Multifunctional ternary deep eutectic solvent-based membranes for the cost-effective ethylene/ethane separation

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ABSTRACT

Membrane technology is a forward-looking approach for gas separation, while the implementation of membrane with high performance for ethylene/ethane separation still challenges the world. Herein, a multifunctional ternary deep eutectic solvent (DES)-based membrane was constructed for the cost-effective ethylene/ethane separation. The incorporation of a sweetener (Al(NO$_3$)$_3$) with the AgNO$_3$/methylacetamide (NMA) mixture to form a ternary DES not only significantly promoted the ethylene/ethane selectivity but also enhanced the long-term stability of resultant membranes, which killed two birds with one stone. Various spectroscopic characterization and quantum mechanical calculations revealed that the complexing interaction between Ag$^+$ and NMA and the complexing interaction between Al$^{3+}$ and NO$_3^-$ weakened the electrostatic interaction between Ag$^+$ and NO$_3^-$, and improved the interaction energy between ethylene molecule and Ag$^+$ carrier. By the synergy effects of two different complexing interactions, the ternary DES-based membranes exhibited high ethylene permeability, ethylene/ethane selectivity and stability, outperforming majority of the previously published data. Therefore, the membranes proved the grand potential for ethylene/ethane separation, and this work will shed light on the design of multifunctional liquid membranes for precise molecular separation.

1. Introduction

Membrane separation continues to attract incomparable research interests due to its high separation efficiency, low energy consumption, small footprint, relative environmental safety, and economic feasibility, accompanying enormous novel membrane materials has been emerged, such as metal/covalent organic framework membranes, bioinspired membranes and two dimensional nanosheet membranes [1–8]. Olefin/paraffin separations, especially ethylene/ethane and propylene/propane separation, have been recognized as one of the seven chemical separations to change the world because of their similar physical-chemical properties and huge global energy consumption. Currently, olefin/paraffin separations heavily rely on the most energy-intensive cryogenic distillation performed at extremely high pressure and low temperature, which accounts for 0.3% of global energy consumption [9,10]. The implementation of membrane-based ethylene/ethane separation instead of cryogenic distillation or integrated with distillation has the grand potential to create significant cost and environmental savings, which remains a great challenge yet critical enterprise toward a sustainable energy future [11,12].

As thirty years passed by, significant advances have been achieved and numerous membrane materials have been manifested the promise for olefin/paraffin separations based on carrier-facilitated transport or molecular sieving mechanism, including polymers of intrinsic micro-porosity membranes (PIMs), carbon molecular sieve membranes and zeolitic imidazolate framework-8 (ZIF-8) membranes [13–16]. For example, Lai reported ultrathin ZIF-8 membranes (500 nm) fabricated by aqueously cathodic deposition method for the propylene/propane separation, which exhibited a superior performance with 182 GPU C$_3$H$_6$ permeance and 142 selectivity [9]. Jeong et al. has constructed ZIF-8 mixed-matrix membranes by the in-situ linker doping method, and the propylene selectivity could reach up to 40 [17]. However, for the ethylene/ethane separation, the selectivity of these membranes are extremely low and less than 10 in most cases, which is far from being commercially attractive [18,19]. Therefore, the exploitation of novel ethylene/ethane separation membranes will be more imperative.

Compared with solid membranes, advanced liquid membranes with carrier-facilitated transport property possess more advantages for ethylene/ethane separation, such as higher ethylene permeability due to the faster transport of gas molecules in liquid than solid, more easy...
fabrication of defect-free membranes, and more tunability of membrane structures via the molecular design [20–23]. As the green solvents have been spotlighted in the chemistry community, including ionic liquids (ILs), deep eutectic solvents (DESs) and porous liquids, the liquid membranes have been updated nowadays and overcame the disadvantages of traditional liquid membranes based on water and volatile organic solvents [24–30]. Dou et al. have investigated the various supported IL and DES membranes for ethylene/ethane separation. Their investigations indicated the membrane permeability and selectivity could be significantly improved by the manipulation of carrier activity through adjusting interactions between ILs or DESs and metal ions, which afforded the promising ethylene/ethane separation, especially for DES based supported liquid membranes [31–35]. However, a trade-off between the selectivity and permeability of DES based membranes still exists. Moreover, further investigations of more effective strategies of carrier activity enhancement and membrane stability are still needed for the development of cost-effective and highly-stable ethylene/ethane separation membranes [36,37].

