

Ionic Liquid as a Solvent and the Long-Term Separation Performance in a Polymer/Silver Salt Complex Membrane

Sang Wook Kang and Kookheon Char*

School of Chemical & Biological Engineering, Seoul National University, Seoul 151-744, Korea

Jong Hak Kim

Department of Chemical Engineering, Yonsei University, Seoul 120-749, Korea

Yong Soo Kang*

Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

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Abstract: The reduction behavior of silver ions to silver nanoparticles is an important topic in polymer/silver salt complex membranes to facilitate olefin transport, as this has a significant effect on the long-term performance stability of the membrane. In this study, the effects of the solvent type on the formation of silver nanoparticles, as well as the long-term membrane performance of a solid polymer/silver salt complex membrane were investigated. These effects were assessed for solid complexes of poly(*N*-vinyl pyrrolidone) (PVP)/AgBF₄, using either an ionic liquid (IL), acetonitrile (ACN) or water as the solvent for the membrane preparation. The membrane performance test showed that long-term stability was strongly dependent on the solvent type, which increased in the following order: IL > ACN >> water. The formation of silver nanoparticles was more favorable with the solvent type in the reverse order, as supported by UV-visible spectroscopy. The poor stability of the PVP/AgBF₄ membrane when water was used as the solvent might have been due to the small amount of water present in the silver-polymer complex membranes actively participating in the reduction reaction of the silver ions into silver nanoparticles. Conversely, the higher stability of the PVP/AgBF₄ membrane when an IL was used as the solvent was attributable to the cooperative coordination of silver ions with the IL, as well as with the polymer matrix, as confirmed by FTIR spectroscopy.

Keywords: ionic liquid, silver, olefin, membrane, stability.

Introduction

Ionic liquids (ILs) are molten salts that are fluidic over a wide temperature range, with higher viscosities (10^{-2} to 10^0 Pa s) than either aqueous ($< 10^{-3}$ Pa s) or organic ($\sim 6 \times 10^{-3}$ Pa s) electrolytes at room temperature. Their potential recyclability, solvating ability of a variety of materials, and negligible vapor pressure are some of their unique attributes. Thus, ionic liquids have recently been targeted as environmentally benign solvent substitutes for conventional volatile solvents in a variety of applications such as chemical synthesis,¹ extractions,^{2,3} dissolution,⁴ polymerization⁵ and catalysis.⁶ Quite recently we also found a new, effective application of ILs in facilitated olefin transport membranes by controlling the strength of the ionic interactions of the silver

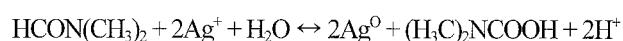
cations and its counter anion (NO₃⁻) in polymer/silver salt complexes.⁷ AgNO₃ has not been effectively used for the polymer/silver salt complexes or silver polymer electrolyte membranes in the separation of propylene/propane mixtures because of its high lattice energy. We reported on the successful use of IL in controlling the interaction between Ag⁺ and NO₃⁻, thus making Ag⁺ more active in silver-olefin complexation and consequently, more active in facilitated olefin transport. The propylene permeance increased from 0.1 to 5.5 GPU (1 GPU = 1×10^{-6} cm³ (STP)/cm² s cmHg) and the mixed gas selectivity of propylene over propane increased from 1.0 to 32.0.⁷

The facilitated olefin transport membranes consisted of a polymer with functional groups and silver ions capable of reversibly reacting with olefin molecules.⁸ Silver polymer electrolyte membranes consisting of AgBF₄ or AgCF₃SO₃ dissolved in either poly(2-ethyl-2-oxazoline) (POZ), poly(*N*-vinyl pyrrolidone) (PVP) or poly(ethylene oxide) (PEO)

*Corresponding Authors. E-mail: khchar@plaza.snu.ac.kr or kangys@hanyang.ac.kr

showed that the mixed gas selectivity of propylene over propane reached 45 and the mixed gas permeance approached 12 GPU.⁸⁻¹²

