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Separation of Olefin/Paraffin Mixtures Using Zwitterionic Silver Complexes as Transport Carriers

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Abstract: Zwitterionic silver nitrate salts of 1-(1-methyl-3-imidazolio)propane-3-sulfonate, 1-(1-methyl-1-pyrrolidinio)propane-3-sulfonate, and 1-(4-methyl-4-morpholio)propane-3-sulfonate have been prepared and tested as carriers for facilitated olefin transport membranes in the separation of ethylene/ethane, propylene/propane, and C_4 mixtures. The interactions of olefins with silver ions bound to sulfonate groups were investigated by FTIR spectroscopy as well as the correlation between the binding affinity of olefins and facilitated transport.

Keywords: ionic liquids • ionomer • membranes • olefins • zwitterions

Introduction

Olefin/paraffin separation by facilitated transport membranes, using silver salts as carriers, is considered as a promising alternative to the conventional energy intensive distillation process.[1–7] The basis for the separation is the ability of silver ions to react reversibly with olefins forming silver–olefin complexes. There have been many reports on the facilitated transport of olefins using supported liquid membranes or dense polymer membranes containing copper or silver ions as carriers.[8–14]

Silver ion confined facilitated membranes, such as dense polymer membranes, however, often suffer from a lack of long-term stability owing to the reduction of silver ions confined in the membrane matrix. In this context, perfluorosulfonated ionomer membranes like Nafion have been intensively studied because the sulfonate groups in Nafion are able to bind silver ions, thereby preventing the reduction of silver ions. However, perfluorosulfonated ionomer membranes often require costly, complicated, and environmentally unfriendly preparation.[15–20] Therefore, the search for new membrane materials that overcome the disadvantages of ion-exchange membranes still remains a challenging problem.

Recently, ionic liquids have attracted much interest as environmentally benign media in many processes, such as organic transformations, electrolytes for batteries and capacitors, extraction, adsorption, nanoparticle formation, and separation processes.[21–28] Accordingly, various types of ionic liquids have been developed for specific purposes.[29–35]

In a previous communication, we demonstrated that zwitterionic imidazolium salts with a covalently bound sulfonate group can be used as an alternative to Nafion in the separation of isoprene from *n*-pentane mixtures.[36]

Continuing this line of study, we report herein on the synthesis and characterization of a series of zwitterionic silver complexes and their performance as carriers for facilitated transport membranes in separating ethylene/ethane and propylene/propane mixtures.

Results and Discussion

1-(1-Methyl-3-imidazolio)propane-3-sulfonate (**1a**), 1-(1-methyl-1-pyrrolidinio)propane-3-sulfonate (**1b**), and 1-(4-methyl-4-morpholinio)propane-3-sulfonate (**1c**) were prepared by the reactions of 1,3-propane sultone with 1-methylimidazole, 1-methylpyrrolidine, or 4-methylmorpholine, as shown in Scheme 1.[30] The formation of a sulfonatopropylated zwitterionic compound was confirmed unambiguously by

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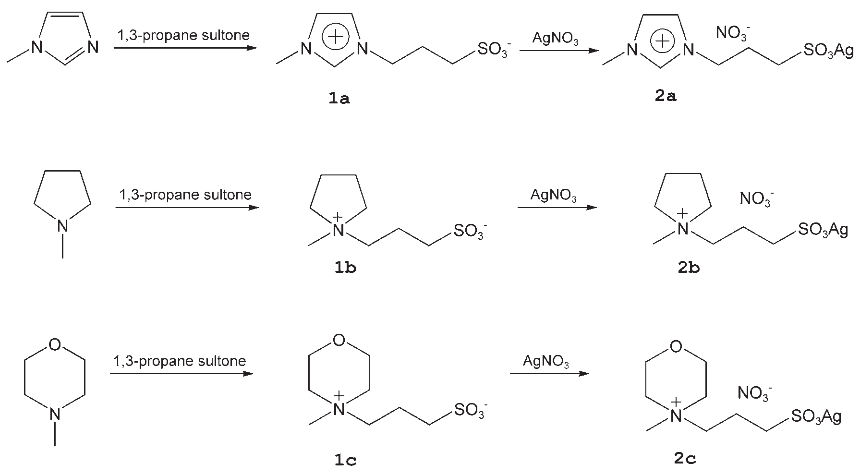

Scheme 1. Synthesis of zwitterionic silver complexes **2a–c**.

