

## Ionic Liquids

### Zwitterionic Silver Complexes as Carriers for Facilitated-Transport Composite Membranes\*\*

Hyunjoo Lee, Dong Bum Kim, Seoung-Hyun Kim,  
Hoon Sik Kim,\* Sung Joon Kim, Dai Ki Choi,  
Yong Soo Kang, and Jongok Won

Silver-based facilitated transport through ion-exchange membranes such as perfluorosulfonated ionomer membrane has

[\*] Dr. H. S. Kim  
Division of Environment and Process Technology, KIST  
39-1, Hawolgokdong, Seongbukgu, Seoul 136-791 (Korea)  
Fax: (+82) 2-958-5859  
E-mail: khs@kist.re.kr  
Dr. H. Lee, Dr. S.-H. Kim, Dr. S. J. Kim, Dr. D. K. Choi, Dr. Y. S. Kang  
Korea Institute of Science and Technology  
D. B. Kim, Prof. J. Won  
Department of Chemistry  
Sejong University  
Seoul (Korea)

[\*\*] We acknowledge financial support by a grant (BC1-108) from Carbon Dioxide Reduction & Sequestration Research Center, one of the 21st Century Frontier Programs funded by the Ministry of Science and Technology of Korean government. We also thank Korea Institute of Science & Technology and Kolon Petrochemical Industry Co. for financial supports.

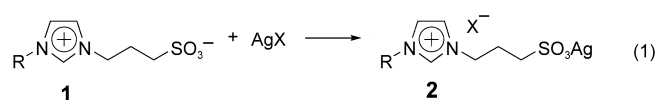
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been considered a promising alternative to low-temperature distillation to separate alkenes from their corresponding alkane.<sup>[1–5]</sup> However, ion-exchange membranes often require costly and complicated preparation steps, and exhibit alkene/alkane selectivity only when the feed mixture is humidified.<sup>[6–7]</sup> Therefore, the exploration of new membrane material to overcome the disadvantages of ion-exchange membranes still remains a challenging problem.

Recently, ionic liquids have attracted increasing interest as environmentally benign media in many organic transformations, as electrolytes for batteries and capacitors, and in extraction, adsorption, nanoparticle formation, and separation processes.<sup>[8–11]</sup> Accordingly, various types of ionic liquids have been developed for specific purposes.<sup>[12–16]</sup> Among ionic liquids reported, we are particularly interested in zwitterionic-type ionic liquids that contain covalently bound anionic sulfonate group, which can be used as a fixed sites to bind silver ions, such as in sulfonated ionomer membranes.<sup>[3]</sup>

Herein, we report on the synthesis and characterization of zwitterionic-type silver complexes, and their performance as carriers for facilitated transport membranes in separating isoprene from a mixture with *n*-pentane. Isoprene/*n*-pentane was chosen as the feed mixture because isoprene is traditionally separated from C5 raffinate by using an energy-intensive extractive distillation owing to azeotrope formation with *n*-pentane.<sup>[17]</sup>

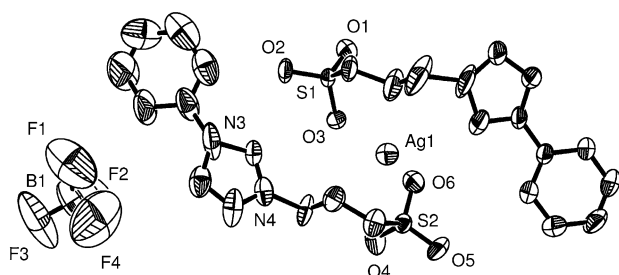
The zwitterionic silver complexes can be easily prepared from silver salts and zwitterionic-type imidazolium compounds that contain a covalently bound sulfonate group as shown in Equation (1).<sup>[14]</sup>



(a: R = Me, b: R = Bu, c: R = Ph; X = NO<sub>3</sub>, ClO<sub>4</sub>, BF<sub>4</sub>)