In this manuscript, a family of multifunctional ternary deep eutectic solvents (type IV DESs) were designed for the first time, which were synthesized by simply mixing a hydrogen bond donor of amide and double metal salts (one is AgNO$_3$ acting as ethylene transport carrier, while the other is a “sweetener” to enhance the carrier activity and solvent stability, such as Al(NO$_3$)$_3$, Cu(NO$_3$)$_2$ and Co(NO$_3$)$_2$). Subsequently, the ternary deep eutectic solvent-based membrane was fabricated by the accommodation of as-design DES within the commercial PVDF microfiltration membrane support, which exhibited high ethylene permeability, ethylene/ethane selectivity and stability, outperforming majority of the published data. Compared with traditional single metal salt based DES, the ternary DES based membranes fostered abundant merits and multi-functionalization: (1) the sweeteners significantly promoted the carrier activity, which endowed the membrane with more flexibility of tuning its combinations of selectively and permeability; (2) the sweeteners favored for the carrier stability, especially for Al(NO$_3$)$_3$, which has been reported to improve carrier activity in polymeric electrolyte membranes for olefin/paraffin separations [37]; (3) ternary DES exhibited more stability than single metal salt based DESs [38]. Moreover, the selected raw materials for DES fabrication are large-scale chemical productions, which are very attractive for the cost-effective practical ethylene/ethane separation. The physical properties of ternary DESs were measured and the DES based membrane morphology was characterized by scanning electron microscope (SEM) and atomic force microscopy (AFM). The chemical interactions and mechanisms of membranes were investigated by various spectroscopic characterization and quantum mechanical calculations. Finally, the mixed gas separation performances were probed and operating conditions were optimized. Our work sheds light on the design of multifunctional DESs for precise molecular separation.

2. Experimental section

2.1. Materials

Ethylene and ethane were supplied by Tianjin Tang Dynasty Gas, Ltd. With a purity of 99.9%. N-Methylacetamide (NMA), Tetramethylurea (TE) were obtained from Beijing J&K Chemical Technology, Ltd. Acetamide (MA) (>99.8 wt %) was purchased by Shanghai Titan Technology, Ltd. Silver nitrate (AgNO$_3$) (99.0 wt %), Aluminum nitrate nonhydrate (Al(NO$_3$)$_3$·9H$_2$O, 98.0 wt %), Cupric nitrate trihydrate (Cu(NO$_3$)$_3$·3H$_2$O, 98.0 wt %) and Cobaltous nitrate hexahydrate (Co(NO$_3$)$_2$·6H$_2$O, 98.0 wt %) were all purchased from Shanghai Aladdin Bio-Chem Technology. The Polynylidenyl fluoride (PVDF) membrane was supplied by Haining Zhongli Filtration Equipment Corporation with the porosity of 75%, the average thickness of 100 μm, and pore size of 0.1 μm. All chemicals were used as received without further purification.

2.2. Synthesis of ternary DESs

Ternary DESs were synthesized via a two-step method. The AgNO$_3$ was selected as carrier, the Al(NO$_3$)$_3$, Cu(NO$_3$)$_2$ or Co(NO$_3$)$_2$ was acted as sweetener, and NMA, TE or MA was chosen as hydrogen-bond donors (HBDs). Taking Ag-Al/NMA DES as an example, Ag-NMA DESs with different molar ratios were prepared by simply mixing AgNO$_3$ powder and NMA (melting point: 26 °C). Then the mixture was stirred at 60 °C for 2 h to form the homogeneous colorless liquid and remained stable at room temperature. Prior to use, the Al(NO$_3$)$_3$·9H$_2$O powder was dried in vacuum at 60 °C for 72 h to remove partial crystalline water. The dehydrated Al(NO$_3$)$_3$·9H$_2$O was added to as-prepared Ag-NMA DESs, followed by stirring at room temperature for 3 h until the transparent liquids were formed. The prepared ternary Ag-Al/NMA DESs were further dried in vacuum at 60 °C for 48 h before membrane fabrication. The water content of ternary DES was detected by the Karl Fischer titration method and did not exceed 1.5 wt%.