X-ray crystallographic analysis of 1-(4-methyl-4-morpholinio)propane-3-sulfonate. The molecular structure of 1-(4-methyl-4-morpholinio)propane-3-sulfonate (**1c**) in Figure 1 clearly shows that the molecule is a zwitterionic salt with a sulfonatopropyl group bonded to a nitrogen atom.

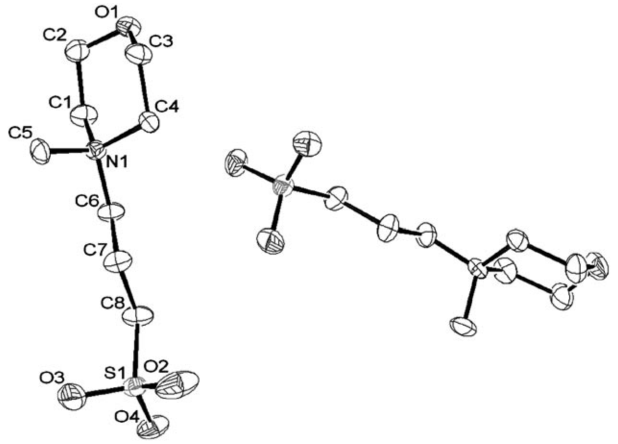

Figure 1. Molecular structure of **1c** with atom labeling. Ellipsoids are shown at the 30 % probability level and the hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: N1−C1 1.508(4), N1−C6 1.514(4), N1−C4 1.508(4), N1−C5 1.509(4), O1−C2 1.420(4), O1−C3 1.428(4), S1−O2 1.439(3), S1−O3 1.441(3), S1−O4 1.454(3), S1−C8 1.762(3); C1–N1–C6 106.0(2), C1-N1-C4 108.3(2), C1-N1-C5 111.4(3), C1-N1-C6 106.0(2), C5-N1-C6 109.7(2), C4-N1-C5 110.4(2), C2-O1-C3 111.2(2), O2-S1-O3 113.0(2), O2-S1-O4 112.53(17), O2-S1-C8 106.52(18), O3-S1-O4 112.19(19), O3-S1-C8 107.26(18), O4-S1-C8 104.64(16).

Zwitterionic silver complexes were prepared by the reaction of silver nitrate with the corresponding zwitterionic salt containing a covalently bound sulfonate group, as shown in Scheme 1.[36]

Elemental and spectroscopic analysis of the zwitterionic silver complexes indicated that all the silver complexes are 1:1 adducts of AgNO$_3$ and a zwitterionic salt. The single-crystal X-ray crystallographic analysis of the 1:1 adducts was unsuccessful because of the failure to obtain suitable crystals. However, the bonding between the silver ion and the sulfonate group was supported by the X-ray structural characterization of the product obtained from 1-(1-phenyl-3-imidazolio)propane-3-sulfonate and AgBF$_4$, which clearly demonstrates that a silver ion is tightly bonded to the sulfonate groups of two sulfonatopropylimidazolium ions.[36]

The prepared zwitterionic silver complexes were tested as olefin transport carriers for the separation of ethylene/ethane, propylene/propane, and C$_4$ olefinic mixtures through composite membranes. The membranes were prepared by casting an aqueous solution of a zwitterionic silver complex onto porous polyester supports. Only defect-free membranes were used for the separation measurements. It was assumed that the membranes were defect-free when the permeability of N$_2$ was too low to be determined in the permeation module.