Zwitterionic silver complexes, **2** were prepared in high yields by the reaction of **1** with a silver salt. Treatment of **1a** with AgBF<sub>4</sub> in THF for 3 h at a room temperature produced **2a**-BF<sub>4</sub> as a white solid. Elemental analysis of **2a**-BF<sub>4</sub> indicated that the complex is a 1:1 addition product of **1a** and AgBF<sub>4</sub>. To confirm this, we attempted a single-crystal X-ray diffraction study of **2a**-BF<sub>4</sub>, but failed to obtain a suitable crystal for the X-ray analysis. Instead, crystals of **2c**-BF<sub>4</sub> were grown in methanol and analyzed by X-ray crystallography (Figure 1).<sup>[18]</sup>

To our surprise, the X-ray study reveals that **2c**-BF<sub>4</sub> is an 1:2 addition product in which the silver ion is coordinated by two sulfopropyl imidazolium ions. It is not certain at the moment why the complex **2c**-BF<sub>4</sub> exists as a 1:2 adduct instead of 1:1, but the bulkiness and/or the electron-withdrawing effect of the phenyl group on the imidazolium moiety is likely to be responsible for the formation of the 1:2 adduct. The silver ion in **2c**-BF<sub>4</sub> is located between two sulfopropyl imidazolium ions and is coordinated by the oxygen atoms of two sulfonate groups. The distances between oxygen atoms of



**Figure 1.** Molecular structure of **2c**-BF<sub>4</sub>. Ellipsoids are shown at 30% probability levels. The unlabeled atoms are carbon atoms and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ag(1)-O(3) 2.314(5), Ag(1)-O(6) 2.369(6), S(1)-O(1) 1.447(6), S(1)-O(2) 1.443(5), S(1)-O(3) 1.465(5), S(1)-O(3)-Ag(1) 137.06(3), O(3)-Ag(1)-O(6) 94.46(2), S(2)-O(6)-Ag(1) 118.02(3).

the sulfonates and the silver ion, Ag(1)-O(3) and Ag(1)-O(6), are 2.314 and 2.369 Å, respectively.

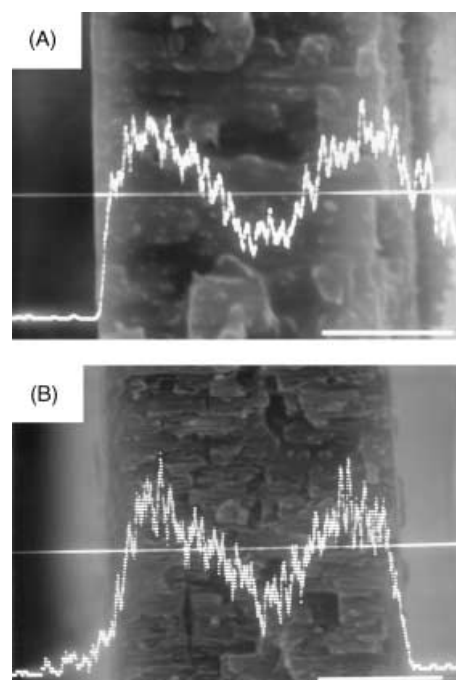
Melting points of the zwitterionic complexes were determined by differentiating scanning calorimetry (DSC). An ionic liquid is defined as the ionic compound that has a melting point lower than 100°C.<sup>[8]</sup> From this point of view, zwitterionic complexes, **2a**-BF<sub>4</sub> and **2c**-BF<sub>4</sub> can be considered as ionic liquids.

Zwitterionic silver complexes were tested as transport carriers for the separation of isoprene from *n*-pentane through composite membranes. The composite membrane was prepared by casting an aqueous solution of a zwitterionic silver complex onto a polyester microporous membrane (47 mm, 0.1 µL, Whatman) by using a coater, and then dried under a vacuum.

