Synergy of high permeability, selectivity and good stability properties of silver-decorated deep eutectic solvent based facilitated transport membranes for efficient ethylene/ethane separation

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ABSTRACT
For ethylene/ethane separation, fabrication of facilitated transport membranes (FTMs) with properties of high ethylene permeability, selectivity, long-term stability and economic feasibility remains a great challenge. In this study, a series of deep eutectic solvents (DESs) containing NO$_3^-$ as anion were designed, synthesized and characterized for the first time. Then, novel DES-FTMs were fabricated successfully through the incorporation of the transport carrier (AgNO$_3$) into as-synthesized DESs. The investigation of structure-performance relationships of FTMs suggested that the hydrogen bond acceptors (HBAs), hydrogen bond donors (HBDs) and carrier concentration could significantly enhance the ethylene/ethane selectivity up to 125. The operating conditions of the separation process were optimized, confirming ethylene/ethane selectivity increased with the decrease of the transmembrane pressure and operating temperature. The synergistic regulation of hydrogen bond and coordination interactions between DES and carrier could tune the interactions between the silver cation and its counter anion, which efficiently promoted the dissociation of carrier and increased carrier activity, leading to high ethylene permeability and ethylene/ethane selectivity. The Brønsted acidic property of HBAs endowed the FTMs with good stability. The low cost and facile availability of the DESs and carrier rendered FTMs with good economic feasibility. This study may reveal the definite potentiality of DES-FTMs in ethylene/ethane separation.

1. Introduction

The separation of olefin/paraffin is very critical for the chemistry industry and is one of the most challenging gas separations due to the similarities in their molecular sizes and physical properties [1,2]. Currently, the industrial practice is to use cryogenic distillation, which is a highly energy-intensive process associated with huge capital and operating costs [3]. Facilitated transport membranes (FTMs), such as polymeric electrolyte membranes [4,5], mixed matrix membranes [6], intrinsic microporous polymeric membranes [7], silver salt/water based liquid membranes [8,9], supported ionic liquid membranes [10], ionic liquid gel membranes [11], polymeric ionic liquid membranes [12], have been evolved as energy-efficient and environmentally friendly alternatives for olefin/paraffin separations due to their advantages of high separation efficiency and low operational cost [5,13-16].

Compared with these membranes in solid state, advanced liquid membranes exhibit much higher olefin permeability, which is very beneficial for industrial application. However, the traditional silver salt/water based liquid membranes experience severe membrane liquid loss due to the evaporation of water [8,9]. Owing to the excellent solvent properties of non-volatility and structural designability, aprotic ionic liquid based FTMs are proposed to carry out olefin/paraffin separations [10,11]. Unfortunately, these membranes suffer from poor performance in terms of selectivity due to the low carrier concentration. Then, our group construct protic ionic liquid based FTMs with high carrier concentration and activity, obtaining high gas permeability and selectivity [17,18]. However, there are growing concerns regarding high cost, complicated preparation, the toxicity and environmental effects of IL based FTMs.

Very recently, the deep eutectic solvent (DES) based FTMs, which combine the outstanding properties of DESs with the advantages of the carrier-facilitated transport, have attracted enormous research attention for olefin/paraffin separations [19,20]. As a new generation of designable and green solvents, DESs are typically obtained by mixing a
quaternary ammonium halide salt, a hydrogen bond acceptor (HBA), with a hydrogen bond donor (HBD, such as urea, glycerol, ethylene glycol, malonic acid), leading to a significant depression of the freezing point [21,22]. DESs possess negligible vapor pressure, high thermal stability, good ionic conductivity and non-flammability [23]. Notably, DESs are inexpensive, synthetically accessible, nontoxic, and biodegradable [24]. Therefore, DESs are becoming increasingly attractive in academia and have been widely used as separation media for gas mixtures [21,25–30]. However, the application of DESs in the olefin/paraffin separations is still in its infancy.