2.3. Ternary DES based membrane fabrication

First, the PVDF membranes were placed in the vacuum at 60 °C for 1 h to remove the trace volatile compounds which adhere to the pores. Then, 3 ml of DESs was spread equably onto the surface of PVDF membranes and impregnated into the membrane’s pores by using a nitrogen pressure of 1 bar in the permeation cell for 10 min. The above procedure was repeated three times to fabricate defect-free membranes. Lastly, the DES based membrane was prepared after removing the excess DES from the membrane’s surface by a tissue.

2.4. Quantum chemical calculation

The quantum chemical calculations about the interaction of ternary DESs and C$_2$H$_4$ were performed using Gaussian 09 program based on density functional theory (DFT). Particularly, the initial structure of C$_2$H$_4$, NMA, AgNO$_3$ and Al(NO$_3$)$_3$ were built by Gauss View 5.0. Several configurations of DESs and DESs-C$_2$H$_4$ complexes were selected by semiempirical optimization at the B3LYP/LANL2DZ and B3LYP/6–311++G(d,p) level through using the Gaussian 09 program to perform density-functional theory (DFT) calculations. All the optimized configurations were validated as minimum by frequency calculation.

2.5. Characterization

The viscosities of ternary DESs were measured by a Brookfield LVDV-II+ Pro viscometer. The melt points of ternary DESs were measured by using a DSC 204 differential scanning calorimeter to heat the samples from −100 °C to 100 °C with a heating rate of 5 °C/min under N$_2$ atmosphere. The morphology of the ternary DES based membrane was observed by the scanning electron microscopy (SEM, Hitachi S-4800) and the atomic force microscope (AFM, Bruker). The elemental composition of SLMs was obtained by energy dispersive spectrometry (EDS, Hitachi S-4800). Fourier transform infrared (FTIR) spectra were carried out using a Bio-Rad FTS-6000 Fourier transform infrared spectrometer. Fourier transform Raman (FT-Raman) spectra were recorded by a Bruker RFS 100 Fourier transform Raman spectrometer. The $^1$H NMR spectra were recorded by a Varian Inova 500 MHz spectrometer using DMSO-d$_6$ as the solvent with tetramethylsilane as the internal standard. Electrospray ionization mass spectrometry (ES-MS) were recorded by the mass spectrometry (Bruker Daltonics AutoflexII LRF200-CID).

2.6. Mixed-gas permeation

The experimental steps of gas separation are described in Fig. 1. The gas tightness of the apparatus was checked by filling nitrogen gas under the constant pressure of 2 bar for 1 h. Ethylene and ethane from the gas
cylinders were mixed in the volume ratio of 1:1 and then the mixed-gas flowed through the permeation cell. The buffer tanks were installed to improve the stability of gas flow and the mass flow controllers were installed to control the flow rate of ethylene and ethane at 30 mL/min (STP). Simultaneously, the sweep gas (N$_2$) flowed through the cell with a flow rate of 20 mL/min (STP). The operation pressure and temperature of the experiments were adjusted by a micrometer value and an air-dry oven, respectively. The compositions of the permeated mixed-gas were analyzed by the online gas chromatograph (GC-2008B, Lunan). The experiment data was recorded in a steady-state for at least 1 h. All the permeation data were measured under the explicit conditions and the experiment was repeated three times under each condition.

The gas permeability through the SLM was calculated according to Eq. (1):

$$P_{m,i} = \frac{J_i \times \delta}{\Delta P_i}$$

where $P_{m,i}$ is the gas permeability of component i through the membrane; $J_i$ is the gas permeation flux through the membrane of component i; $\delta$ is the membrane thickness; $\Delta P_i$ is the transmembrane pressure difference.

To verify the accuracy of experiments, the standard deviation of permeability was calculated according to Eq. (2):

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(P_{m,i} - P_m')^2}{3}}$$

where $P_{m,i}$ is the individual permeability data; $P_m'$ is the average of the permeability data; $\sigma$ is the standard deviation of permeability. In all experiments, the standard deviation of permeability data was lower than 0.05, proving the reliability of permeability data.