Figure 2 and Figure 3 show the changes in selectivity for ethylene over ethane and the flux of permeated gases with time at room temperature through the membranes. The selectivities for ethylene over ethane ranged between 50 and 58 depending on the zwitterionic silver complex employed. The imidazolium-based silver complex **2a** showed the highest selectivity, whereas the pyrrolidinium-based complex **2b** exhibited the lowest selectivity. The fluxes were measured after 5 h of separation measurements using a bubble flow

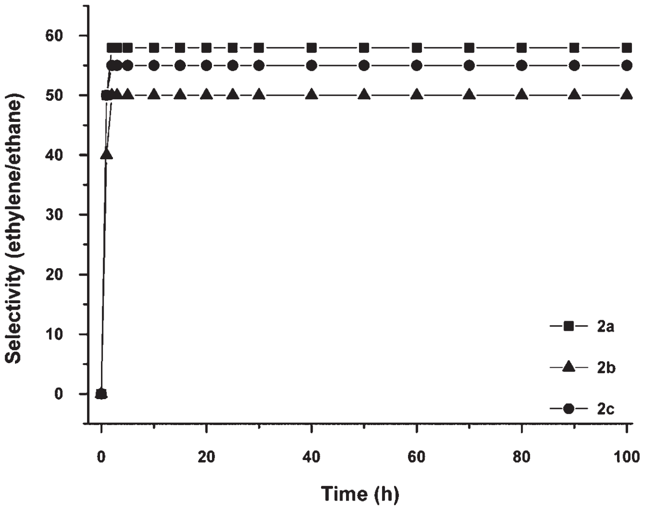

Figure 2. Change in selectivity for ethylene over ethane with time for various membranes containing zwitterionic silver complexes.

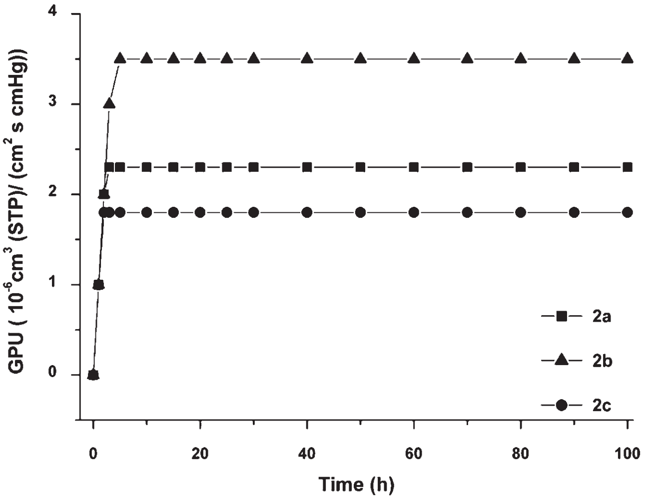

Figure 3. Change in flux of a permeated ethylene/ethane mixture with time for various membranes containing zwitterionic silver complexes.

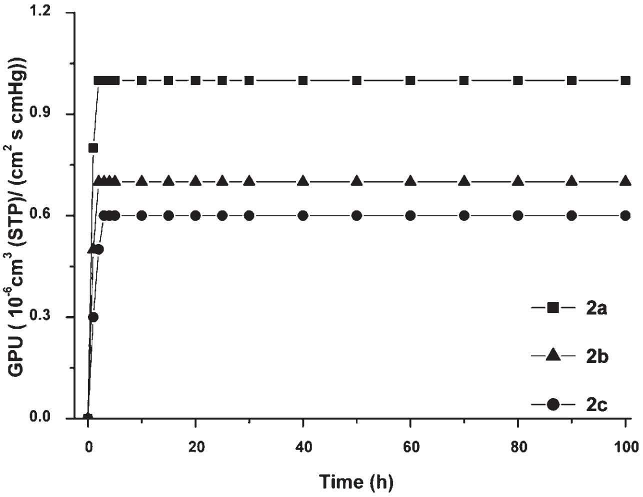

Figure 5. Change in flux of a permeated propylene/propane mixture with time for various membranes containing zwitterionic silver complexes.

meter. In contrast with the observed selectivity, the highest and lowest fluxes were achieved with **2b** and **2c**, respectively (see Figure 2). The high flux through the **2b**-containing membrane seems to be attributable to the greater solubility of the ethylene/ethane mixture in **2b** than in **2a** and **2c**.