It has been well established that Cu(I) salts can form π-complexes with olefin molecules, which have been utilized as olefin carriers to accelerate the transport of ethylene [31]. In 2017, for the first time, Sun et al. [31] reported DES-FTMs based on cuprous chloride (CuCl) and 1-butyl-3-methylimidazolium chloride for the separation of ethylene/ethane mixture, where the anionic clusters such as [CuCl2]− and [Cu(Cl)4]2− formed between the Cl− with CuCl acted as the carrier to facilitate ethylene transport. Yang et al. [32] reported bimetallic (CuCl, ZnCl2) DES-FTMs for the ethylene/ethane separation. Bin et al. [19,33] designed a series of CuCl/DES-FTMs containing different HBDs for the ethylene/ethane separation, where the carrier activity was enhanced by the hydrogen-bond interactions. However, the ethylene/ethane selectivity and ethylene permeability of these CuCl/DES-FTMs are relatively low and still to be improved.

Compared with Cu(I) salts, silver salts such as AgCF3SO3 and AgBF4 have the strength of effective facilitated transport of olefins [4]. Therefore, it can be anticipated that silver salt based DES-FTMs will exhibit great potential for the olefin/paraffin separations. In spite of their tremendous potential, only one study reported the use of silver salt based DES-FTMs for ethylene/ethane separation [20]. This lacuna is as a consequence of the chemical reaction between halide ion of DES (Cl− or Br−) and silver cation, which deprives the ability of silver ion to transport olefin. Previous study reported a particular strategy to construct DESs from silver trifluoromethanesulfonate (AgCF3SO3) and acetamide, which were used as promising media for the ethylene/ethane separation, the markedly high selectivity and permeability were obtained [20]. Unfortunately, this strategy is not a generic road for designing new DESs and only few DESs can be obtained based on this strategy. Moreover, high cost of AgCF3SO3 and potential degradation are the huge obstacles for future industrial use.

Therefore, exploration of ultra-stable and cost-efficient silver salt based DES-FTMs with high separation performances may lead to a qualitative leap in olefin/paraffin separations. Inspired by the structural designability of DESs, in this study, a series of novel DESs containing NO3− as anion were synthesized for the first time. Then, novel DES-FTMs were successfully fabricated through the incorporation of the transport carrier (AgNO3) into DESs, which obtained high ethylene permeability, ethylene/ethane selectivity, good stability and economic feasibility [34].

2. Experimental

2.1. Materials

Ethylene and ethane gases were purchased from Tianjin Shengtang Gas Co., Ltd (China) with a minimum purity of 99.9 mol%. Dimethylamine (40 wt%), triethylamine, nitric acid (65–68 wt%), glycerol, ethylene glycol, triethylene glycol and silver nitrate (99.5 wt%) were all supplied from Shanghai Aladdin Biochem Technology Co., Ltd. (China) and used as received. The nylon microporous support was obtained from Haining Zhongli Filtering equipment Co., Ltd (China) with average pore size of 0.1 µm, porosity of 70%, thickness of 100 µm and diameter of 75 mm.

![Diagram of DES and HBAs](image)

Fig. 1. (a) A synthetic route to prepare HBAs and DESs investigated in this study; (b) the picture of the prepared DESs.

2.2. Synthesis of HBAs and DESs

DESs were prepared from the right combination of HBAs and HBDs. Dimethylammonium nitrate ([DMA·NO3], Tm = 75 °C) and triethylammonium nitrate ([TEA·NO3], Tm = 113 °C), were chosen as HBAs, and ethylene glycol (EG), glycerol (G) and triethylene glycol (TEG) were chosen as HBDs.

The HBAs were synthesized following a similar procedure described elsewhere [35]. In short, the nitric acid (0.2 mol) was slowly dropped into the methanol solution of triethylamine (0.2 mol) at 0 °C or below with rapid stirring. The mixture was further reacted for 8 h at RT, and then was concentrated by rotary evaporation. Subsequently, the HBA powder was crystallized from concentrated liquid at 0 °C with slow stirring. Finally, the HBA powder was washed by acetone (50 mL) for three times and dried under vacuum for 24 h at 65 °C. The structures of the [DMA·NO3] and [TEA·NO3] were confirmed by 1H NMR and FTIR measurements. Then, the synthesis of DESs was conducted as reported previously [36,37] and their water contents of the DESs were determined to be less than 500 ppm by Karl–Fischertitration method (Fig. 1).