Maintaining a stable separation performance over time through membranes is critical for applications. Unfortunately, a gradual decrease in separation performance over time through silver polymer electrolyte membranes has frequently been observed,¹³ primarily because of a loss of carrier activity by the reduction of silver ions to metallic silver. This reduction originates from the fact that the polymer matrices, such as POZ, PVP or PEO, play a role as a reducing agent for silver ions.^{14,15} Isabel and Luis explained that *N,N*-dimethylformamide (DMF) in water causes the silver ions to be reduced as follows:¹⁶



Because the structure of PVP, which has amide groups, is similar to DMF, a similar reduction behavior is expected in the presence of water. It has been also reported that alcohols participate in the reduction reaction of silver ions.¹⁷ Therefore, the use of alternative solvents other than water or alcohols is desirable.

It is known that AgBF_4 is most active in olefin-complexation and thus frequently used as an olefin carrier for facilitated transport. But it is readily reduced to metallic silver and loses its carrier activity, resulting in a rapid deterioration in the separation performance with time. Therefore, it is highly desirable to prolong the separation performance when AgBF_4 is used for silver polymer electrolytes.

In this paper, we introduced an IL and acetonitrile (ACN) as alternative solvents to prepare silver polymer electrolyte membranes to prolong the separation performance of propylene/propane mixtures over time.

Experimental

Silver tetrafluoroborate (AgBF_4 , 99%), poly(*N*-vinyl pyrrolidone) (PVP, $M_w = 1.3 \times 10^6$ g/mol) were purchased from Aldrich Chemical Co. The ionic liquid, 1-butyl-3-methylimidazolium nitrate ($\text{BMIM}^+\text{NO}_3^-$) was purchased from C-TRI Co. All the chemicals were used as received. 0.05 g of PVP was dissolved in 0.95 g of ionic liquid. The (PVP in IL)/ AgBF_4 membranes were prepared by dissolving AgBF_4 in the ionic liquid solution containing 5 wt% PVP. (PVP in ACN)/ AgBF_4 membranes were prepared by dissolving 0.39 g of AgBF_4 in a solution consisting of 0.2 g PVP and 0.8 g ACN. The (PVP in water)/ AgBF_4 membrane was prepared by dissolving 0.39 g of AgBF_4 in a solution consisting of 0.2 g PVP and 0.8 g water. The solutions were then coated onto the polysulfone microporous membrane support (Seahan Industries Inc., Seoul, Korea) using an RK Control Coater (Model 101, Control Coater RK Print-Coat instruments LTD, UK). The water and ACN were evaporated in a light-protected convection oven at room tempera-

ture under a stream of nitrogen, and then the membranes were dried completely in a vacuum oven for two days at room temperature. It should be noted that the IL is hardly volatile and is mostly present in the membranes of (PVP in IL)/ AgBF_4 . Permeation tests were performed in a stainless steel separation module as described elsewhere.⁸ The gas flow rates, represented by gas permeance, were determined using mass flow controllers (MFC). The unit of the gas permeance is GPU, where 1 GPU = 1×10^{-6} cm³ (STP)/(cm² s cmHg). Mixed gas (50:50 vol% of propylene:propane mixture) separation properties of the membranes were evaluated by gas chromatography (Hewlett Packard) equipped with a TCD and a unibead 2S 60/80 packed column.

Infrared measurements were performed on a Perkin-Elmer FTIR spectrometer; 64-200 scans were signal-averaged at a resolution of 4 cm⁻¹. For UV-visible spectroscopy, solutions of PVP/ AgBF_4 with the same polymer concentration in a solvent of 0.5 wt% were dropped and spread on each quartz window by spin-coating. The quartz windows were dried under a nitrogen atmosphere for 2 h at room temperature and further dried in a vacuum oven for 2 days. UV-visible spectra were measured with spectrophotometer (Hewlett-Packard) over a range of 190 to 900 nm.