The zwitterionic silver complexes were also tested as carriers for the separation of a propylene/propane mixture. However, unlike in the separation of the ethylene/ethane (50/50) mixture, the highest selectivity and flux were achieved with membranes containing **2c** and **2a**, respectively (Figure 4 and Figure 5). The reasons for the different behavior of each zwitterionic complex in the separation of ethylene/ethane and propylene/propane mixtures is not clear at the moment, but it is likely that the difference is somewhat influenced by the different π–π complexation ability of each of the zwitterionic silver complexes with ethylene and propylene.

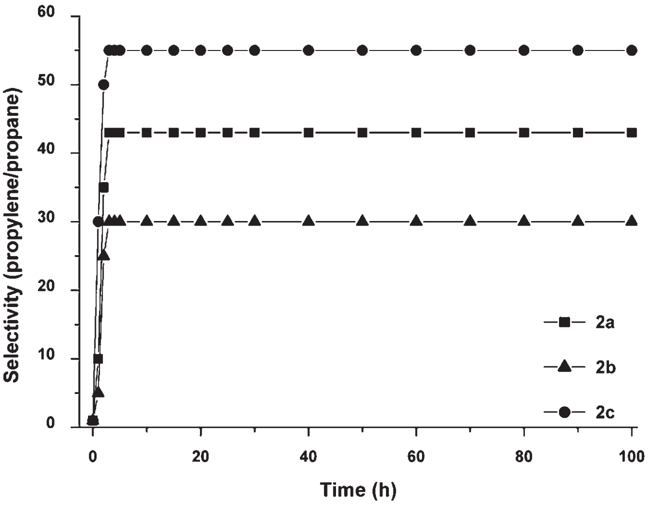

Figure 4. Change in selectivity for propylene over propane with time for various membranes containing zwitterionic silver complexes.

The interaction of olefins with silver ions confined to a carbonyl-containing polymer electrolyte membrane has been demonstrated clearly by FTIR spectroscopy,[3,4] but the interaction of olefins with silver ions bound to sulfonate groups has never been investigated. For this reason, we conducted a FTIR spectroscopic investigation of the interaction of sulfonate-bound silver ions with propylene using **2b**. For simplicity, spectra were recorded using **2b** as a background. Figure 6a and 6b show the IR spectra of free propylene and 1,3-butadiene, respectively. When the IR cell containing a film of **2b** was pressurized with 30 psig of propylene, a new peak associated with the C=C stretching frequency of the coordinated propylene appeared at 1587.7 cm^{-1}, which is about 77 cm^{-1} lower than the C=C stretching frequency of free propylene at 1664 cm^{-1} (see Figure 6c). The new peak remained even after a long period of N_2 flushing (Figure 6d). Interestingly, the peak at 1587.7 cm^{-1} was replaced by a new peak at 1548.5 cm^{-1} corresponding to coordinated 1,3-butadiene upon exposure of the propylene-coordinated **2b** to 2 atm of 1,3-butadiene for 2 min followed by purging with N_2 (Figure 6e). This result is a clear indication that an olefin coordinated to silver ions can be easily exchanged by an incoming olefin, as shown in Scheme 2. With such a rapid olefin exchange process, olefins can diffuse from the feed stream across the membrane to the permeate side, thereby resulting in selective separation of olefin from a paraffin mixture.

Figure 7 demonstrates the binding affinity of C_4 olefins to silver ions in **2b.** When the film of **2b** was exposed to 20 psig of a 1-butene/isobutylene (v/v = 50/50) mixture for 2 min and then purged with N_2 for 3 min, the IR spectrum (Figure 7d) showed a peak centered at around 1589.1 cm^{-1}.

This peak most likely corresponds to a mixture of coordinated 1-butene and isobutylene. Deconvolution of the peak shows that the 1-butene-coordinated species is predominant. On the other hand, exposure of the membrane to 20 psig of