2.3. Dissolution of silver salt

The above as-synthesized DESs served as solvents for the dissolution of AgNO3 to obtain reactive liquids. The desired amount of AgNO3 was added into the DES, and then the mixture was agitated with a magnetic stirrer at 65 °C for several hours (1–3 h). Homogeneous transparent reactive liquids with molar concentration of AgNO3 between 0.5 and 5 mol/L were obtained directly.

2.4. Preparation of FTMs

The nylon membrane was used as the support because of its well-known thermal, chemical, mechanical stability and could be easily wetted by the AgNO3/DESs (contact angles ≤ 15°). FTMs were fabricated through the pressure-based technique described elsewhere [19]. For each AgNO3/DES, 3 mL reactive liquid was spread on the membrane surface and was impregnated into the membrane pores at a transmembrane pressure of 1 bar in a circular membrane cell. The impregnation was repeated for three times to ensure that the membrane pores were completely filled with the AgNO3/DES. The DES-FTMs were successfully prepared and characterized by field emission scanning electron microscope (SEM, Hitachi S-4800).
2.5. Characterization

The viscosities and densities were determined by Viscometer (Brookfield LVDV-II+Pro, ± 1% in relation to full scale) and Densimeter (Anton Paar DMA 5000 type automatic densimeter, 0.0001 g/cm³) at 25 °C, respectively. The melting points of DESs were determined with a differential scanning calorimeter (DSC 204) by heating the samples from −120 to 100 °C at a heating rate of 5 °C/min in N₂ atmosphere. The thermal characterization were conducted on a thermal gravimetric analyzer (Netzsch TG 209) by heating the samples from RT to 800 °C with a heating rate of 10 °C/min in N₂ atmosphere. The 1H NMR spectra were recorded on the spectrometer (VARIA INOVA 400 MHz) using d₆-DMSO as the solvent with TMS as the internal standard. The Fourier transform infrared spectra (FTIR) were recorded on a spectrometer (Bio-Rad FTS 6000) at a resolution of 4 cm⁻¹ with 32 scans. Fourier transform Raman spectra (FT-Raman) were carried out by a spectrometer (Bruker RFS 100) at a resolution of 2 cm⁻¹ with 250 scans.

2.6. Determination of gas permeability

The gas permeability was measured according to the same procedure reported in our previous work [19,31,33], and the experimental apparatus employed for gas separation is depicted in Fig. 2. During the measurement, the feed stream (50:50 vol% ethylene/ethane) was supplied at a total flow rate of 60 mL/min (STP), while the nitrogen as sweep gas at the rate of 20 mL/min (STP), the pressure and operating temperature were adjusted by micrometric valves and an air blowing thermostatic oven, respectively. The compositions of gases were analyzed by the online gas chromatography.

The permeation experiments were performed at desired conditions, the permeability through the FTMs was determined according to Eq. (1):

\[ P_{m,i} = \frac{\Delta P}{\delta} J_i \]  

where \( P_{m,i} \) is the gas permeability through the membrane of the component \( i \), \( J_i \) is the permeation flux of component \( i \) through the membrane; \( \delta \) is the membrane thickness and \( \Delta P \) is the partial pressure gradient across the membrane. All the experiment data was obtained through at least three parallel experiments, and the standard deviation \( \sigma \) of permeability data was defined as Eq. (2):

\[ \sigma = \sqrt{\frac{\sum_{n=1}^{n} (P_{m,i} - \bar{P}_m)^2}{n}} \]  

where \( P_{m,i} \) is the individual experimental data point of the permeability, \( \bar{P}_m \) is the average of the data and \( n \) is the number of measurements for each data point. In all cases, the standard deviation \( \sigma \) of permeability data was lower than 5%, concluding that there was a good experimental reliability. The selectivity through the FTMs was determined according to Eq. (3):

\[ S_{ij} = \frac{P_{m,i}}{P_{m,j}} \]  

3. Results and discussion

3.1. The physical properties of DESs

Table 1 lists the compositions, melting points, densities, ion conductivities and the viscosities of the studied DESs. The novel DESs exhibited significant depression of the melting points in comparison with the corresponding HBAs and HBDs forming them and their points ranged from −95 to −75 °C (Table 1), which indicated they were attractive media for practical purposes [38]. Furthermore, the melting points of DESs could be tuned by varying the molar ratio of HBA to HBD. The viscosity values covered the range from 7.9 to 170.3 cp, which were significantly lower than those observed with traditional DESs based on the choline chloride [37,39]. The low viscosities of the DESs are favorable to the mass transfer within DESs, thus guaranteeing high C₆H₄ permeability of FTMs.