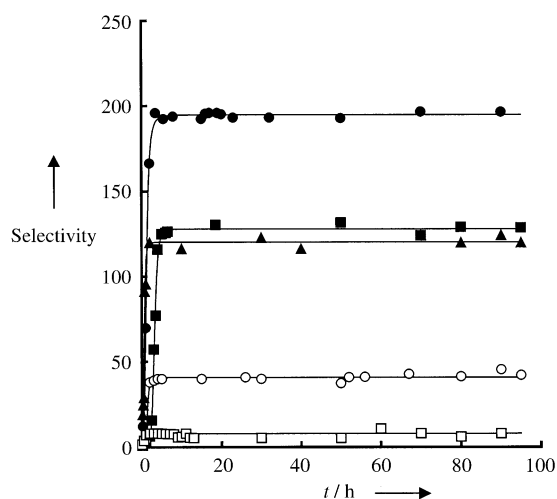
SEM-WDS (WDS = wavelength-dispersive spectrometry) photographs in Figure 2 display the cross sections of the prepared composite membrane containing **2a**-BF<sub>4</sub> before and after transportation study. The white solid lines denote the distribution of silver across the membrane. WDS images clearly show that **2a**-BF<sub>4</sub> is immobilized in the porous structure of the polyester membrane and distributed mostly at the inlet and outlet of the pores.

A comparison of the WDS images before and after use of the membranes indicates that the initial distribution of **2a**-BF<sub>4</sub> remains almost unchanged during the separation process. It is hard to figure out the state of the carriers immobilized in the pores of the membrane. From the SEM images shown in the Supporting Information, the carriers seem to exist as a thin film on the inlet surface of the polyester membrane. However, in the pores of the membrane, the carriers are likely to be in a well-dispersed solid state, which might transform into a swollen gel film upon interaction with a feed mixture.

Figure 3 shows the selectivity of isoprene over *n*-pentane with time through composite membranes containing zwitterionic silver complexes as transport carriers. The selectivity was strongly dependent on the types of counterions of the zwitterionic silver complexes in the membranes. In contrast to polymer membranes that consist of polyvinyl alcohol and silver salts in which the counterion effect was negligible,<sup>[19]</sup> the zwitterionic complex prepared from AgNO<sub>3</sub> showed much higher selectivity than those from AgBF<sub>4</sub> and AgClO<sub>4</sub>.



**Figure 2.** Cross section SEM-WDS photograph of the composite membrane containing **2a**-BF<sub>4</sub> A) before, and B) after 10 h of use. Bar = 10 µm



**Figure 3.** Change of selectivity of isoprene over *n*-pentane with time for various membranes containing zwitterionic silver complexes; ● **2a**-NO<sub>3</sub>, ■ **2a**-ClO<sub>4</sub>, ▲ **2a**-BF<sub>4</sub>, ○ **2b**-BF<sub>4</sub>, □ **2c**-BF<sub>4</sub>.

Investigation of the anion effect on isoprene transport is in progress. The selectivity also varied significantly with the change of alkyl group on the imidazolium cations. Of the zwitterionic silver complexes that have the BF<sub>4</sub><sup>-</sup> counterion, **2a**-BF<sub>4</sub> exhibits the highest selectivity and **2c**-BF<sub>4</sub> the lowest. The lower performance of phenyl-substituted imidazolium silver complex, **2c**-BF<sub>4</sub> can be largely attributed to the fact that the vacant site of silver ion is occupied by an additional sulfopropyl imidazolium ion, thereby blocking the coordination of isoprene to the silver ion to a certain extent. The

selectivities for isoprene over *n*-pentane increased rapidly with time up to about 2 h and then remained nearly constant throughout the experiments, thus demonstrating the stability of zwitterionic silver complexes towards reduction of the silver ions. In fact, the initial white color of the membrane was retained even after a long period of use. This result is a clear indication that the reduction of silver ions did not occur during the separation process. Such a high stability of silver ions in zwitterionic complexes is believed to stem from the strong interaction of silver ion with the sulfonate groups and a favorable electronic effect of the sulfopropyl imidazolium ions.