The selectivity of the gas through the membrane was defined according to Eq. (3):

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

3. Results and discussion

3.1. Fabrication of ternary DESs and membrane

The synthesis of multifunctional ternary deep eutectic solvents comprises two steps: the synthesis of Ag-amide DES with different HBDs; the addition of sweetener within Ag-amide DES to obtain ternary DESs. As shown in Fig. 2, all the ternary DESs were the homogeneous and transparent liquids at room temperature, which were highly stable. After storing in the lab for one month, their appearances remained unchanged and no precipitation was observed, which meant they were attractive for the fabrication of DES based membranes. The DES based membranes were fabricated by impregnating the as-synthesized ternary DES within PVDF support by pressure-based technique [39, 40]. The photographs of PVDF support and DES based membranes were also shown in Fig. 2. Due to the colorless of Ag-NMA and Ag-Al/NMA DESs, the appearances of DES based membranes exhibited no obvious change compared with the PVDF support.

3.2. Physical properties of ternary DESs

The main physical properties of the Ag-NMA and ternary DESs were measured and recorded in Table 1. As shown in Table 1, the DESs formed by AgNO$_3$ and NMA exhibited a low melting point and viscosity. It was a remarkable fact that the addition of sweetener significantly affected the viscosity of ternary DESs. The viscosity was dependent on the molecular interactions among the components, and the increase of viscosity of the ternary DESs was attributed to the newly formed complexing interactions. As the temperature increases, the viscosity of DESs decreased gradually because of the weakening molecular interactions. The viscosity of ternary DES reported here was much lower than the widely used choline chloride-glycerol based DESs. The lower viscosity of DESs was conducive to the transport of gas in membranes and beneficial to the improvement of permeability.

3.3. Morphology of ternary DES-based membranes

The morphology of ternary DES-based membranes was observed by SEM and AFM. As shown in Fig. 3a–c, the PVDF support was a highly
porous material with hierarchical and irregular pore structure, which had interconnected macropores in the range of 200 nm–1 μm. After impregnating DES within PVDF support for one time, most of pores were filled with ternary DES benefiting from the positive capillary forces, but some pores remained partially unfilled. When the impregnation was repeated for three times, almost all the support pores were saturated by the homogeneously distributed ternary DES. The surface of the as-fabricated ternary DES based membrane was relatively smooth and no obvious defects were observed, which confirmed the successful fabrication of DES based membranes. The EDS mapping was also conducted.

Table 1
Physical properties of multifunctional ternary DESs, melting point and viscosity.

<table>
<thead>
<tr>
<th>DES</th>
<th>Melting point (°C)</th>
<th>Viscosity (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25 °C</td>
<td>35 °C</td>
</tr>
<tr>
<td>Ag/NMA(1:4)</td>
<td>78.08</td>
<td>25.72</td>
</tr>
<tr>
<td>Ag-Co/NMA(1:0.4:4)</td>
<td>73.64</td>
<td>153.28</td>
</tr>
<tr>
<td>Ag-Al/NMA(1:0.4:4)</td>
<td>51.54</td>
<td>102.72</td>
</tr>
<tr>
<td>Ag-Al/NMA(1:0.33:4)</td>
<td>54.52</td>
<td>84.23</td>
</tr>
<tr>
<td>Ag-Al/NMA(1:0.28:4)</td>
<td>57.92</td>
<td>71.24</td>
</tr>
</tbody>
</table>

Fig. 2. The photographs of ternary DES and the corresponding membranes, (a) Ag/NMA, (b) Ag-Al/NMA (1:0.4:4), (c) Ag-Co/NMA (1:0.4:4), (d) Ag-Co/NMA (1:0.4:4), (e) pristine PVDF support, (f) Ag/NMA based SLMs, (g) Ag-Al/NMA based SLMs.

