

Effect of Plasticizers on the Formation of Silver Nanoparticles in Polymer Electrolyte Membranes for Olefin/Paraffin Separation

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The effect of plasticizers such as dioctyl phthalate, diphenyl phthalate, dioctyl terephthalate, ethylene carbonate, glycerol, and sucrose on the performance and stability of polymer electrolyte membranes consisting of AgBF_4 and poly(vinylpyrrolidone) (PVP) or poly(2-ethyl-2-oxazoline) (POZ) has been investigated for the separation of propylene/propane gas mixtures. The mixed gas permeances and selectivities for propylene over propane on AgBF_4 –PVP and AgBF_4 –POZ membranes without a plasticizer continuously decreased with time due to the reduction of silver ions in the membrane. Reduction of silver ions to silver nanoparticles in AgBF_4 –PVP membrane was confirmed by transmission electron microscopic (TEM) analysis. Among the plasticizers tested, the presence of dioctyl or diphenyl phthalate was found to improve the stability and performance of the membranes significantly. On the other hand, the performance of the membranes containing glycerol or sucrose as a plasticizer rapidly deteriorated even faster than that of the membranes without a plasticizer. TEM analysis of the membranes shows that the rate of silver nanoparticle formation is greatly reduced by the addition of a phthalate, but accelerated by the presence of glycerol.

Introduction

Olefin/paraffin separation using facilitated transport membranes has been of interest for some years.^{1–14} Recently, several studies on solid polymer membranes containing silver salt as carriers for the facilitated transport of olefin have been reported.^{4–14} Polymers such as poly(ethylene oxide) (PEO),^{4,5} poly(2-ethyl-2-oxazoline) (POZ), poly(vinylpyrrolidone) (PVP),^{6–10} polyacrylamide,¹¹ poly(vinyl methyl ketone),¹³ and cellulose

acetate¹⁴ containing polar groups in their chains have been used as polymer matrix to dissolve the silver salts for the olefin-facilitated transport. However, the silver salt-polymer electrolytes exhibit severe disadvantages that affect the commercialization of this separation process. One major drawback observed on these membranes is their poor stability, leading to rapid degradation in the membrane performance. Therefore, the stabilization of the silver ions, confined in the membrane matrix, is a challenging topic as it could lead to promising impacts on membrane science and separation technology. For this reason, we have undertaken our study to increase the stability of the polymer electrolyte membrane containing silver ions.

PVP and POZ are often used as polymers in the preparation of silver salt–polymer electrolytes for olefin/paraffin separation.^{6–10} However, PVP and POZ are also known as reducing agents for silver ions^{15,16} and protecting agents for silver colloids.^{17,18}

Recently, we reported the effect of phthalates in preventing the reduction of silver ions and enhancing the performance of olefin/paraffin separation for AgBF_4 –PVP membranes.¹⁹ Here, we report the detailed study of the effect of several plasticizers on the stability and

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Table 1. Plasticizers Selected for Study and Their Properties

Plasticizer type	Chemical Structure	Plasticizer type	Chemical Structure
Dioctyl phthalate (DOP)		Sucrose	
Diphenyl phthalate (DPP)		Glycerol	
Dioctyl terephthalate (DOT)		Ethylene carbonate	