The permeation fluxes measured were  $8 \times 10^{-9}$  for **2a**-NO<sub>3</sub>,  $9 \times 10^{-9}$  for **2a**-BF<sub>4</sub>,  $6 \times 10^{-9}$  for **2a**-ClO<sub>4</sub>,  $9 \times 10^{-9}$  for **2b**-BF<sub>4</sub>, and  $4 \times 10^{-10}$  mol cm<sup>-2</sup> s<sup>-1</sup> for **2c**-BF<sub>4</sub>. As expected from the reduced number of silver ions present in the membrane, **2c**-BF<sub>4</sub> gave the lowest flux, but other zwitterionic silver complexes exhibited similar permeation fluxes. The initial fluxes were maintained throughout the separation experiments.

The membranes containing zwitterionic silver complexes were also effective for the separation of mixtures of 1-pentene and *n*-pentane. When **2a**-NO<sub>3</sub> and **2a**-BF<sub>4</sub> were used as carriers, selectivities of 93 and 47 were obtained, respectively. The lower selectivities for 1-pentene compared with those for isoprene can be attributed to the fact that the binding ability of 1-pentene to silver ions is weaker than that of isoprene.

It should be mentioned here that this is the first attempt to use ionic liquid-based silver complexes as carriers for the facilitated transport membranes in separating unsaturated compounds from their corresponding alkanes. More importantly, the membranes containing zwitterionic silver complexes are easier to prepare, more stable, and more selective for separating isoprene from *n*-pentane compared with conventional ion-exchange membranes.

Efforts to improve the performance of the membranes by modifying the imidazolium moiety in the zwitterionic silver complexes are in progress as well as the detailed investigation of the effect of water on the performance and stability of the membranes.

## Experimental Section

Compounds **1a**, **1b**, and **1c** were prepared by treating 1,3-propane sultone with the corresponding 1-alkyl or 1-phenylimidazole, similarly to the literature procedure employed for the preparation of 1-ethyl-3-sulfopropyl imidazolium compound.<sup>[14]</sup> Isoprene and *n*-pentane were purchased from Aldrich and distilled prior to use. All other chemicals were obtained from Aldrich and used as received. Melting points were measured by using a DSC (TA Instruments).

**2a**-BF<sub>4</sub>: A solution of AgBF<sub>4</sub> (11 mmol) in THF (30 mL) was treated with **1a** (10 mmol) at room temperature for 3 h. The solution was filtered, washed with THF to remove unconverted AgBF<sub>4</sub>, and dried under a reduced pressure to give air stable white solid. Yield: 96%; mp 94.9°C; elemental analysis calcd (%): C 21.08, H 3.03, N 7.02; found: C 21.12, H 3.05, N 7.00; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C):  $\delta$  = 2.17 (m, 2H; CH<sub>2</sub>), 2.78 (t, 2H; CH<sub>2</sub>), 3.75 (3, 3H; CH<sub>3</sub>), 4.22 (t, 2H; CH<sub>2</sub>), 7.30 (s, 1H; CH), 7.38 (s, 1H; CH), 8.61 ppm (s, 1H; CH).

**2a**-NO<sub>3</sub>: AgNO<sub>3</sub> (11 mmol) was treated with **1a** (10 mmol) in MeOH (30 mL) at room temperature for 3 h. The solution was

filtered to remove unconverted AgNO<sub>3</sub>, and the solvent was removed under vacuum to give an air-stable white solid. Yield: 97%; mp: 119.9°C; elemental analysis calcd (%): C 22.47, H 3.23, N 11.23; found: C 22.63, H 3.21, N 11.20; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C):  $\delta$  = 2.17 (m, 2H; CH<sub>2</sub>), 2.77 (t, 2H; CH<sub>2</sub>), 3.74 (3, 3H; CH<sub>3</sub>), 4.21 (t, 2H; CH<sub>2</sub>), 7.29 (s, 1H; CH), 7.30 (s, 1H; CH), 8.61 ppm (s, 1H; CH).