3.2. Characterization of DESs

The liquid structure of DESs was investigated by the 1H NMR and FTIR spectra. As shown in Fig. 3, when the [TEANo₃] was mixed with G to form DESs, the N-H of [TEANo₃] G 1:1 gradually shifted to up-field with the molar ratio of [TEANo₃] G 1:1 to 1:3. Meanwhile, the O-H of G in the DESs also shifted to up-field, e. g. from 4.508 ppm for G to 4.452, 4.434, 4.411 ppm for DESs with molar ratios of 1:3, 1:2, and 1:1, respectively.

As seen from Fig. 4, FTIR spectra of DESs exhibited the characteristic bands of [TEANo₃] and G. The broad peaks between 3600 and 3200 cm⁻¹ were attributed to the broadening of O-H, which confirmed the formation of hydrogen bonds in DESs. Compared with pure [TEANo₃], the stretching vibrations of NH₃⁺ and NO₃⁻ exhibited different degrees of blue shifts for the DESs with different molar ratios. The characterization results confirmed that the intercalation of the [TEANo₃] by the G disrupted the long-range ordered structure of [TEANo₃] and frustrated cation-anion electrostatic interactions. Moreover, the intramolecular hydrogen-bond networks of [TEANo₃] and G were destroyed and the intermolecular hydrogen-bond networks of DESs were built [40]. The reconstruction of hydrogen-bond networks of G-cation and G-anion led to strong charge transfer from cation and anion.
anion to G, thus generating homogeneous and stable DESs [41,42].

As seen from Fig. 5, the TGA of the [TEA·NO₃]-G (1:1) based DES revealed that the prepared DESs possessed satisfactory thermal stability and the weight loss temperature due to the initial decomposition occurred at 200 °C.

3.3. Morphological studies of FTMs

The SEM images of the nylon support and FTMs are presented in Fig. 6. The SEM images showed great differences between the support and FTMs, including top surface and cross section. It was evident that the nylon support was a highly porous material with a network of macro-pores of about 0.1 µm. After immobilization of AgNO₃/DES in the nylon support, the pores of the membranes were saturated by the homogeneously distributed AgNO₃/DES and hardly any excess AgNO₃/DES liquid accumulated on the external surface of the membranes, which was due to the relatively low viscosity of AgNO₃/DES. As shown in Fig. 6C₂, the structure of the nylon support was sponge-like and some void spaces existed. After impregnation, almost all the voids were completely filled with AgNO₃/DES liquid (Fig. 6C₂). The SEM micrographs confirmed the successful fabrication of FTMs.

3.4. The structure-performance relationship of FTMs

The gas separation performances of FTMs with the molar ratio of HBA to HBD (1:1) were measured and the results are shown in Figs. 7a-

![Fig. 3. The liquid structure of DESs: ¹H NMR spectra of different DESs.](image)

![Fig. 4. FTIR spectra of [TEA·NO₃], [G], and DESs prepared with [TEA·NO₃] and [G] at different molar ratios.](image)
As shown in Figs. 7a-7b, the DES-FTMs obtained high ethylene permeability and ethylene/ethane selectivity. For example, the ethylene permeabilities of the [DMA·NO₃]-EG and [TEA·NO₃]-EG based FTMs reached up to 785 and 643 Barrers, respectively. The ethylene/ethane selectivity of the [TEA·NO₃]-G based FTMs approached to 100. The satisfactory separation performances were probably attributable to the good disassociation of silver salt, thus obtaining a carrier with high activity. As also shown in Figs. 7a-7b, both HBDs and HBAs greatly affected the separation performances of FTMs. Compared with HBAs, HBDs had greater influence on the separation performances of the membranes. As seen from Fig. 7a, the effect of the HBDs on the gas permeability was as follows: EG > TEG > G. In contrast, the HBAs had a complicated effect on the gas permeability, if the EG and TEG were chosen as HBDs, the values of ethylene and ethane permeabilities followed the order: [TEA·NO₃] < [DMA·NO₃], while, for the G based DESs, the order was reversed. As shown in Fig. 7b, for DESs prepared with the same HBDs, the [TEA·NO₃] based DESs possessed improved ethylene/ethane selectivity compared to [DMA·NO₃] based DESs. While for HBAs, the G based DESs were more efficient than the others, which was probably due to the different interactions between carrier and HBAs.