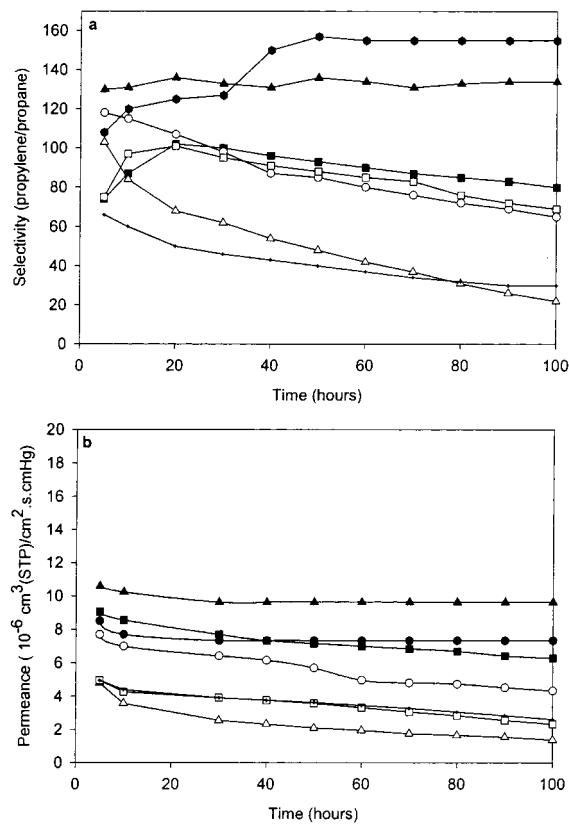


Figure 1. Selectivity and permeance of PVP- AgBF_4 membrane with or without plasticizers with time: (a) selectivity; (b) permeance. (-●- 2% dioctyl phthalate, -▲- 2% diphenyl phthalate, -■- 2% dioctyl terephthalate, -○- 2% sucrose, -△- 2% glycerol, -□- 2% ethylene carbonate, and -+- without plasticizer).

performance of AgBF_4 -PVP and AgBF_4 -POZ membranes. The effect of plasticizer on the interaction of silver ions with polymer has also been investigated using FT-IR spectroscopy and transmission electron microscopy (TEM).

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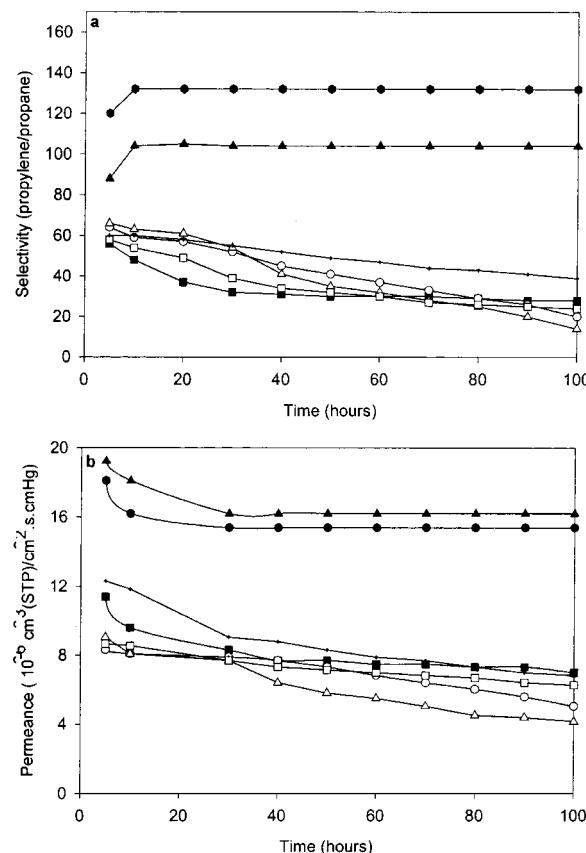


Figure 2. Selectivity and permeance of POZ- AgBF_4 membrane with or without plasticizers with time: (a) selectivity; (b) permeance. (-●- 2% dioctyl phthalate, -▲- 2% diphenyl phthalate, -■- 2% dioctyl terephthalate, -○- 2% sucrose, -△- 2% glycerol, -□- 2% ethylene carbonate, and -+- without plasticizer).

Experimental Section

Materials. Silver tetrafluoroborate, poly(2-ethyl-2-oxazoline), dioctyl phthalate, diphenyl phthalate, dioctyl terephthalate, ethylene carbonate, glycerol, and sucrose were purchased from Aldrich Chemical Co. Poly(vinylpyrrolidone) ($M_w = 1 \times 10^6$) was obtained from Polyscience. All the chemicals were used as received.