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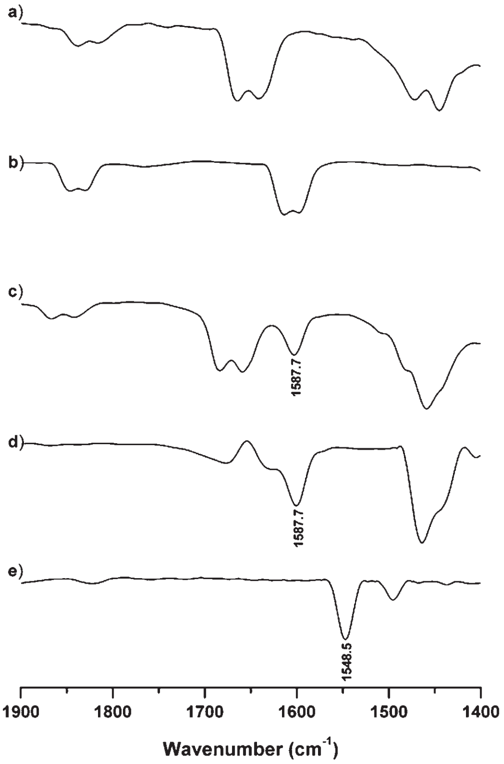


Figure 6. FTIR spectra showing the interactions of **2b** with propylene and 1,3-butadiene: a) free propylene; b) free 1,3-butadiene; c) **2b**+propylene; d) sample in (c) after N_2 purge; e) sample in (d)+1,3-butadiene followed by N_2 purge.

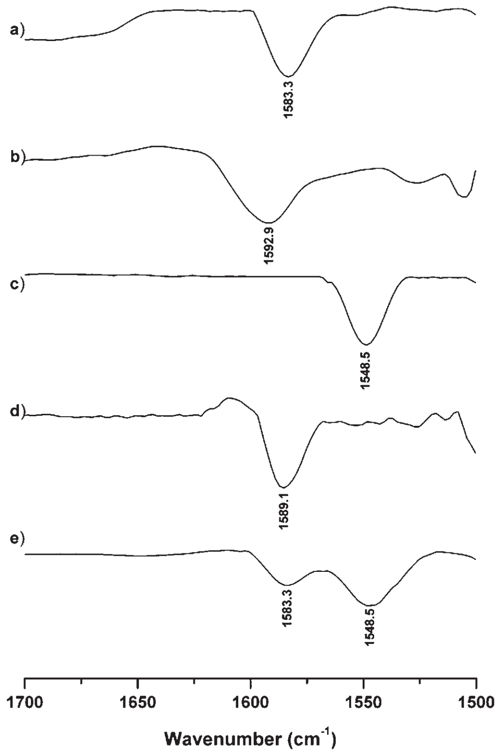


Figure 7. FTIR spectra showing the interactions of **2b** with mixtures of 1-butene/isobutylene and 1-butene/1,3-butadiene: a) **2b**+1-butene followed by N_2 purge; b) **2b**+isobutylene followed by N_2 purge; c) **2b**+1,3-butadiene followed by N_2 purge; d) **2b**+1-butene/isobutylene followed by N_2 purge; e) **2b**+1-butene/1,3-butadiene followed by N_2 purge.

a 1-butene/1,3-butadiene (v/v = 50/50) mixture for 2 min and subsequent treatment with N_2 for 3 min led to peaks corresponding to coordinated 1-butene and 1,3-butadiene, approximately in a ratio of 1:2 (Figure 7e), indicating that 1-butene has a lower binding affinity than 1,3-butadiene. From the IR spectroscopic results, it is likely that 1,3-butadiene has the highest binding affinity to silver ions of 1-butene, isobutylene, and 1,3-butadiene.

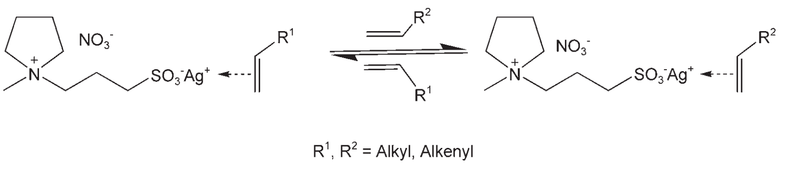
To correlate the binding affinity of C_4 olefins to silver ions in the membrane with olefin transport, 1-butene/1,3-butadiene (v/v = 50/50), 1-butene/isobutylene (v/v = 50/50), and isobutylene/1,3-butadiene (v/v = 50/50) were separated using **2b** at 25 °C and 20 psig of feed pressure. As shown in Figure 8, the selectivities were found to be around 2.3 for 1,3-butadiene/1-butene, 1.7 for 1-butene/isobutylene, and 4.1 for 1,3-butadiene/isobutylene, respectively. The order of facilitated olefin transport is 1,3-butadiene > 1-butene > isobutylene, which is in good agreement with the order of olefin binding affinity to silver ions.