It was apparent that the molar ratio of HBA to HBD also played a vital role in the physical-chemical properties of DESs, thus manipulating the separation performances of FTMs. Therefore, the effect of molar ratio on the gas separation performance was evaluated with the [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs. As shown in Fig. 7c, for the [DMA·NO₃]-G based FTMs, both ethylene and ethane permeabilities decreased with the molar ratio changing from 1:1 to 1:3. In the case of [TEA·NO₃]-G based FTMs, the ethylene permeability followed the order: [TEA·NO₃]-G (1:1) > [TEA·NO₃]-G (1:3) > [TEA·NO₃]-G (1:2), which was the combined contribution of carrier facilitated transport and Fickian diffusion. For example, the ethylene permeabilities were 305, 109, 134 Barrers at the molar ratio of [TEA·NO₃] to G of 1:1, 1:2, 1:3, respectively. The ethane permeability exhibited same variation trend, which was in well agreement with the viscosity of DES and further confirmed the C₂H₆ transport was dependent on the Fickian diffusion. As shown in Fig. 7d, the ethylene/ethane selectivities of [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs both increased as the molar ratio of HBA to HBD increased from 1:3 to 1:1. The ethylene/ethane selectivities were 70 and 98 for the [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs when the molar ratio of HBA to HBD was 1:1.

3.5. The effect of silver salt concentration

Interestingly, high solubility (up to 5 mol/L) could be achieved for AgNO₃ in the DESs, which indicated good compatibility between the carrier with DESs. As shown in Fig. 8, for [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs, the ethylene permeability was almost two order of magnitude higher than that of C₂H₆ because of different transport

Fig. 5. TGA and DTG studies of DESs.

Fig. 6. The microscopic morphology of FTMs was investigated by SEM.
mechanisms. In addition to normal Fickian diffusion, ethylene can reversibly coordinate with the carrier inside FTMs, thus facilitating the transport of ethylene. As expected, as the silver salt concentration changed from 0 to 5 mol/L, the ethylene permeabilities increased from 25 to 308 Barrers and from 15 to 190 Barrers for [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs, respectively. This behavior could be explained by that the increase of silver salt concentration increased the number of available carrier for the facilitated ethylene transport. In contrast, the ethane permeability decreased with silver salt concentration increasing, mainly due to the structural compactness of the DESs or the salting-out effect (Fig. 8). As a result, the selectivity sharply increased. For example, the ethylene/ethane selectivity of [TEA·NO₃]-G based FTMs reached up to 125 at AgNO₃ concentration of 5 mol/L, which indicated that the DES-FTMs are promise as the ethylene/ethane separation platform.

3.6. The effects of operating temperature and transmembrane pressure

The optimization of the operation temperature and pressure is very helpful for the separation process design and the effects of the operating temperature and transmembrane pressure have been discussed by using [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs (molar ratio 1:1). As shown in Fig. 9a, with the transmembrane pressure increasing from 0.1 to 0.5 bar, the ethylene permeabilities of [DMA·NO₃]-G and [TEA·NO₃]-G based FTMs significantly decreased from 305 to 222 Barrers and from 190 to 136 Barrers, respectively, which indicated that the transport of ethylene was mainly dependent on the carrier-facilitated transport. The carrier saturation restricted the future improvement of ethylene permeability at high pressure, thus leading to the negative correlation between the C₂H₄ permeability and transmembrane pressure. In contrast, the ethane permeability almost remained unchanged. As a result, the ethylene/ethane selectivity decreased with the increase of transmembrane pressure (Fig. 9c). Therefore, the low transmembrane pressures were preferred.