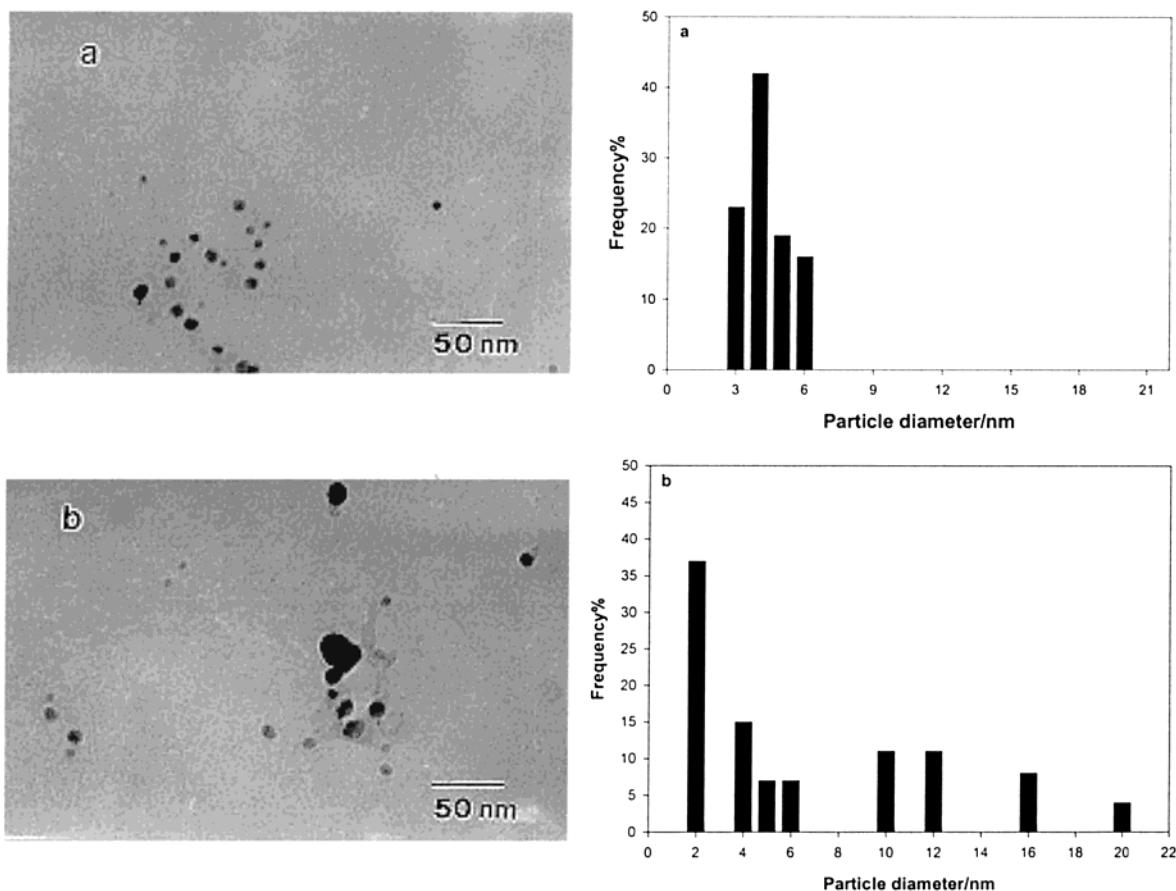


Figure 3. Transmission electron micrographs and corresponding size histograms of silver nanoparticles in PVP–AgBF₄ membrane (a) just after the preparation and (b) after 1 week of preparation.

AgBF₄-PVP and AgBF₄-POZ Membranes for Permeation Measurements. Polymer electrolyte solutions containing equimolar amounts of AgBF₄ and a polymer were prepared by dissolving AgBF₄ in 20 wt % PVP or POZ in methanol. 2 wt % of plasticizer with respect to PVP or POZ was added to these solution when needed. The solution was then coated onto polysulfone microporous membrane support (SEAHAN Industries Inc., Seoul, Korea) using an RK Control Coater. The solvent was evaporated in a light-protected convection oven at 25 °C under a stream of nitrogen, and then the membrane was dried completely in a vacuum oven for 24 h at room temperature. The thickness of the top polymer electrolyte layer was ca. 1 μm. Permeation tests were performed in a stainless steel separation module as described elsewhere.¹² The flow rates of mixed gas and sweep gas (helium) were controlled using mass flow controllers. The gas flow rates represented by gas permeance were determined using a soap bubble flow meter. Mixed-gas (50:50 vol % of propylene/propane mixture) separation properties of the membranes were evaluated by gas chromatography (Gow-Mac) equipped with a TCD and a unibead 2S 60/80 packed column.

Characterization. Transmission electron micrographs were obtained from a Philips CM30 microscope operating at 300 kV. Membranes for TEM were prepared by casting a methanol solution of PVP (20 wt %) containing AgBF₄ and/or a plasticizer (2 wt % of PVP) on a glass plate and dried for 2 h in a light-protected convection oven at 25 °C under nitrogen. The membrane was dissolved in methanol and a drop of this colloidal silver dispersion was placed onto a standard copper grid. For IR measurements, the methanol solution containing a silver salt, polymer, and a plasticizer was coated onto a 25 mm × 3 mm CaF₂ window and dried under a vacuum. The coated window was placed in a specially designed gas cell together with an uncoated window.²⁰ IR spectra were recorded

on a Mattson Infinity spectrophotometer equipped with MCTA detector.