Experiments to separate *cis*-2-butene/*trans*-2-butene and 1-butene/*trans*-2-butene were also conducted, but, as shown in Figure 9, the separation factors were as low as 1.6 and 2.1, respectively.

Even though the selectivity of one olefinic isomer over another is not high, it is possible that fine-tuning of the facilitated carriers could improve the selectivity.

The selectivities for ethylene over ethane and for propylene over propane increased rapidly to 40–60 in 2–5 h, depending on the type of zwitterionic silver complex employed, and then remained nearly constant throughout the experiments, demonstrating the stability of zwitterionic silver complexes towards reduction of the silver ions. In fact, the initial white color of the membranes was retained even after 100 h of use. Such a high stability of zwitterionic complexes can be ascribed to the strong interaction of silver ions with the sulfonatopropyl groups of the zwitterionic compounds.

Note that ionomer membranes containing zwitterionic silver complexes as carriers are much easier to prepare and more cost effective than con-



Scheme 2. Reversible olefin exchange on zwitterionic silver complex **2b**.

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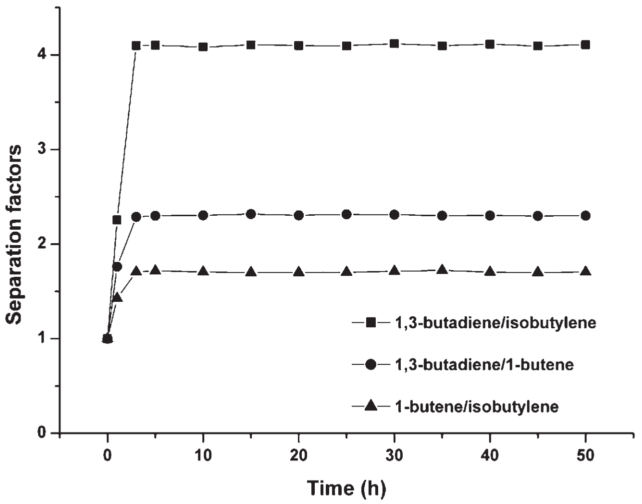

Figure 8. Separation factors for 1-butene/isobutylene, 1,3-butadiene/1-butene, and 1,3-butadiene/isobutylene mixtures through a **2b**-containing membrane.

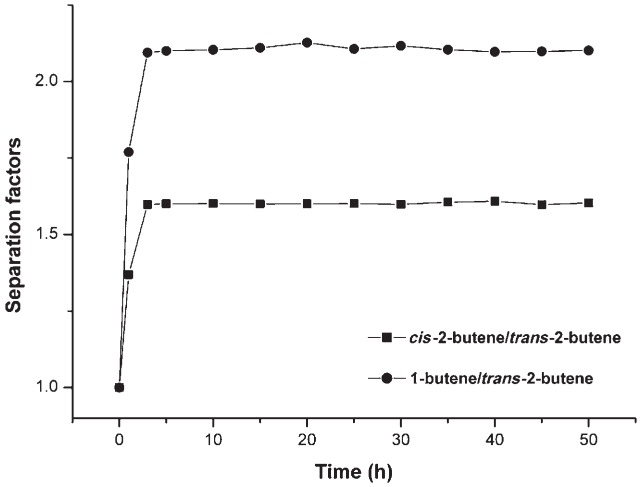

Figure 9. Separation factors for *cis*-2-butene/*trans*-2-butene and 1-butene/*trans*-2-butene mixtures through a **2b**-containing membrane.

ventional fluorinated ionomer membranes. More importantly, membranes containing zwitterionic silver complexes are highly effective for separating olefins from paraffin mixtures.

