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Abstract

Cellulose triacetate (CTA) is a workhorse polymeric membrane material for industrial CO₂/CH₄ separation. This study investigates the doping of CTA with ionic liquids (ILs) to reduce the crystallinity of the CTA and enhance its affinity with CO₂, thus increasing CO₂ permeability and CO₂/light gas selectivity. CTA films doped with 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][dca]) were prepared; and the effect of IL loading on properties of the CTA, such as crystallinity, density, degradation temperature, glass transition temperature, and gas transport properties, were determined. The IL doping reduces the glass transition temperature and degree of crystallinity of CTA, increasing gas diffusivity and permeability. The IL doping also increases CO₂/CH₄ solubility selectivity and CO₂/N₂ permeability selectivity, due to the affinity of these ILs with CO₂, compared to light gases such as CH₄ and N₂. This study demonstrates a promising route in manipulating the morphology and gas transport properties of semi-crystalline polymers by doping with ILs.

Keywords: Cellulose triacetate; membrane CO₂ separation; ionic liquids

1. Introduction

Membrane technology has emerged as an important gas separation technology due to its inherent advantages such as small equipment footprint, easy maintenance, and high energy efficiency [1-3]. Polymeric membranes based on cellulose triacetate (CTA) have become the dominant choice for the removal of CO₂ from natural gas for offshore applications, and they are emerging as a technology for onshore CO₂ separations competitive with conventional technologies such as amine absorption [1-5]. As an off-the-shelf material, CTA is semi-crystalline, and the crystal domains are not accessible to gas sorption and diffusion, thus decreasing the CO₂ solubility, diffusivity, and permeability [6-8]. The low CO₂ permeability results in large membrane area required and thus relatively high capital and operation costs, which are partially ascribed to the prevention of the wide implementation of the membrane technology.

Numerous novel polymers have been designed and tailored for membrane CO₂/CH₄ separation, aiming to increase polymer size-sieving ability and thus CO₂/CH₄ diffusivity selectivity [9-14]. However, when exposed to real natural gas streams containing highly plasticizing components such as hexane and toluene, these polymers significantly sorb these hydrocarbons and thus lose size-sieving ability, leading to deteriorated CO₂/CH₄ separation performance [15, 16]. CTA retains high performance for CO₂/CH₄ separation under practical operating conditions with heavy hydrocarbons present, largely due to its high CO₂/CH₄ solubility selectivity which may not be affected by the plasticization induced by the heavy hydrocarbons [2, 17]. The high CO₂/CH₄ solubility selectivity in CTA can be further enhanced by lowering the operating temperature [18], though the polymer plasticization by the heavy hydrocarbons becomes more significant due to their increased solubility at lower temperatures.

Various approaches have been explored to enhance the CO₂/CH₄ separation properties in CTA-based materials as a continuing effort to sharpen the competitiveness of the membrane technology. For example, liquid poly(ethylene glycol) has been added into CTA to form mixed matrix membranes [19] or polymer blends [20] to improve CO₂/CH₄ selectivity. Recently, cellulose acetate (CA) with hydroxyl groups was modified by grafting with vinyltrimethoxysilane and then cross-linking, leading to a modified CA containing 15 wt.% element Si and an estimated 50 wt.% CA [4]. The CO₂ permeability increased from 5.0 Barrers for the neat CA to 139 Barrers for the modified one, presumably due to the decrease in crystallinity and increase in polymer chain flexibility [4]. However, the CO₂/CH₄ selectivity remained unchanged [4].