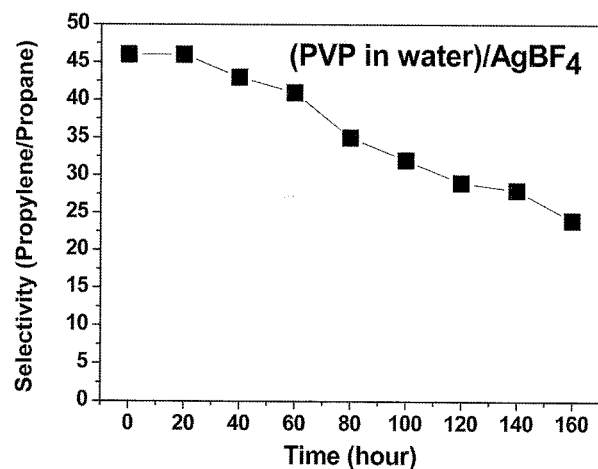
Results and Discussion

Separation Performance with Time. Figure 1 shows membrane selectivities with respect to propylene/propane of the (PVP in water)/ AgBF_4 , (PVP in ACN)/ AgBF_4 and (PVP in IL)/ AgBF_4 membranes as a function of time. The molar ratio of silver ions to the monomeric units of PVP was fixed at 1:1 or $[\text{C}=\text{O}]:[\text{Ag}]=1:1$. Both (PVP in water)/ AgBF_4 and the (PVP in ACN)/ AgBF_4 membranes showed an initial selectivity of about 40 and an initial permeance of about 12 GPU. On the other hand, the (PVP in IL)/ AgBF_4 membrane showed a selectivity of 7.2 and a permeance of 3.6 GPU.

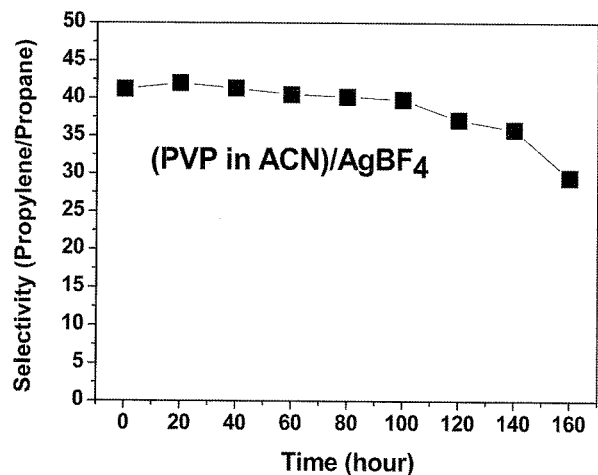
The relatively poor separation performances of the (PVP in IL)/ AgBF_4 membrane are explained as follows. First, the concentration of silver ions in the (PVP in IL)/ AgBF_4 membrane was much lower than the other two even at the same $[\text{C}=\text{O}]:[\text{Ag}]=1:1$ because the IL was scarcely volatile and thus mostly (~95 wt% in the total membrane) remained in the membranes. In other words, the carrier concentration was low compared to the others, resulting in a poor separation performance. Secondly, the propylene or propane solubilities may be much lower in the (PVP in IL)/ AgBF_4 membrane than the others because of the presence of the ionic liquid which is rather polar in nature. Thirdly, the (PVP in IL)/ AgBF_4 membrane was much thicker than the other two membranes, resulting in low permeance.

As the time for the separation experiments increased, the (PVP in water)/ AgBF_4 membrane showed a rapid decrease in separation performance with respect to time as shown in

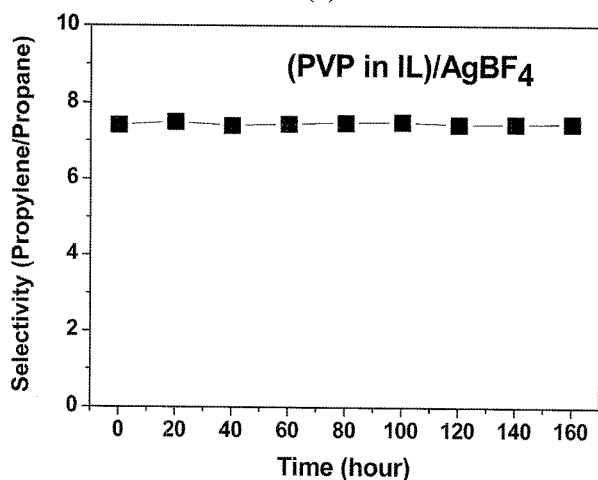
Figure 1(a). The (PVP in ACN)/AgBF₄ membrane showed a rather stable separation performance up to 100 h, after