Conclusion

Silver nitrate complexes of 1-(1-methyl-3-imidazolio)propane-3-sulfonate, 1-(1-methyl-1-pyrrolidinio)propane-3-sulfonate, and 1-(4-methyl-4-morpholinio)propane-3-sulfonate were found to be highly effective carriers for facilitated transport ionomer membranes in the separation of ethylene/ethane, propylene/propane, and olefinic C_4 mixtures.

An FTIR study has demonstrated that silver ions bound to the sulfonatopropyl groups of **2b** interact with propylene to form propylene-coordinated **2b**, which in turn transforms into 1,3-butadiene-coordinated **2b** upon contact with 1,3-butadiene. This behavior indicates that an olefin coordinated to silver ions can be easily exchanged with an incoming olefin. Such a rapid olefin exchange process could be the driving force for olefins to diffuse from the feed stream across the membrane to the permeate side, resulting in selective separation of an olefin from a paraffin mixture.

Experimental Section

Method and materials: All manipulations were carried out under argon unless otherwise stated. The solvents were freshly distilled before use according to literature procedures. 1-Methylimidazole, 1-methylpyrrolidine, 4-methylmorpholine, 1,3-propane sultone, and silver nitrate were purchased from Aldrich Chemical Co. and used as received. Ethylene, ethane, propylene, propane, 1-butene, isobutylene, and 1,3-butadiene were obtained from Sinyang Gas Co. Gas chromatographic analyses of feed mixtures and permeates were conducted on a Gaw-Mac gas chromatograph equipped with a TCD and Unibead 2S 60/80 column. ^{1}H NMR spectra were recorded on a Varian Unity 300 spectrometer. Elemental analysis was carried out by using a Perkin-Elmer 2400 CHNS analyzer.

Synthesis of zwitterionic salts: Zwitterionic salt **1a** was prepared by reacting 1,3-propane sultone with 1-methylimidazole, similarly to the literature procedure employed in preparing the 1-ethyl-3-sulfonatopropylimidazolium compound.[30] 1-(1-Methyl-1-pyrrolidinio)propane-3-sulfonate (**1b**) was prepared as follows. In a 100-mL flask, 1-methylpyrrolidine (8.52 g, 0.1 mol) was refluxed with 1,3-propane sultone (13.44 g, 0.11 mol) in acetone (30 mL) for 6 h. After the reaction was complete, the precipitates were filtered, washed with acetone to remove any remaining 1,3-propane sultone, and dried under reduced pressure to give an air-stable white solid. Yield: 96%. ^{1}H NMR (300 MHz, D_2O, 25 °C): $\delta=2.24$ (m, ^3J(H,H) = 9.6 Hz, 4H; CH_2), 2.28 (t, ^3J(H,H) = 6.0 Hz, 2H; CH_2), 3.00 (t, ^3J(H,H) = 7.5 Hz, 2H; CH_2), 3.10 (s, 3H; CH_3), 3.52 (t, ^3J(H,H) = 3.9 Hz, 2H; CH_2), 3.57 (m, ^3J(H,H) = 6.0 Hz, 2H; CH_2), 3.61 ppm (t, ^3J(H,H) = 1.2 Hz, 2H; CH_2); Elemental analysis calcd (%) for $C_8H_{17}NO_3S$: C 46.35, H 8.27, N 6.76; found: C 46.37, H 8.30, N 6.73.

Compound **1c** was prepared in a similar manner to that employed in synthesizing **1b**, by refluxing 4-methylmorpholine (10.12 g, 0.1 mol) with 1,3-propane sultone (13.44 g 0.11 mol) in acetone (30 mL) for 6 h. Yield: 96%. ^{1}H NMR (300 MHz, D_2O, 25 °C): $\delta=2.27$ (m, ^3J(H,H) = 4.2 Hz, 2H; CH_2), 3.01 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_2), 3.24 (s, 3H; CH_3), 3.56 (t, ^3J(H,H) = 4.5 Hz, 4H; CH_2), 3.66 (t, ^3J(H,H) = 5.2 Hz, 2H; CH_2), 4.07 ppm (t, ^3J(H,H) = 6.0 Hz, 4H; CH_2); elemental analysis calcd (%) for $C_8H_{17}NO_4S$: C 43.03, H 7.67, N 6.27; found: C 42.97, H 7.70, N 6.28.