Fig. 3. Characterizations of DES based membranes. (a–c) SEM images of PVDF support (a) and Ag-Al/NMA based membranes (b–c), the scale is 5 μm. (d–g) EDS mapping of Ag-Al/NMA based membranes, Al (d), Ag (e), C (f) and F (g), the scale is 200 nm. (h–m) AFM images of PVDF (h, j) and Ag-Al/NMA based membranes (k, m).
to identify the distribution of DES in the membrane and the element distributions of Al, Ag, C, and F were shown in Fig. 3d–g. The elementals of Ag and Al were introduced by ternary DESs, while fluorine existed in the PVDF support. As indicated by the Al and Ag distributions, the ternary DES was homogeneously accommodated in the support, the observation of F element suggested the accumulation of DES on the membrane surface and the dark regions meant the valleys. As shown in 3D AFM images (Fig. 3j–m), the brighter area presented the higher part of the membrane after the impregnation of DES in the PVDF support. As indicated by the Al and Ag distributions, the average roughness (Ra) of the membrane decreased significantly from 295 nm to 76 nm, which was in coordination with the SEM results.

3.4. Molecular interactions within membranes

The molecular interactions within ternary DES based membranes, including hydrogen-bond interaction, complexing interaction and electrostatic interaction, were gained by $^1$H NMR and ATR-FTIR characterizations, which offered a deep insight of carrier-activity enhancement mechanism and separation performances of the membrane. As shown in Fig. 4a, the chemical shifts of 1.857 ppm, 2.651 ppm and 7.939 ppm in the pure NMA spectrum were ascribed to the $-\text{CH}_3(2)$, $-\text{CH}_2(1)$ and $-\text{NH}-(3)$, respectively. Upon mixing with AgNO$_3$ to form Ag/NMA DES, the chemical shift of $-\text{NH}-(3)$ moved to up-field from 7.939 ppm to 7.798 ppm, which suggested the destruction and reconstruction of hydrogen-bond interaction. The intermolecular hydrogen-bond interaction (N–H...O=C) of NMA was partly destructed by adding AgNO$_3$ and new hydrogen-bond interaction between $-\text{NH}$– group and NO$_3^-$ was constructed. When the sweetener was added to construct ternary DES with different molar ratios, the $-\text{NH}$– group shifted very slightly, which was probably due to the interference of deuteration reagent. The hydrogen-bond interaction was further investigated by ATR-FTIR. In the case of NMA, the N-H asymmetric stretching and symmetric stretching vibrations of NMA occurred at 3291 cm$^{-1}$ and 3108 cm$^{-1}$, respectively. Regarding Ag/DES, the N-H asymmetric stretching and symmetric stretching vibrations exhibited blue shifts, appearing at 3296 cm$^{-1}$ and 3116 cm$^{-1}$, respectively. As for the ternary DES, the addition of sweetener made the N-H stretching vibrations continue to the blue shifts, located at about 3308 cm$^{-1}$ and 3120 cm$^{-1}$ for all the ternary DES with different sweeteners. These behaviors further confirmed the destruction and reconstruction of hydrogen-bond interaction. However, it should be noted that the newly formed hydrogen-bond interaction between $-\text{NH}$– group and NO$_3^-$ was weaker than that of NMA. Therefore, the N-H stretching vibrations gradually exhibited blue-shifts when the addition of carrier (AgNO$_3$) and sweeteners.

The complexing interaction between the metal ion and NMA was also characterized by ATR-FTIR. As shown in Fig. 4b, the peaks at 1632 cm$^{-1}$ and 1557 cm$^{-1}$ in NMA spectrum were assigned to the stretching vibrations of C–O and C-N groups. Upon the addition of single metal salt, the C–O stretching vibration exhibited red shifts with different extents, moving from 1632 cm$^{-1}$ to 1616 cm$^{-1}$ for Ag/NMA, from 1632 cm$^{-1}$ to 1621 cm$^{-1}$ for Al/NMA, from 1632 cm$^{-1}$ to 1617 cm$^{-1}$ for Cu/NMA, and from 1632 cm$^{-1}$ to 1624 cm$^{-1}$ for Co/NMA, respectively. Therefore, the complexing interaction between metal ion and C=O of NMA followed the order: Ag$^+$ > Cu$^{2+}$ > Al$^{3+}$ > Co$^{2+}$. Moreover, the addition of metal salt induced the appearance of the resonance structure of NMA and rendered the C-N with partial double bond character, which resulted in the blue shifts of C-N stretching vibration. As shown in Fig. 4c, the C=O stretching vibration continued to slight red shifts for Ag-Al/NMA.