As seen from Fig. 9b, the higher operating temperature was, the higher gas permeability could be achieved. Higher temperatures meant lower viscosities of the DESs, which favored the gas diffusion. However, the ethylene permeability increased more slowly than that of ethane. For instant, the ethylene permeability for [TEA·NO₃]-G based FTMs concentration increasing, mainly due to the structural compactness of the DESs or the salting-out effect (Fig. 8). As a result, the selectivity sharply increased. For example, the ethylene/ethane selectivity of [TEA·NO₃]-G based FTMs reached up to 125 at AgNO₃ concentration of 5 mol/L, which indicated that the DES-FTMs are promise as the ethylene/ethane separation platform.

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increased by 1.5 times (from 308 to 458 Barrers), while the ethane permeability increased by nearly two times (from 3.1 to 5.9 Barrers). This was supposed that the high temperature weakened the complexation between the carrier and ethylene and greatly decreased the ethylene solubility in the FTMs [31,43], thus resulting in the slower increase of ethylene permeability. As a result, the ethylene/ethane selectivity decreased from 98 to 77 for [TEA·NO3]-G based FTMs and from 70 to 55 for [DMA·NO3]-G based FTMs, respectively (Fig. 9d).

3.7. The stability of DES-FTMs

The instability is the great obstacle for the application of FTMs, which is caused by carrier deactivation or poisoning. The carrier poisoning mainly derives from the reduction by exposure to visible light, ultraviolet light or by reducing gases such as hydrogen and the reaction with H2S and C2H2. In this study, the [DMA·NO3]-G and [TEA·NO3]-G based FTMs (molar ratio 1:1) were held for more than 160 h to evaluate the stability of the membranes. As shown in Fig. 10, the gas permeability increased quickly at the initial stage. Then, the gas permeability remained almost unchanged during medium-term run. The results clearly showed that the prepared membranes had great potential for medium-term operation, which was very beneficial for the application of DES-FTMs from an economic aspect.

Moreover, we have stored DES-FTMs without any protection or stored the membranes in the hydrogen atmosphere for six months. The color and the gas separation performances of the DES-FTMs remained unchanged, which indicated good stability. However, it should be pointed out that DES-FTMs may suffer from the loss of separation performances in the presence of impurities such as H2S and C2H2. The one solution to silver ion poisoning by sulfur compounds or C2H2 was to use pretreatment to reduce these species to very low concentrations or remove these species completely. Another feasible solution was to use the peroxide/acid vapor phase treatment to stabilize membrane performance, which has been proposed by the Merkel et al. [44].

Fig. 9. The effect of transmembrane pressure (a) and operating temperature (b) on gas permeability; the effect of transmembrane pressure (c) and operating temperature (d) on the gas selectivity. (Conditions: 298.15 K or 0.1 bar transmembrane pressure, 4 mol/L silver salt concentration).

Fig. 10. Medium-term stability of DES-FTMs. (Conditions: 0.1 bar transmembrane pressure, 298.15 K, 4 mol/L silver salt concentration, 60 mL/min).
Table 2, it was remarkable the performances of the PVDF-HFP/AgBF4 membrane for ethylene/ethane separation and polymeric electrolyte separation membrane for propylene/propane separation, which were reported by Ortiz and Kang, respectively [5,45]. However, the ethylene permeability as well as ethylene/ethane selectivity measured in this study were higher than most results in the literature. It was apparent that the DES-FTMs containing silver salt as carrier exhibited better separation performances than those containing copper salt as carrier. Compared with IL based membranes, the prepared DES-FTMs obtained comparable permeability and superior selectivity at the same carrier concentration, which indicated the DESs offered tremendous opportunities and open intriguing perspectives for enhancing the separation performances of FTMs. Due to the slower gas diffusion in the solid, the polymeric ionic liquid membranes presented lower permeability than the IL and DES based FTMs.