Results and Discussion

Membrane prepared from a methanol solution of 1:1 molar ratio of carbonyls of PVP or POZ and AgBF₄ shows high selectivity and permeance for olefin/paraffin separation. A maximum selectivity of 60 for propylene over propane was observed with the AgBF₄-PVP membrane initially. However, the selectivity and permeance decrease with time as shown in Figures 1 and 2. This decrease in selectivity is ascribed to the reduction of silver ions to silver nanoparticles in the membrane. The formation of silver nanoparticles in the membrane was confirmed by TEM analysis. Figure 3 shows the TEM micrographs of the membrane prepared using a AgBF₄-PVP solution in methanol in a 1:1 molar ratio in the absence of a plasticizer. Figure 3a indicates the presence of silver nanoparticles of size less than 6 nm with narrow distribution in the AgBF₄-PVP membrane just after the preparation. The size and distribution of the nanoparticles, however, increase significantly after 1 week of preparation due to the formation, aggregation, and growth of the particles as shown in Figure 3b. The particle distribution is wide with a size range of 2–20 nm. From the TEM and permeation results, it is likely that the presence of nanoparticles of size approximately 10 nm does not greatly affect the permeance of propylene. However, the selectivity and permeance is found to decrease with time presumably due to the increase in size and distribution of silver nanoparticles.

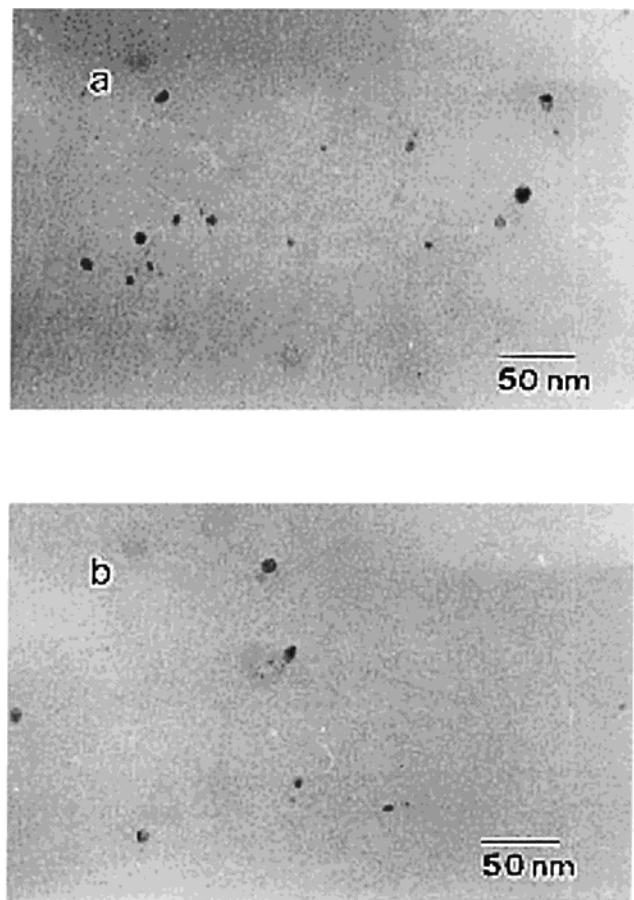
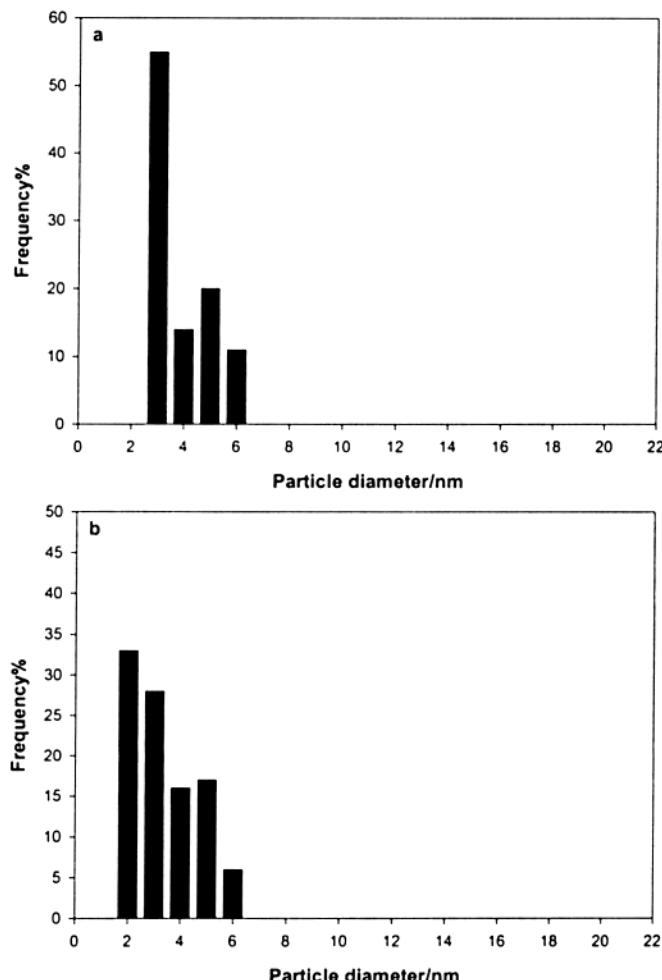