Synthesis of zwitterionic silver complex, **2a**: $AgNO_3$ (1.693 g, 11 mmol) was treated with **1a** (2.043 g, 10 mmol) in MeOH (30 mL) at room temperature for 3 h. The solution was filtered to remove excess $AgNO_3$ and the filtrate was evaporated under vacuum to give **2a** as an air-stable white solid.

Yield: 97%. ^{1}H NMR (300 MHz, D_2O, 25 °C): $\delta=2.32$ (m, ^3J(H,H) = 3.8 Hz, 2H; CH_2), 2.92 (t, ^3J(H,H) = 4.0 Hz, 2H; CH_2), 3.90 (s, 3H; CH_3), 4.20 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_2), 7.29 (s, 1H; CH), 7.30 (s, 1H; CH), 8.61 ppm (s, 1H; CH); elemental analysis calcd (%) for $C_8H_{17}NO_4S$: C 22.47, H 3.23, N 11.23; found: C 22.63, H 3.21, N 11.20.

Zwitterionic silver complexes **2b** and **2c** were prepared similarly to **2a**.

2b: Yield: 93%. ^{1}H NMR (300 MHz, D_2O, 25 °C): $\delta=2.22$ (m, ^3J(H,H) = 3.2 Hz, 4H; CH_2), 2.24 (t, ^3J(H,H) = 2.7 Hz, 2H; CH_2), 3.00 (t, ^3J(H,H) = 7.2 Hz, 2H; CH_2), 3.10 (s, 3H; CH_3), 3.50 (t, ^3J(H,H) = 4.7 Hz, 2H; CH_2), 3.53 (m, ^3J(H,H) = 4.5 Hz, 2H; CH_2), 3.55 ppm (t, ^3J(H,H) = 1.8 Hz, 2H; CH_2); elemental analysis calcd (%) for $C_8H_{17}N_2O_6AgS$: C 25.48, H 4.54, N 7.43; found: C 25.45, H 4.57, N 7.42.

2c: Yield: 94%. ^{1}H NMR (300 MHz, $[D_2]H_2O$, 25 °C): $\delta=2.27$ (m, ^3J(H,H) = 3.2 Hz, 2H; CH_2), 3.03 (t, ^3J(H,H) = 8.0 Hz, 2H; CH_2), 3.24 (s, 3H; CH_3), 3.52 (t, ^3J(H,H) = 4.8 Hz, 4H; CH_2), 3.64 (t, ^3J(H,H) = 3.5 Hz, 2H; CH_2), 4.07 ppm (t, ^3J(H,H) = 4.6 Hz, 4H; CH_2); elemental analysis calcd (%) for $C_8H_{17}N_2O_7AgS$: C 24.44, H 4.36, N 7.13; found: C 24.45, H 4.38, N 7.10.

FTIR experiments: The samples for the FTIR experiments were prepared by coating a 25×3 mm CaF_2 window with an aqueous solution of 10 wt% **2b**. The coated window was then vacuum-dried for 2 h at room temperature. The coated and uncoated CaF_2 windows were placed in a specially designed gas cell because the silver–olefin interaction is sensitive to moist water.[37,38] FTIR spectra were recorded with a Mattson Infinity spectrophotometer.

X-ray crystallographic study: Single crystals of **1c** suitable for X-ray diffraction studies were grown in methanol at −10 °C. Diffraction measurements were made with an Enraf CAD-4 automated diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The ORTEP structure and crystal data are presented in the Supporting Information.

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_2O) onto a polyester microporous membrane support (0.1 μm, 47 mm, Whatman Industries Inc.) using a coater knife. 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.

To perform the separation measurements the dense membranes were placed in a stainless steel separation module with an olefin/paraffin (50/50) gas mixture, as described elsewhere.[39] The flow rates of the feed mixtures were controlled by using mass flow controllers. The total feed pressure of the mixed gas was set at 20 psig using back-pressure regulators. The permeated gases were analyzed using a Gaw-Mac gas chromatograph equipped with a TCD and Unibead 2S 60/80 column.

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