An alternative approach explored in this work is to dope CTA with ionic liquids (ILs). ILs are salts that are liquid at temperatures up to 100 °C with low vapor pressure and strong solvation ability for dissolving various organic and inorganic materials [14, 21-24]. ILs (such as imidazolium- and pyridinium-based ones) have also been extensively investigated for the dissolution of cellulosic materials [25, 26], since ILs can disrupt the hydrogen bonding in CTA and thus decrease the crystallinity [27-31]. More importantly, ILs have been extensively investigated for CO₂/CH₄ and CO₂/N₂ separation via absorption or membrane technology, due to the affinity between certain ILs and CO₂ [32-39], leading to high CO₂/CH₄ and CO₂/N₂ solubility selectivity [14, 23, 24, 33, 40]. For example, the three typical polymers considered for CO₂/CH₄ separation, CTA, Matrimid[®] 5218 polyimide [41], and cross-linked poly(ethylene oxide) [16], exhibit the CO₂/CH₄ selectivity of 9.1, 6.2 and 12, respectively. The details are shown in Table S1 of the Supplemental Information. On the other hand, two common ILs, [emim][BF₄] and [emim][dca], exhibit CO₂/CH₄ selectivity of about 20, which is among the highest selectivity

values for ILs studied [34]. Therefore, these two ILs are chosen in this study as dopants. The chemical structures of CTA and the two ILs are shown in Fig. 1. Although these ILs have been extensively used to blend with a variety of polymers to improve their gas separation properties [14, 24, 42-45], their doping with semi-crystalline CTA has not been studied yet.

Fig. 1. Chemical structures of (a) cellulose triacetate (CTA), (b) [emim][BF₄], and (c) [emim][dca]. The CTA structure is simplified by omitting the residual hydroxyl groups considering the high degree of acetylation of 2.87.

The objective of this work was to investigate the effects of the IL doping on the morphology and CO₂/CH₄ separation properties of CTA-based membranes. Two ILs were chosen, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF₄]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][dca]), due to their high CO₂/CH₄ solubility selectivity [34]. The effect of the IL doping on polymer properties such as crystallinity, degradation temperature and glass transition temperature is determined. The pure-gas CH₄ and CO₂ solubility and CH₄, N₂, and CO₂ permeability were determined as a function of IL doping levels, and the gas diffusivity was calculated. These doped CTA materials were also evaluated for CO₂/N₂ separation due to the high CO₂/N₂ solubility selectivity in these ILs. This work provides a new route in modifying CTA to enhance its performance of CO₂ removal from mixtures with light gases such as CH₄ and N₂.

2. Materials and experimental methods

2.1. Materials

The CTA was provided by Cameron CYNARA[®] with a degree of acetylation of 2.87 and a molecular weight of ~100,800 g/mole. [Emim][BF₄] and [emim][dca] were purchased from IoLiTec Ionic Liquids Technology, Inc. (Tuscaloosa, AL) and used as received. Anhydrous dichloromethane (>99.8%) and iso-octane (>99%) were purchased from Aldrich Chemical Company (St. Louis, MO) and used as received. Pressurized gases of CO₂, CH₄ and N₂ with ultrahigh purity (99.999%) were purchased from Praxair Inc. (Tonawanda, NY).

2.2. Preparation of thin films

Thin films of IL-doped CTA were prepared by solvent casting as follows. CTA and IL in predetermined amounts were dissolved in dichloromethane, and the mixture was stirred overnight to form a homogeneous solution. The solution was then poured into a leveled glass petri dish. After drying in the air at ambient temperature overnight, the films were placed in a vacuum oven for 3 h at 65 °C to completely remove the dichloromethane (which has a boiling temperature of 40 °C). The films were then stored at ambient temperature in a vacuum desiccator to avoid the sorption of water from the ambient. The prepared films have a thickness of 50-100 μm.

2.3. Density measurement

The density of the polymer films was determined via the buoyance method at room temperature using a Mettler-Toledo analytical balance (Model XS 64) equipped with a density

kit. Iso-octane was used as the auxiliary liquid due to the negligible sorption in the polymers, and the polymer density, ρ_P , was calculated using eq. 1 as below [8]:

$$\rho_P = \frac{M_{air}}{M_{air} - M_{liquid}} (\rho_{air} - \rho_{liquid}) + \rho_{liquid} \quad (1)$$

where M_{air} and M_{liquid} are the weights of the film in air and in the auxiliary liquid, respectively.

The ρ_{air} and ρ_{liquid} are the densities of air and the auxiliary liquid, respectively.