Fig. 4. Investigation of interactions within the membranes by $^1$H NMR and ATR-FTIR spectroscopy. (a) $^1$H NMR spectra of Ag-Al/NMA DESs with different molar ratios. (b) ATR-FTIR spectra of single metal based DESs. (c) ATR-FTIR spectra of ternary DESs with different sweeteners. (d) ATR-FTIR spectra of ternary DESs with different amides.
and Ag-Cu/NMA, shifting from 1616 cm\(^{-1}\) to 1613 cm\(^{-1}\), while the C=O stretching vibration of Ag-Co/NMA remained almost unchanged due to the weakest interaction between Co\(^{2+}\) and NMA. The red shift of C=O stretching in ternary DES was possibly derived from two following factors: (1) the newly formed interaction between metal ion of sweetener and C=O upon its addition; (2) the addition of metal ion could coordinate more NO\(^3\) to form the complex, which crippled the electrostatic interaction between Ag\(^{+}\) and NO\(^3\) and favored the dissociation of AgNO\(_3\), thus leading to the reinforced interaction Ag\(^{+}\) and C=O group of NMA. We speculated the latter fact was dominated, which was also confirmed by the highest wavenumbers of NO\(^3\) stretching vibration of Ag-Co/NMA remained almost unchanged due to the weakest interaction between Al\(^{3+}\) and NO\(^3\). Moreover, the ion clusters of [NO\(_3\)(NMA)\(_2\)]\(^{-}\) and [NO\(_3\)(NMA)\(_4\)]\(^{-}\) further demonstrated the newly formed hydrogen-bonding interaction between NO\(^3\) and NMA, which was in well agreement with ATR-FTIR results. FT-Raman spectroscopy is a more straightforward method for the investigation of NO\(^3\) cluster. It is widely acknowledged that the NO\(^3\) stretching vibration bands of free ions, contact ion pairs, and higher-order ionic clusters locate at 1035, 1040 and 1045 cm\(^{-1}\), respectively. As shown in Fig. 5b, the stretching vibration bands of NO\(^3\) in the Ag/NMA and Al/NMA occurred at 1037 cm\(^{-1}\) and 1045 cm\(^{-1}\), which indicated the stronger ability of Al\(^{3+}\) to coordinate NO\(^3\) than that of Ag\(^{+}\). For the ternary Ag-Al/NMA DES, the stretching vibration band of NO\(^3\) appeared at 1041 cm\(^{-1}\), which suggested that the electrostatic interaction between Ag\(^{+}\) and NO\(^3\) was weakened by complexing interaction of Al\(^{3+}\) and NO\(^3\), thus increasing the interaction between ethylene molecule with carrier and obtaining high separation selectivity [42].

The interactions within the DES based membranes were further investigated by quantum mechanical calculations. The optimized structures of NMA, Ag-NMA, Ag-Al/NMA are shown in Fig. 5c–g. Mixing AgNO\(_3\) with NMA to form Ag-NMA DES made the bond length of C=O increase from 1.2223 Å to 1.2451 Å and also induced the bond length of C-N to decrease from 1.3601 Å to 1.3372 Å, which suggested the interaction between Ag\(^{+}\) and C=O of NMA and the appearance of resonance structure of NMA (Fig. 5c and d). As for the ternary Ag-Al/NMA...
NMA DESs, the Al$^{3+}$ coordinate the NO$_3^-$ of AgNO$_3$, which weakened the electrostatic interaction between Ag$^+$ and NO$_3^-$, thus leading to the increase of Ag-O bond length from 2.6471 Å to 2.9238 Å and from 2.1313 Å to 2.2628 Å (Fig. 5f). The weakened electrostatic interaction between Ag$^+$ and NO$_3^-$ enhanced the complex between ethylene molecules and silver ions. The addition of Al(NO$_3$)$_3$ sweetener into Ag-NMA to prepare ternary DES improved the interaction energy between C$_2$H$_4$ and Ag$^+$ carrier from −75.4 kJ/mol to −183.8 kJ/mol, which could significantly improve the ethylene/ethane selectivity.

