both PVA and CPVA/$AgBF_4$ complex membranes.This composition corresponds to 6:1 mole ratio of [OH]:[Ag] or ([OH]+[CHO]):[Ag], suggesting each silver ion in the membrane is coordinated by six oxygens. The decrease of selectivity above this critical composition may come from the presence of ion pairs or higher order ionic aggregates, producing interfacial defects between polymer matrix and the salt. This is supported by the increase of propane permeance through both PVA and CPVA membranes, from 0.01 to 1.32 GPU and from 0.01 to 0.81 GPU, respectively, even though it is not clearly shown in Fig. 1(a).

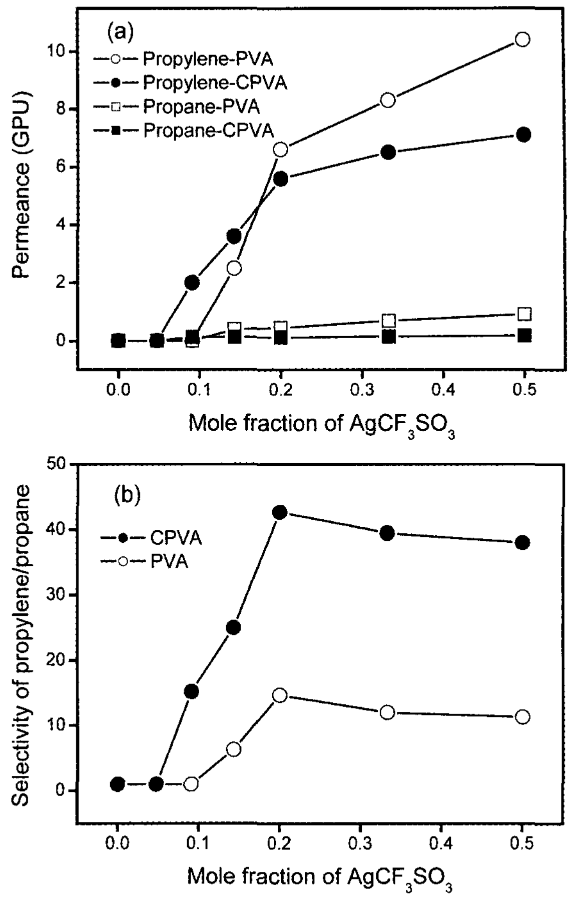

Fig. 2. The separation properties of PVA and CPVA/$AgCF_3SO_3$ complex membranes as a function of silver mole fraction; (a) the permeances of propylene and propane and (b) the selectivity of propylene over propane.

The separation performances for the CPVA and PVA membranes complexed with $AgCF_3SO_3$ were measured and presented in Fig. 2. The behaviors of separation property for the membranes containing $AgCF_3SO_3$ were not greatly different from those containing $AgBF_4$, in the point that 1) threshold concentration for CPVA membranes was lower than PVA membranes, 2) the propylene permeances increased almost linearly with an increase of silver concentration above threshold concentration. However, it should be noted that the composition of maximum selectivity for the membranes corresponds to 5:1, which is higher than the membranes containing $AgBF_4$. This result is presumably attributed to the different coordination atmosphere be-