2.4. X-ray diffraction and thermal analysis

Wide-angle X-ray diffraction (WAXD) was conducted to evaluate the crystallinity of the IL-doped CTA films at room temperature. An Ultima IV X-ray diffractometer (Rigaku Corporation, Tokyo, JP) with a Cu K α radiation (wavelength of 1.54 Å) was used at a scan range of 5-40° and a scan rate of 0.5°/min. The degree of crystallinity was estimated using the Rigaku PDXL software by comparing the CTA/IL diffraction patterns to those of the CTA crystalline structure in the ICDD database and normalizing both the crystalline and amorphous peaks [46, 47].

Thermogravimetric analysis (TGA) was conducted using a TG 209 F1 (NETZSCH Group, Germany) in the temperatures range from 25 °C to 600 °C with a heating rate of 10 °C/min under an argon flow rate of 40 mL/min. The degradation temperature was taken at the first derivative peak of the thermogravimetric curve using the Proteus Thermal Analysis software [48].

Thermal transitions in the polymer blends were determined using differential scanning calorimetry (DSC, Q2000, TA Instruments, New Castle, DE). The measurement was conducted at a heating rate of 20 °C/min under a nitrogen gas flow of 50 mL/min. The films were scanned in the range of -80 °C to 300 °C for CTA, and -80 °C to 200 °C for the IL-doped CTA. The highest temperature for the IL-doped CTA was set as 200 °C to avoid degradation during the

scanning. The glass transition temperature was taken as the midpoint of the heat capacity step change using the Universal Analysis software from TA Instruments [49].

2.5. Permeation and sorption measurement

The pure-gas N₂, CH₄, and CO₂ permeability values of the IL-doped CTA films were determined using a constant volume/variable pressure apparatus at 35 °C [50]. Gas permeability was calculated from the steady-state rate of pressure increase in a fixed downstream volume [8, 50]. There appears no leakage of the ILs from the films onto the filter paper beneath after the IL-doped CTA samples were exposed to the high pressures.

The pure-gas CO₂ and CH₄ solubility values of the polymer films were measured using a gravimetric microbalance apparatus (IGA 001, Hiden Isochema, Warrington, UK) at 35 °C and pressures up to 14 atm [51]. The apparatus had a resolution of 0.1 µg, and the effect of buoyancy on the readings was considered using the Archimedes' principle. Polymer films of 60-100 mg with a thickness of ~40 µm were utilized. Prior to gas sorption measurements, the sample was dried and degassed for at least 8 h at 35 °C to remove all volatile impurities sorbed in the sample. Ultrahigh purity gas passed through a low temperature trap with a blend of liquid N₂ and iso-octane (at -107 °C) to remove any possible contaminants before entering the sorption chamber [52]. Gas sorption at each pressure was deemed to have reached equilibrium once the microbalance reading remained unchanged for at least 30 minutes. The gas sorption was derived from the weight change of the polymer samples with a compensation of buoyancy effect [51, 52]. The uncertainty of gas permeability and solubility is estimated using an error propagation method and uncertainty for each determined parameter [53].

3. Results and discussion

3.1. Morphology

Figs. 2a and 2b present representative WAXD spectra for CTA doped with [emim][BF₄] and [emim][dca], respectively. Pure CTA exhibits two main peaks at $2\theta = 8^\circ$ and 17° , indicating the crystalline, and the amorphous phase of CTA, respectively [6, 54, 55]. In general, the WAXD peak intensity at $2\theta = 8^\circ$ for the CTA/IL blends decreases with increasing the IL content, indicating that the addition of IL reduces the CTA crystallinity.

Fig. 2. X-ray diffraction patterns of CTA doped with (a) [emim][BF₄] and (b) [emim][dca]. The numbers by the spectra indicate the overall IL weight percentage in the CTA/IL blends.