3.6. The structure-performance relationship

The relationship of membrane structure-performance for ethylene/ethane separation was investigated. The permeation was driven by the transmembrane pressure difference on both sides of the membrane. Compared with sole Fickian diffusion of ethane, ethylene could occur through the DES based membrane. As shown in Fig. 6a, the permeability of ethylene through based DES membranes followed the order: Ag-Cu/ NMA (681.99 Barrer) > Ag/NMA (482.24 Barrer) > Ag-Al/NMA (458.48 Barrer) > Ag-Co/NMA (264.05 Barrer), which was determined by both the carrier activity and viscosity of the DES. The ethylene/ethane selectivity of ternary DES based membranes was much higher than Ag/NMA based membrane and followed the order: Ag-Al/NMA (14.68) > Ag-Co/NMA (14.51) > Ag-Cu/NMA (10.21) > Ag/NMA (7.22). Compared with Ag/NMA based membrane, the addition of Al(NO$_3$)$_3$ sweetener nearly improved the selectivity by twice. As suggested by the above characterizations, Al$^{3+}$ coordinated the NO$_3^-$ of AgNO$_3$, which weakened the electrostatic interaction between Ag$^+$ and NO$_3^-$ and could significantly promote the interaction energy between C$_2$H$_4$ and Ag$^+$ carrier, thus improving the ethylene/ethane selectivity. Moreover, the selectivity of Ag-Al/NMA was superior to the selectivity of Ag-Cu/ NMA, which illustrated that the complexing interaction between sweetener and NO$_3^-$ was dominated factor to determine the carrier activity compared to its interaction with NMA, which was consistent with the results of ATR-FTIR. As shown in Fig. 6b, the selectivity of ternary DES based membranes with different amides was arranged as follows: Ag-Al/ MA (28.54) > Ag-Al/NMA (14.68) > Ag-Al/TE (4.59). It should be noted that moderate complexing interaction could favor for the dissociation of carrier and improve the Ag$^+$ activity. However, too much strong complexing interaction could significantly reduce the positive charge density of Ag$^+$ and whittle the Ag$^+$ activity.

As depicted in Fig. 6c, the ethylene permeability decreased from 592.38 Barrer to 338.04 Barrer as the decrease of AgNO$_3$ concentration from (1.4:0.4:4) to (0.6:0.4:4). Meanwhile, the permeability of ethane increased from 15.48 Barrer to 33.97 Barrer, in good agreement with the opposite trend of the viscosity of ternary DES. The decrease of AgNO$_3$ concentration led to the loss of the Ag$^+$ carries coordinated with C$_2$H$_4$ inside the membrane. Hence, the selectivity decreased gradually from 27.33 to 7.11. As shown in Fig. 6d, the ethylene/ethane selectivity decreased from 22.75 to 13.21 with the decrease of Al(NO$_3$)$_3$, which further convinced the important role of sweetener.

3.7. Optimization of the separation process

The membrane separation process was also optimized, including operating temperature, transmembrane pressure, feed ratio, and sweep gas flow rate. As depicted in Fig. 7a, the permeability of ethylene and ethane both increased with the rising of operating temperature. This was caused by the decrease of viscosity of ternary DES with the increase of temperature. Lower viscosity is more conducive to the diffusion of the gas through DES based membrane. Whereas, ethylene/ethane selectivity decreased gradually, which illustrated that the complexation reaction between Ag$^+$ and ethylene was exothermic. The temperate rise would weaken the interaction between the ethylene molecules and DES. As can be seen from Fig. 7b, with the transmembrane pressure difference increasing, the permeability of ethane almost remained a stable level but the permeability of ethylene decreased obviously. The permeation of

![Fig. 6](Image)