3.9. The separation mechanism

Investigation of separation mechanism is valuable for the understanding of the gas separation performances, which will be significant for the development of molecule design of novel DESs based FTMs for the ethylene/ethane separation. The ethane permeability depended on the Fickian diffusion. In contrast, ethylene could reversibly coordinate with the silver ions in the DESs to form [Ag(C2H4)n]+ at the feed side, increasing the solubility of ethylene. Then, the resultant [Ag(C2H4)n]+ complex diffused through the DES based membranes from the high-pressure feed side to the low-pressure permeate side, where the decomplexation took place and released the ethylene. Therefore, the ethylene permeability was mainly determined by the activity of silver ions and the number of effective carrier (dissociation behaviors of AgNO3), which were determined by the interactions between the AgNO3 and DESs. The moderate interactions between AgNO3 and DESs could weaken the interaction between silver cation and the counter anion (NO3-), thus increasing the interactions between the silver cation and C2H4 and further enhancing the facilitated ethylene transport.

The quantitative information on the dissociation behaviors of AgNO3 in the DESs has been provided by the FT-Raman spectroscopy. Note that the NO3- stretching bands at 1034, 1040, and 1045 cm⁻¹ are assigned to free ions, ion pairs, and ion aggregates, respectively [50]. As shown in Fig. 11a, the ion aggregates and ion pairs continued to increase with the addition of AgNO3 into DES. As shown in Fig. 11a, the ion aggregates and ion pairs continued to increase with the addition of AgNO3 into DES. As shown in Fig. 11b, interestingly, the fraction of the free ions and ion pairs continued to increase with the addition of AgNO3 into DES, which was probably due to the destruction of electrostatic interactions between the cation and anion as well as the reconstruction of hydrogen-bond interactions between NO3- and G. The results of FT-Raman indicated that DESs were the good solvents for silver salts and conducive to the dissociation of the silver salt (AgNO3), thus guaranteeing that the DESs based FTMs obtained excellent ethylene/ethane separation performances.

FIIR spectra have been used to gain insight into the interactions between AgNO3 and DESs. As shown in Figs. 11d-11f, Upon incorporation of AgNO3, the O-H stretching modes of G and TEG
exhibited different degrees of red shifts, which demonstrated that the silver ions were coordinated by the OH through an electron donation to the vacant 5s orbital of silver ions \[51\]. It also should be noted the coordinative interactions between AgNO_{3} and TEG were stronger than that between AgNO_{3} and G. In contrast, the O-H stretching mode of EG almost remained unchanged. In brief, the interactions between silver ions and HBDs were extremely low for the EG, medium for G and strong for TEG. Combination the results with the above separation performance of DESs based FTMs, we concluded that moderate interactions between silver ions and HBDs were beneficial for enhancement of facilitated C_{2}H_{4} transport due to the weakened interactions between Ag\(^{+}\) and NO\(_{3}\)^{-}. However, too strong interactions decreased the positive charge density of silver cation, thus crippling the coordination ability of silver ions with ethylene to some extent. Therefore, the skillful selection of HBDs is important for designing DESs to achieve efficient ethylene/ethane separation.

4. Conclusion

In summary, a series of novel DESs containing NO\(_{3}\)^{-} as anion were designed and synthesized. The physical property measurements suggested their low melting points and viscosities. The liquid structure characterizations revealed that the reconstruction of hydrogen-bond networks of G-cation and G-anion led to strong charge transfer from cation and anion to G, thus generating homogeneous and stable DESs. The thermal stability evaluation indicated their good thermal stability. Then, novel FTMs were prepared and their successful fabrication was confirmed by SEM images. The as-prepared FTMs exhibited excellent ethylene permeability and high ethylene/ethane selectivity, which could be tuned by the skillful combination of HBA and HBDs or variation of the molar ratio of HBA to HBD. The lower transmembrane pressure meant higher gas permeability and selectivity. The increase of operating temperature increased the ethylene permeability but decreased ethylene/ethane selectivity. The investigation of separation mechanism indicated that the DESs were ideal solvents for the activation of silver ions, which was attributable to the unique liquid structure of DESs, the moderate interactions between silver ions and HBD as well as the reconstruction of hydrogen-bond interactions between NO\(_{3}\) and G. Therefore, together with the inherent advantages of DESs, the good separation performance and stability would position this new class of DESs based FTMs potential for the ethylene/ethane separation.

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