(a)



(b)



(c)

Figure 1. Separation performance: mixed-gas selectivity of (a) 1:1 (PVP in water)/AgBF₄, (b) 1:1 (PVP in ACN)/AgBF₄, and (c) 1:1 (PVP in IL)/AgBF₄ membranes with time (40 psig and 20 °C).

which a deterioration of the separation performance was gradually observed (Figure 1(b)). On the other hand, selectivity and permeance of the (PVP in IL)/AgBF₄ membrane were nearly constant for the duration of the experiment, up to 160 h (Figure 1(c)), implying that the activity of silver ions as olefin carriers is very stable. A detailed mechanism of the improvement in the separation performance with time in the (PVP in IL)/AgBF₄ membrane will be discussed below.

Interactions of Silver Ions with IL and PVP. The interactions of silver cations with the ionic liquid and PVP were investigated by FTIR spectroscopy. Figure 2 shows the FTIR spectra recorded between 4000 and 3000 cm⁻¹ for the (PVP in water)/AgBF₄ and the (PVP in ACN)/AgBF₄ membranes. The broad band at around 3500 cm⁻¹ associated with OH groups indicates the presence of water for the (PVP in water)/AgBF₄ a with negligible amount of water for the (PVP in ACN)/AgBF₄ membranes. The (PVP in water)/AgBF₄ retained the OH band even after vacuum conditions (10⁻⁵ Torr at room temperature) for 3 days. Since the retained water plays a key role as a reducing agent for silver ions,¹⁸ the (PVP in water)/AgBF₄ membrane showed much poorer stability regarding separation than the (PVP in ACN)/AgBF₄ membrane.

To elucidate a mechanism for the more stable separation performance for the (PVP in IL)/AgBF₄ membrane, the FTIR spectra of the IL (BMIM⁺NO₃⁻), neat PVP, and (PVP in IL) containing various molar ratios of the silver salt are shown in Figure 3. The peak centered at approximately 1670 cm⁻¹ was ascribed to the carbonyl (C=O) stretching vibration of the neat PVP. The decrease of the carbonyl peak intensity at 1670 cm⁻¹ with the concomitant increase at 1636 cm⁻¹ of the (PVP in IL)/silver salt complex demonstrated a specific interaction between the carbonyl oxygen of the PVP and silver cations. At the same time, the free NO₃⁻ peak at 1360 cm⁻¹ shifted to 1288 cm⁻¹ upon forming a