Figure 4. Transmission electron micrographs and corresponding size histograms of silver nanoparticles in PVP–AgBF₄ membrane containing 2% dioctyl phthalate (a) just after the preparation and (b) after 1 week of preparation.

We studied the effect of several plasticizers on the long-term stability and performance of AgBF₄–PVP or AgBF₄–POZ membranes. The plasticizers studied includes dioctyl phthalate, diphenyl phthalate, dioctyl terephthalate, ethylene carbonate, glycerol, and sucrose. Table 1 shows the structure of the plasticizers studied to determine the effect of plasticizer on the performance and stability of silver polymer electrolyte membranes. Figures 1 and 2 show the propylene/propane mixed gas separation properties of the membranes containing plasticizers (2 wt % of polymer) in AgBF₄–PVP or POZ–AgBF₄ membranes. The presence of a plasticizer in the AgBF₄–PVP membrane gives an increase in the initial selectivity of the membrane for the propylene gas with an increase in permeance. This increase in selectivity is attributed to the increase in the mobility of silver ions in the polymer electrolyte. It is important to mention here that the ionic mobility and conductivity of lithium ions in PEO-based lithium polymer electrolytes can be significantly increased by the incorporation of a plasticizer.^{21–25}

As shown in Figure 1, the selectivity and permeance of the membrane containing dioctyl phthalate or diphenyl



yl phthalate are high and remain constant with time for the AgBF₄–PVP membrane. On the other hand, the selectivity and permeance for the AgBF₄–PVP membrane containing ethylene carbonate or dioctyl terephthalate was high in the beginning, but it decreased gradually with time, indicating the slow reduction of silver ions in the membrane. The performance AgBF₄–PVP membranes containing glycerol or sucrose rapidly deteriorated even faster than that of the membrane without a plasticizer. This rapid decrease can be attributed to the fact that the formation of silver nanoparticles is facilitated in the presence of polyols.^{26,27}

The AgBF₄–POZ membrane containing a phthalate gives outstanding long-term stability with enhanced selectivity and permeance, as shown in Figure 2. However, unlike in PVP–AgBF₄ membranes containing a plasticizer, AgBF₄–POZ membranes containing plasticizer such as dioctyl terephthalate or ethylene carbonate show no increase in the initial selectivity or permeance. AgBF₄–POZ membranes containing glycerol or sucrose give a slightly enhanced initial selectivity, but the decrease in the selectivity and permeance is more rapid than that for the membrane without a plasticizer as in the case of PVP–AgBF₄ membranes.