Table 1 summarizes the degree of crystallinity (w_c) for the IL-doped CTA estimated by analyzing the WAXD patterns using the Rigaku PDXL software. [Emim][dca] is slightly more effective than [emim][BF₄] in disrupting the CTA crystallization. As the [emim][dca] content increases from 0 wt% to 50 wt%, the crystallinity decreases from 28 wt% to 6.8 wt%. At 10 wt% IL loading, however, the CTA crystallinity increases, presumably because the IL may provide the polymer chains higher mobility for assembling and thus crystallization. Further

increase in the IL content starts to decrease significantly the degree of crystallinity due to the CTA decrystallization and the IL dilution. The crystallization suppression of the CTA has been ascribed to the disruption of hydrogen bonds among the OH, esters, and ether oxygen groups, which is critical for the CTA chains to pack efficiently and then crystallize [27-31].

Table 1

Density, degree of crystallinity (w_c), amorphous phase IL weight fraction ($w_{am,IL}$) and volume fraction ($\phi_{am,IL}$) of the IL-doped CTA films at 22 °C

IL content (wt%)	CTA/[emim][BF ₄]				CTA/[emim][dca]			
	ρ_P (g/cm ³)	w_c	$w_{am,IL}$	$\phi_{am,IL}$	ρ_P (g/cm ³)	w_c	$w_{am,IL}$	$\phi_{am,IL}$
0	1.286	0.28	0	0	1.286	0.28	0	0
10	1.293	0.37	0.16	0.16	1.288	0.32	0.15	0.16
20	1.307	0.21	0.25	0.25	1.271	0.22	0.26	0.28
40	1.313	0.13	0.46	0.45	1.231	0.11	0.45	0.48
50	1.322	0.098	0.55	0.55	1.211	0.068	0.54	0.57

Table 1 presents the composition of CTA and IL in the amorphous phase, assuming that the crystal phase is pure CTA and that the amorphous phase is a mixture of CTA and IL. This assumption is valid, since the characteristic peak for the crystalline phase in the blends is consistent with that of pure CTA. As expected, the IL content in the amorphous phase (*i.e.*, $w_{am,IL}$) is also higher than that in the overall films.

Table 1 also summarizes the density of the IL-doped CTA films. Since the blends are comprised of a crystalline CTA phase and an amorphous phase containing CTA and IL, the following equation can be derived based on the additive model [8, 56]:

$$\frac{1}{1-w_c} \left(\frac{1}{\rho_P} - \frac{w_c}{\rho_c} \right) = \frac{1}{\rho_{am,CTA}} + \left(\frac{1}{\rho_{IL}} - \frac{1}{\rho_{am,CTA}} \right) w_{am,IL} \quad (2)$$

where ρ_c is the density of the crystalline CTA with a reported value 1.45 g/cm³ [57], $\rho_{am,CTA}$ is the density of the amorphous phase CTA with a reported value 1.24 g/cm³ [57] and ρ_{IL} is the IL density. The ρ_{IL} value is 1.282 g/cm³ for [emim][BF₄] and 1.101 g/cm³ for [emim][dca] at 20 °C [58]. As shown in Fig. S2 in the Supplementary Information, the density data can be well described by the model using eq. 2, corroborating the two-phase model in the IL-doped CTA (*i.e.*, a crystalline CTA phase and an amorphous phase consisting CTA and IL).

Within the amorphous phase of the blends, the volume fraction of CTA ($\phi_{am,IL}$) can be expressed as:

$$\phi_{am,IL} = \frac{w_{am,IL} / \rho_{IL}}{w_{am,CTA} / \rho_{am,CTA} + w_{am,IL} / \rho_{IL}} \quad (3)$$

The results have been recorded in Table 1, which will be used later to correlate the gas transport properties of the blends with those of the individual components.