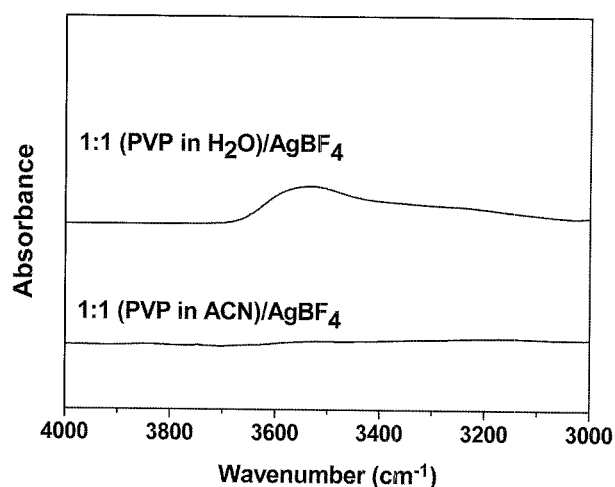
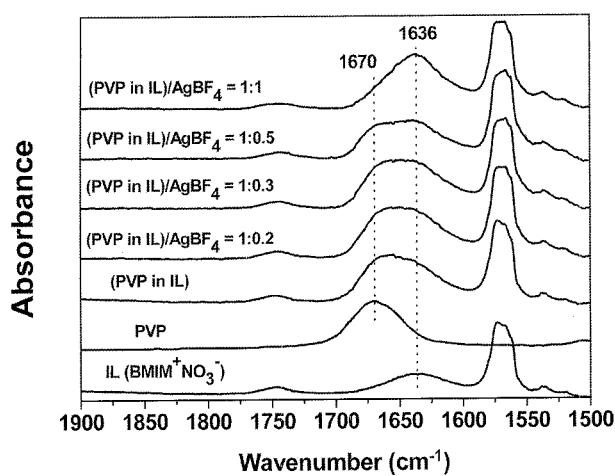
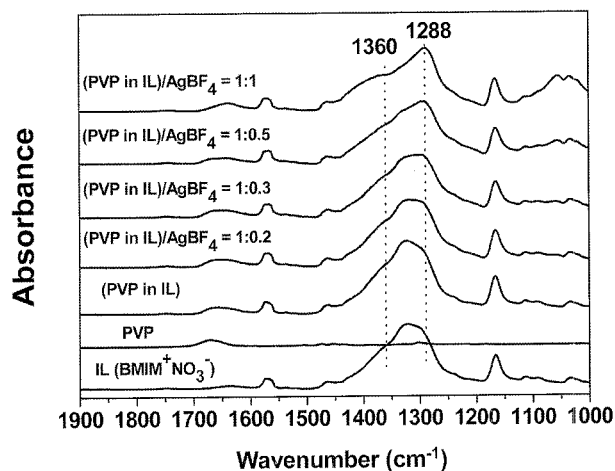


Figure 2. FTIR spectra of 1:1 (PVP in water)/AgBF₄ and 1:1 (PVP in ACN)/AgBF₄ in the range between 4000 and 3000 cm⁻¹.



(a)



(b)

Figure 3. FTIR spectra of ionic liquid (BMIM⁺NO₃⁻), neat PVP, (PVP in IL) and (PVP in IL)/AgBF₄ complexes with different mole ratios of the monomeric unit of PVP to silver ion.

NO₃⁻ complex with silver cations,¹⁹ as shown in Figure 3(b). Note that the NO₃⁻ peak shape of the IL does not change upon mixing with PVP, suggesting that no significant interaction between the IL and PVP occurs. Therefore, it could be said that the silver ions are coordinated by both the carbonyl oxygens of the PVP and the NO₃⁻ of the ionic liquid.

The peak shift of the carbonyl group in PVP was compared in three systems, i.e. (PVP in water)/AgBF₄, (PVP in ACN)/AgBF₄ and (PVP in IL)/AgBF₄ complexes, as shown in Figure 4. This figure shows that the free carbonyl peak at 1670 cm⁻¹ shifted to 1620 cm⁻¹ for both (PVP in water)/AgBF₄ and (PVP in ACN)/AgBF₄ while it shifted to 1636 cm⁻¹ for the (PVP in IL)/AgBF₄ complex. The degree of the peak shifting was much larger for the (PVP in water)/AgBF₄ and (PVP in ACN)/AgBF₄ than that for the (PVP in IL)/AgBF₄ complex, suggesting that the interaction of the silver cation with the carbonyl oxygens was stronger than that with the IL. In addition, the weak interaction between