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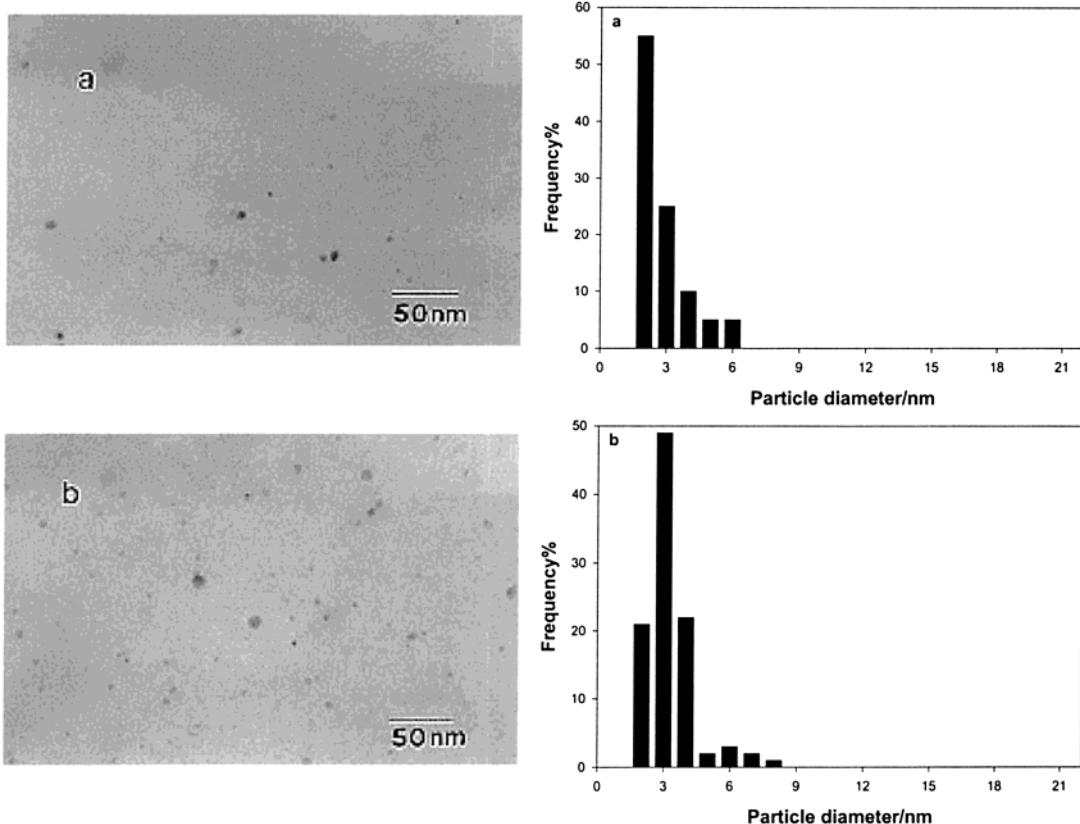


Figure 5. Transmission electron micrographs and corresponding size histograms of silver nanoparticles in a PVP–AgBF₄ membrane containing 2% glycerol (a) just after the preparation and (b) after 24 h of preparation.

For further evidence on the stabilization of silver ions in the polymer matrix, we carried out TEM analysis of the membrane containing a plasticizer. The TEM image of the membrane containing diethyl phthalate (2 wt % of PVP), taken just after the preparation, shows a much smaller number of silver nanoparticles in comparison with that of AgBF₄–PVP membrane. The TEM image of the membrane, taken after 1 week, shows no appreciable change in particle size and distribution, indicating that diethyl phthalate plays a role in preventing the reduction of silver ions in AgBF₄–PVP membranes (Figure 4). Such a stabilization of silver ions in the membrane is likely to be attributed to the strong interaction of the two ester groups of phthalate with silver ions through a chelation mode, thereby stabilizing the silver ions in the membrane. On the other hand, the incorporation of glycerol into the AgBF₄–PVP membrane results in a significant increase in the particle size and distribution with time. The TEM of the AgBF₄–PVP membrane containing glycerol as a plasticizer just after preparation and after 24 h is shown in Figure 5. On dissolution of the membrane containing glycerol in methanol after 1 week of preparation we observed the deposition of silver particles, which indicate the rapid formation and growth of silver particles.