Fig. 3 shows the mass loss of the CTA/IL blends in the TGA runs with a temperature ramp rate of 10 °C/min. There is an initial weight loss at about 50 °C, presumably due to loss of the remaining dichloromethane (with a boiling temperature of 40 °C) in the blends. The estimated values of decomposition temperature (T_d) and the corresponding weight loss are recorded in Table 2. The measured T_d values of both pure CTA and the ILs are consistent with the literature findings [6, 55, 59, 60]. Addition of the ILs clearly decreases the degradation temperature of CTA. These results suggest that the dissolved ILs disrupt the CTA chain packing, lowering the energy requirement to break the inter- and intra-bonding between polymer chains and rendering them more labile. It should be pointed out that the degradation behavior may change with the temperature ramp rate.

For the CTA/[emim][BF₄] blends, the degradation occurs in two steps when the [emim][BF₄] loading is 20% or higher. The first degradation step is attributed to the degradation of CTA due

to its lower T_d value of 309 °C, and it is also confirmed by the weight loss of the first step. [Emim][BF₄] seems to be able to partially disrupt the CTA chain packing, and the T_d value decreases with increasing the [emim][BF₄] content. The second degradation step is attributed to the degradation of [emim][BF₄], since the second T_d value is almost the same as that of pure [emim][BF₄].

Fig. 3. TGA thermograms of CTA doped with (a) [emim][BF₄] and (b) [emim][dca] with a temperature ramp rate of 10 °C/min. The numbers by the degradation curves denote the IL weight percentage in the blends.

Table 2

Glass transition temperature (T_g), decomposition temperature (T_d) and weight losses (L_1 and L_2) at the T_d 's of the CTA/IL blends

IL content (wt.%)	CTA/[emim][BF ₄]					CTA/[emim][dca]	
	T_g (°C)	1 st T_d (°C)	L_1 (%)	L_2 (%)	Measured w_{IL}	T_g (°C)	T_d (°C)
0	198	309	86	0		198	309
10	113	289	70	7.4	0.09	111	N/A
20	107	279	64	16	0.16	100	218
40	45	268	46	37	0.43	55	219
50	11	259	39	46	0.53	-1	219
100	-92	412	83	0		-104	275

Assuming that the first-step mass loss is for CTA only and the second step is for [emim][BF₄] only, the following equation can be derived:

$$w_{IL} = \frac{L_2/L_{IL}}{L_1/L_{CTA} + L_2/L_{IL}} \quad (4)$$

where L_1 and L_2 are the mass loss at the 1st and 2nd degradation step, respectively. L_{CTA} and L_{IL} are the mass loss for the pure CTA and [emim][BF₄], respectively. As shown in Table 2, the compositions estimated from the TGA results are very close to that used for the preparation of the blends, validating the hypothesized degradation mechanism in the CTA/[emim][BF₄] blends.

The T_d values for the CTA/[emim][dca] blends are lower than those of the CTA/[emim][BF₄] blends, suggesting that the dca⁻ anion is more effective than BF₄⁻ in interacting with CTA and thus affording decrystallization. The CTA/[emim][dca] blends have an almost constant T_d value, while the CTA/[emim][BF₄] blends show a decrease in the first T_d decrease with increasing the IL loading.

As shown in Table 2, the increase in the IL loading decreases the T_g value of the blends, suggesting an increase in the polymer chain mobility. The films become rubbery at the room temperature (22 °C) when the IL content is 50 wt%. For the blends containing 40% and 50% [emim][BF₄], two separate T_g values are observed, indicating phase separation. Phase separation has also been reported in blends of poly(methyl methacrylate) and ILs [21]. For the CTA/[emim][dca] blends, there is only one T_g at higher IL loading levels, suggesting that homogenous mixtures were obtained and that [emim][dca] is more compatible with CTA than [emim][BF₄]. The detailed DSC curves are shown in Fig. S3 in the Supplemental Information.

The w_c for the pristine CTA can be estimated by comparing the exothermic crystallization at around 220 °C and the endothermic melting at around 290 °C [6]:

$$w_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_{fusion}} \quad (5)$$

where ΔH_m (J/g) is the enthalpy of melting, ΔH_c (J/g) is the enthalpy of crystallization, and ΔH_{fusion} (J/g) is the enthalpy of fusion (or melting) for a perfect CTA crystallite. ΔH_{fusion} has been estimated to be about 34.4 J/g [6]. The obtained w_c is 0.28, which is consistent with that from the XRD characterization (0.28), as shown previously in Table 1.