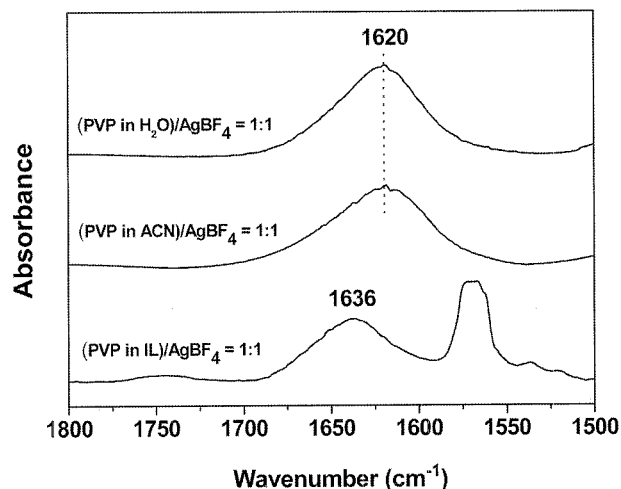


Figure 4. FTIR spectra of 1:1 (PVP in water)/AgBF₄, 1:1 (PVP in ACN)/AgBF₄ and 1:1 (PVP in IL)/AgBF₄ complexes.

the silver cation with the IL associated with the small carbonyl peak shift suggests that the charge density of the silver cations would be lower for the (PVP in IL)/AgBF₄ complex compared to those for the (PVP in water)/AgBF₄ and (PVP in ACN)/AgBF₄. This may also suggest a low olefin carrier activity for the latter and consequently, a smaller facilitated transport. This could also contribute a poor separation performance for the (PVP in IL)/AgBF₄ membrane. Therefore, it could be concluded that silver ions were additionally coordinated with the ionic liquid together with the carbonyl group of the PVP.

Reduction of Silver Ions to Metallic Silver. UV-Visible spectroscopy has been employed to investigate the reduction of silver cations to metallic silver. This is because UV-visible spectra are known to be quite sensitive to the formation of metallic silver nanoparticles. Figure 5 compares the absorption spectra for the (PVP in water)/AgBF₄, (PVP in ACN)/AgBF₄ and (PVP in IL)/AgBF₄ complexes with varied UV irradiation time. UV irradiation was carried out in order to accelerate the reduction reaction of the silver ions to metallic silver, and thus to investigate the formation kinetics of silver nanoparticles in polymer/silver salt complexes. For UV irradiation, a Spectrolinker (Spectronics Corporation, model: XL-1000 UV Crosslinker, U.S.) was used and the irradiation intensity was 4,000 μW/cm². A broad absorption maximum at around 420 nm is attributed to the surface plasmon excitation when silver nanoparticles are formed.²⁰ It is generally accepted that the height of the surface plasmon peak is associated with the amount of the silver nanoparticles.²⁰ The intensity of the plasmon peak in the (PVP in water)/AgBF₄ complex increased with increasing UV-irradiation time due to the formation of silver nanoparticles. The intensities are much smaller in the (PVP in IL)/AgBF₄ complex than those in the (PVP in ACN)/AgBF₄ and (PVP in IL)/AgBF₄ complex at any given time, indicating that the former has a