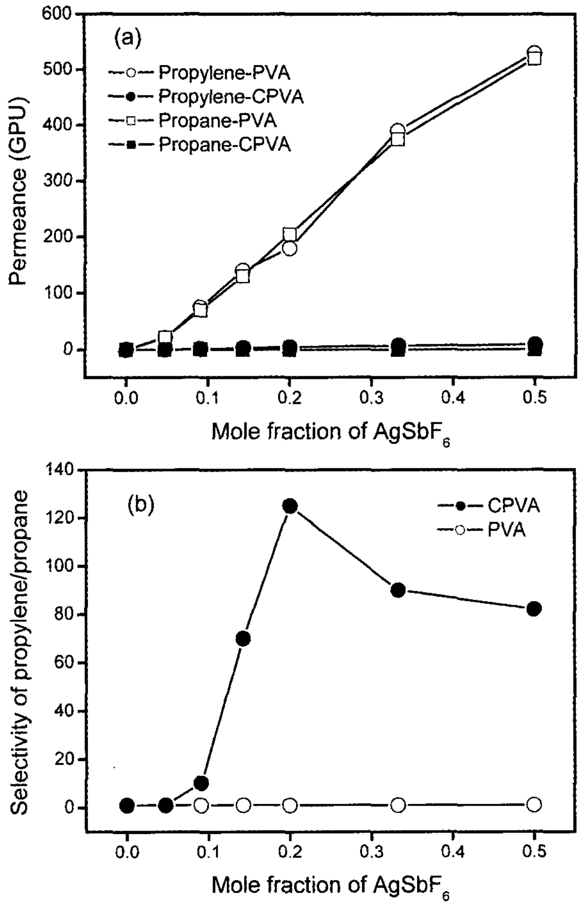

Fig. 3. The separation properties of PVA and CPVA/$AgSbF_6$ complex membranes as a function of silver mole fraction; (a) the permeances of propylene and propane and (b) the selectivity of propylene over propane.

tween oxygen and silver ions, and the difference of the most favorable coordination numbers of the two salts [15,26].

The separation properties of the membranes containing $AgSbF_6$ were completely different from the membranes containing other two salts, as seen in Fig. 3. First, PVA/$AgSbF_6$ membranes hardly exhibited facilitated propylene transport, presenting very low selectivity of propylene/propane mixtures as unity. Second, the permeances of propylene and propane through PVA/$AgSbF_6$ membranes were almost identical each other and both increased with an increase of salt concentration. It might be originated from poor solubility of $AgSbF_6$in PVA[29]. However, the CPVA/$AgSbF_6$ membranes exhibited the selectivity as high as 128 at 0.2 of silver mole fraction. These results represent that 1) silver ions coordinated to aldehyde groups are more effective in facilitated olefin transport than those coordinated to hydroxyl groups, and 2) facilitated olefin transport through PVA membranes in the solid state is only observed when the PVA is crosslinked.

Table 1. The Separation Properties of PVA and CPVA/silver Salt Complex Membranes at 0.2 of Silver Mole Fraction

Salt	Polymer matrix	Permeance (GPU)	Selectivity
$AgBF_4$	PVA	21.9	76.3
	CPVA	20.7	99.7
$AgCF_3SO_3$	PVA	6.6	14.7
	CPVA	5.6	42.7
$AgSbF_6$	PVA	213.4	1.0
	CPVA	4.1	125.2
$AgNO_3$	PVA	0.3	1.0
	CPVA	0.2	1.9

The separation properties through PVA and CPVA complex membranes with four kinds of silver salt at 0.2 of silver mole fraction were compared and summarized in Table 1. The results show that 1) CPVA membranes always exhibited higher selectivity than PVA membranes, but slightly lower permeance of propylene, 2) $AgBF_4$ membrane was the most effective facilitated transport membrane for the separation of propylene/propane mixtures, 3) facilitated olefin transport through $AgSbF_6$ membranes in the solid state was only observed when the PVA is crosslinked, and 4) $AgNO_3$ membranes did not exhibit facilitated transport irrespective of the crosslinking of the membranes.

4. Conclusions

Facilitated transport membranes were preparedby the complexation of PVA and CPVA with silver salt and their separation properties of propylene/propane mixtures were investigated. Upon the crosslinking of PVA, the selectivity increased significantly whereas the propylene permeance decreased to some degree. The separation properties were also strongly dependent on the kind of silver salt. The use of $AgBF_4$ produced the highest separation performance whereas that of $AgNO_3$ hardly exhibited facilitated propylene transport irrespective of crosslinking of the membranes. It was also found that the threshold concentrations of silver salt were sensitive to the crosslinking of membranes but not the kind of salt.

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