Other zwitterionic silver complexes were prepared in a similar manner to that of **2a**-BF<sub>4</sub> or **2a**-NO<sub>3</sub>.

**2a**-ClO<sub>4</sub>: Yield: 98%; mp: 103.4°C; elemental analysis calcd (%): C 20.43, H 2.94, N 6.81; found: C 20.62, H 3.01, N 6.78; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C):  $\delta$  = 2.16 (m, 2H; CH<sub>2</sub>), 2.77 (t, 2H; CH<sub>2</sub>), 3.74 (3, 3H; CH<sub>3</sub>), 4.21 (t, 2H; CH<sub>2</sub>), 7.29 (s, 1H; CH), 7.36 (s, 1H; CH), 8.60 ppm (s, 1H; CH).

**2b**-BF<sub>4</sub>: Yield: 97%; mp: 104.0°C; elemental analysis calcd (%): C 27.24, H 4.11, N 6.35; found: C 27.34, H 4.10, N 6.41; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C):  $\delta$  = 0.78 (t, 3H; CH<sub>3</sub>), 1.18 (m, 2H; CH<sub>2</sub>), 1.72 (m, 2H; CH<sub>2</sub>), 2.19 (m, 2H; CH<sub>2</sub>), 2.79 (t, 2H; CH<sub>2</sub>), 4.07 (t, 2H; CH<sub>2</sub>), 4.24 (t, 2H; CH<sub>2</sub>), 7.39 (s, 1H; CH), 7.41 (s, 1H; CH), 8.69 ppm (s, 1H; CH).

**2c**-BF<sub>4</sub>: Yield: 97%; mp: 77.4°C; elemental analysis calcd (%): C 39.63, H 3.88, N 7.70; found: C 39.80, H 3.92, N 7.68; <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O, 25°C):  $\delta$  = 2.63 (m, 2H; CH<sub>2</sub>), 2.86 (t, 2H; CH<sub>2</sub>), 4.35 (t, 2H; CH<sub>2</sub>), 7.50 (s, 5H; C<sub>6</sub>H<sub>5</sub>), 7.60 (s, 1H; CH), 7.76 (s, 1H; CH), 9.17 ppm (s, 1H; CH).

Single crystals of **2c**-BF<sub>4</sub> suitable for X-ray diffraction studies were grown in methanol at -10°C.

Performance of membranes: Composite membranes were prepared by casting an aqueous solution of a zwitterionic silver complex (2.0 mmol in 0.5 mL H<sub>2</sub>O) onto a polyester microporous membrane support (0.1  $\mu$ m, 47 mm, Whatman Industries Inc.) by using a coater. The coated membrane was dried in an oven at room temperature for 12 h under a stream of nitrogen, and then further dried in a vacuum oven at 40°C for 24 h. The separation of isoprene/*n*-pentane (50:50 wt. %) was performed at room temperature with the cast membranes in a module.<sup>[20]</sup> Helium gas (10 mL min<sup>-1</sup>) was used as a sweep gas and the flow rate of He was controlled by using a mass flow controller. A mixture of isoprene/*n*-pentane (10 mL, *v/v* = 50:50) was charged into a FEP tube attached to the lid of the module. The permeate was collected at -20°C in a trap filled with *n*-heptane and analyzed by gas chromatography (Younglin, Model 600D equipped with an FID and a unibead 2S 60/80 packed column).

Received: December 29, 2003 [Z53632]

**Keywords:** facilitated transport · ionic liquids · membranes · silver · zwitterions

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