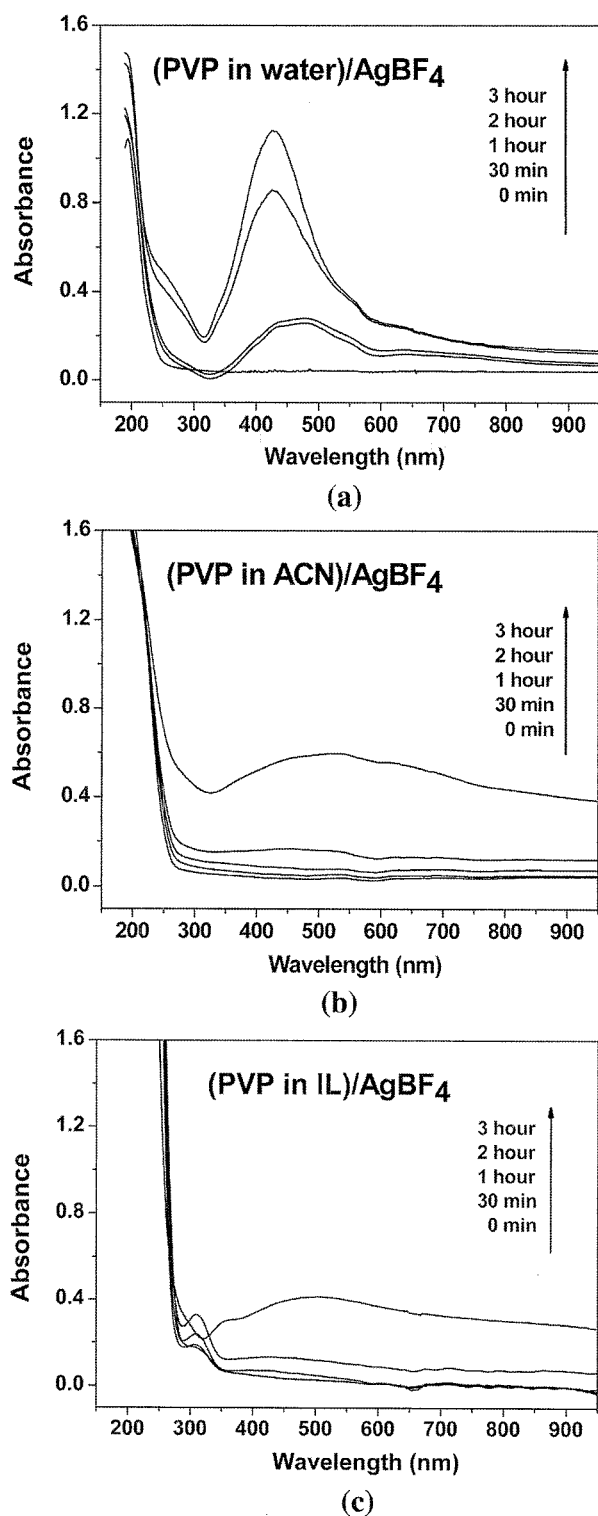


Figure 5. The UV-visible spectra of (a) 1:1 (PVP in water)/AgBF₄, (b) 1:1 (PVP in ACN)/AgBF₄, and (c) 1:1 (PVP in IL)/AgBF₄ membrane with varying UV irradiation time.

higher concentration of silver nanoparticles than the latter two. Furthermore, it was observed that the formation of silver nanoparticles was retarded or completely inhibited in

the presence of IL, compared to the presence of water and ACN, which is in consistent with the much prolonged separation performance that was observed over time.

Conclusions

The ionic liquid prolongs the separation performance of olefin/paraffin mixtures over time, but shows a rather poor separation performance compared to acetonitrile and water. The poor separation performance may be attributable to several factors: (1) less positively charged silver ions due to the rather weak interactions between the silver ions and the ionic liquid, (2) a low concentration of the silver cation olefin carrier, and (3) a longer effective thickness associated with the presence of a nonvolatile ionic liquid. More importantly, it is expected that the silver ions coordinated by the IL are more stable than those coordinated by carbonyl oxygen as confirmed by FTIR spectroscopy. Conclusively, the ionic liquid may play an important role in prohibiting the reduction reaction of silver cations to metallic silver and consequently in improving stable separation performance over time.

The effect of solvent, i.e. IL, ACN and water, was investigated with respect to the long-term stability of the polymer/silver salt complex membranes together with a correlation with the reduction behavior of silver ions to silver nanoparticles. It was found that the 1:1 (PVP in ACN)/AgBF₄ and 1:1 (PVP in IL)/AgBF₄ complex membranes were more stable with time in the separation of propylene/propane mixtures than the 1:1 (PVP in water)/AgBF₄ complex membrane. It is believed that the deterioration of the long-term stability in the (PVP in water)/AgBF₄ membrane over time is attributable to the role of the trace water that remains in the membranes as a reducing agent. Furthermore, the higher stability of the 1:1 (PVP in IL)/AgBF₄ complex membranes could be explained by the fact that the silver ions coordinated with the IL are more stable than those coordinated with carbonyl oxygen as confirmed by FTIR spectroscopy. Therefore we succeeded in preparing a long-term stable membrane for olefin/paraffin separation by using an ionic liquid as an alternative solvent.

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