**Fig. 6.** The investigation of structure-performance relationship. Effects of different sweeteners (a), different amides (b), AgNO$_3$ concentrations (c), and different Al(NO$_3$)$_3$ concentrations (d) on the permeability and selectivity of ternary DES based membranes at 298K under 0.1 bar transmembrane pressure.
ethane molecules in membrane depended on Henry’s law, thus the permeability was unchanged with the higher transmembrane pressure difference. As for ethylene, the interaction between Ag\(^{+}\) and ethylene made the major contribution to permeation, and the complexation sites of Ag\(^{+}\) carrier were saturated with the transmembrane pressure increasing. Therefore, the selectivity of ethylene/ethane decreased correspondingly. As shown in Fig. 7c, the ethylene permeability decreased from 1059.23 Barrer to 147.25 Barrer and the ethane permeability increased from 13.73 Barrer to 60.09 Barrer with the feed ratio of ethylene/ethane changed from 50:10 to 10:50. Hence, the ethylene/ethane selectivity was more challenging. Finally, a higher rate of sweep gas could remove ethylene on the permeation side more efficiently, increasing the driving force for permeation.

3.8. Long-term stability and comparison

The experiment for long-term separation of ternary DES based membrane was also measured to check for the stability of membrane. The membrane based on Ag-Al/NMA (1:0.4:4) worked at 298 K, a transmembrane pressure of 0.1 bar and a sweep gas rate of 20 mL/min. As shown in Fig. 8a, the permeability of ethylene and ethane remained nearly unchanged and the selectivity remained stable in 160 h. The result proved that the membrane could maintain durable performance during long-term operation, mainly because of the better stability of AgNO\(_3\) compared with other silver salts and the presence of Al(NO\(_3\))\(_3\) sweetener. Furthermore, as shown in Fig. 8b, the performances of the ternary DES based membrane in this study were superior to those of the polymeric, CMS, MMMs and most of previously reported IL/DES based membranes. The ternary DES based membranes exhibited high ethylene permeability and ethylene/ethane selectivity. All the above results clearly showed the application potential of the Al-Ag/NMA based membrane for ethylene/ethane separation.

4. Conclusion

In summary, for the first time, a series of multifunctional ternary DESs were designed by mixing the HBD of amide, AgNO\(_3\) and a sweetener such as Al(NO\(_3\))\(_3\), Cu(NO\(_3\))\(_2\) or Co(NO\(_3\))\(_2\), and then the ternary DES-based membranes were fabricated successfully by the impregnation of as-designed DES within PVDF support, whose morphology was observed by SEM and AFM. The investigations of molecular interactions within ternary DES based membranes by \textsuperscript{1}H NMR and ATR-FTIR suggested that the hydrogen-bond interaction within NMA and electrostatic interaction between Ag\(^{+}\) and NO\(_3\) were weakened by the newly formed complexing interaction between the metal ion and C=O group of NMA, which promoted carrier activity. The MS, FT-Raman and quantum mechanical calculation exhibited that the Al\(^{3+}\) of sweetener coordinated with the NO\(_3\), which weaken the electrostatic interaction between Ag\(^{+}\) and NO\(_3\), further enhanced the carrier activity. The investigation of structure-performance revealed that the molecular interactions within membranes could be tuned by HBD, molar ratio, and the content and type of sweetener. By the elaborate combination of HBD, sweetener and carrier, the membranes exhibited excellent comprehensive performance, including high ethylene permeability, high selectivity and durable stability. Finally, the optimization of separation process including operational temperature, transmembrane pressure, feed ratio and sweep gas flow rate was investigated, which contributed to the highly-efficient membrane process. This work offers a creative strategy of carrier activity enhancement and membrane stability, which opens novel avenues for the development of cost-effective, highly-efficient and durable ethylene/ethane separation membranes.

Fig. 7. Optimization of operating conditions for highly efficient separation process. Effects of (a) operating temperature, (b) transmembrane pressure, (c) feed ratio, (d) sweep gas flow rate on permeability and selectivity of Ag-Al/NMA DES (1:0.4:4) based membranes.
Declaration of competing interest

The authors declared that they have no conflicts of interest to this work.

CRediT authorship contribution statement

Bin Jiang: Conceptualization, Writing - original draft. Junhan Zhou: Validation, Formal analysis, Investigation, Writing - original draft. Mi Xu: Investigation, Writing - review & editing. Haozhen Dou: Methodology, Data curation, Writing - review & editing. Haiming Zhang: Software. Na Yang: Funding acquisition. Luhong Zhang: Resources, Writing - review & editing, Supervision, Project administration.

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