The color change of the membrane from colorless to dark brown also indicates the formation of silver nanoparticles in the membrane. Initially, colorless AgBF₄–PVP membrane without a plasticizer attained gradual coloration with time and became dark brown in a week. The coloration was more rapid for the membrane containing glycerol or sucrose. However, no coloration was observed for the membrane containing diethyl

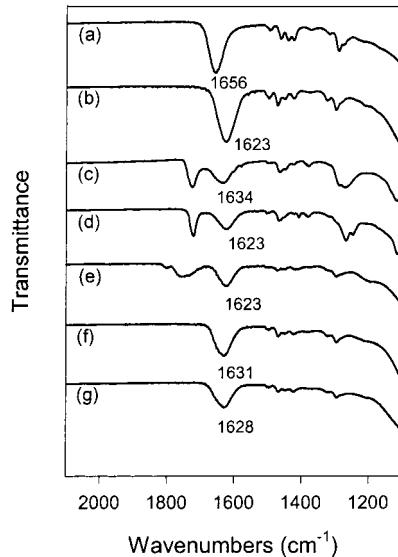


Figure 6. IR spectral changes of carbonyl groups of PVP upon interaction with AgBF₄ and a plasticizer in the molar ratio of 1:1:1: (a) PVP, (b) PVP–AgBF₄, (c) PVP–AgBF₄–diethyl phthalate, (d) PVP–AgBF₄–diethyl terephthalate, (e) PVP–AgBF₄–ethylene carbonate, (f) PVP–AgBF₄–glycerol, and (g) PVP–AgBF₄–sucrose.

phthalate, even after 3 days. Only a slight yellow coloration was observed after 1 week.

Figure 6 presents the FT-IR spectra in the carbonyl-stretching region of pure PVP, AgBF₄–PVP membrane in the molar ratio 1:1, and AgBF₄–PVP-plasticizer in the molar ratio 1:1:1. On incorporation of AgBF₄ to PVP in the molar ratio of 1:1, the carbonyl stretching band of PVP shifts from 1667 to 1623 cm⁻¹ due to the

coordination of carbonyl oxygen of PVP to silver ions. The coordinated carbonyl stretching band of PVP shifts from 1623 to 1634 cm^{-1} upon incorporation of dioctyl phthalate to PVP–AgBF₄ membrane in the molar ratio of 1:1, indicating the strong interaction of dioctyl phthalate with silver ions. On the other hand, no peak shift is observed for the coordinated carbonyl groups of PVP on incorporation of dioctyl terephthalate in the molar ratio of 1:1. This difference between phthalate and terephthalate seems to be originated from the difference in bonding mode. Phthalate can form a chelating bond to silver ions by using two adjacent ester groups, while terephthalate cannot. The coordination of carbonyl groups of PVP to silver ions is not influenced by the incorporation of ethylene carbonate. However, as shown in Figure 6f,g, the incorporation of glycerol and sucrose shifts the coordinated PVP carbonyl stretching frequency from 1623 to 1631 cm^{-1} and 1628 cm^{-1} , respectively. This further confirms the effect of chelation of two vicinal oxygen atoms of glycerol and sucrose to silver ions. Even though glycerol and sucrose strongly interact with silver ions through forming chelating bonds, the stabilities of silver ions in the membranes are extremely low. As mentioned earlier, this can be ascribed to the reducing effect of hydroxyl groups in glycerol and sucrose.²⁶

As in the case of Li polymer electrolytes containing phthalates, the strong interaction of phthalates with silver ions through a chelation is likely to facilitate the dissociation of silver salts to silver ions, thereby improving the permeation of propylene.²⁴ In addition to the facilitating role of phthalates to dissociate silver salts to silver ions, phthalates seem to function as stabilizers to prevent the reduction of silver ions to silver nano-

particles and also to prevent the aggregation of silver nanoparticles to a bigger size.

Conclusions

The silver polymer electrolyte membranes show high selectivity for propylene/ propane separation, but the selectivity is found to continuously decrease with time, due to the reduction of silver ions to silver nanoparticles. The formation of silver particles in the membranes has been confirmed by TEM analysis.

The addition of small amounts of plasticizer can significantly affect the selectivity and permeance for AgBF₄–PVP membranes. Phthalates such as dioctyl and diphenyl phthalates significantly increase the membrane stability with an enhancement in the selectivity and the permeance for the AgBF₄–PVP and AgBF₄–POZ membranes. On the other hand, plasticizers containing polyols such as glycerol and sucrose decrease the selectivity and permeance with time due to the rapid reduction of silver ions in the membranes. TEM analysis shows that the formation of silver nanoparticles can be greatly retarded by the presence of dioctyl phthalate in the membrane. IR studies show that the silver ions are more strongly held by the two ester groups of phthalates by forming chelating bonds and thus the interaction with the carbonyl groups of polymer to silver ions is reduced by the presence of a phthalate.

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