The effect of the polymer blend composition on T_g can be described using the Gordon-Taylor equation as shown below [61]:

$$T_g = \frac{w_{am,CTA}T_{g,CTA} + Kw_{am,IL}T_{g,IL}}{w_{am,CTA} + Kw_{am,IL}} \quad (6)$$

where K is an adjustable parameter. Fig. 4 presents the best fitting of the T_g values determined from DSC using eq. 6 with a K value of 1.4 for CTA/[emim][BF₄], and 1.5 for CTA/[emim][dca]. The data can be satisfactorily described by the model, considering the complicated morphology in these blends. In the fittings, the lower T_g values for the blends containing 40% and 50% [emim][BF₄] are used, with the assumption that the phase with the lower T_g is dominant in the amorphous phase. The fitting results further corroborate this assumption.

Fig. 4. Effect of the IL weight fraction in the amorphous phase ($w_{am,IL}$) on the glass transition temperature (T_g) of the CTA/IL blends. The curves are best fittings based on eq. 6 with a K value of 1.4 for CTA/[emim][BF₄], and 1.5 for CTA/[emim][dca].

3.2. Gas permeability of the CTA/IL blends

Fig. 5 shows the pure-gas permeability at pressures of 4.4, 7.8, and 11.2 atm for the CTA/IL blends at 35 °C. The permeability values have an uncertainty of $\pm 10\%$ based on the error propagation analysis [8, 53], which was also confirmed by the measurement of multiple films. Both pure-gas CH₄ and N₂ permeability values are independent of the feed pressure, indicating that these polymer films are defect-free macroscopically. On the other hand, the pure-gas CO₂ permeability increases with increasing pressures by as much as 33% and 26% for blends of CTA/[emim][BF₄] and CTA/[emim][dca], respectively, largely due to the CO₂ plasticization [6, 17]. The CTA doped with 10% IL shows lower permeability than the pristine CTA, presumably due to the higher crystallinity in the doped CTA. Further increase in the IL content increases the pure-gas permeability, presumably due to the reduced degree of crystallinity and the increased polymer chain mobility (or T_g), as shown in Tables 1 and 2.

(a)

(b)

(c)

(d)

Fig. 5. Effect of feed gas pressure on pure-gas permeability at 35 °C: (a) CH₄ in CTA/[emim][BF₄]; (b) CH₄ in CTA/[emim][dca]; (c) N₂ in CTA/[emim][BF₄]; (d) N₂ in CTA/[emim][dca]; (e) CO₂ in CTA/[emim][BF₄]; (f) CO₂ in CTA/[emim][dca]. The numbers by the lines indicate the IL weight percentage in the blends. 1 Barrer = 10⁻¹⁰ cm³ (STP) cm/(cm² s cmHg).

Gas permeability (P_A) in nonporous polymers is usually expressed by eq 7 below [62]:

$$P_A = S_A \times D_A \quad (7)$$

where S_A is the solubility coefficient and D_A is the average effective diffusion coefficient through the film. For gas transport in semi-crystalline polymers, the crystalline domains are typically not accessible to penetrant sorption and diffusion, and the following equations are often used [8, 63, 64]:

$$S_{A,sc} = S_{A,am} \times \phi_{am} \quad (8)$$

$$D_{A,sc} = D_{A,am} \times \phi_{am} \quad (9)$$

$$P_{A,sc} = P_{A,am} \times \phi_{am}^2 \quad (10)$$

where the subscript of “am” and “sc” indicates the properties in the wholly amorphous phase, and semi-crystalline polymers, respectively.

Fig. 6 presents the estimated amorphous phase permeability, which can also be related to that of the individual components using the following equation [65, 66]:

$$\ln P_{am} = \phi_{am,CTA} \ln P_{am,CTA} + \phi_{am,IL} \ln P_{IL} \quad (11)$$

where $P_{am,CTA}$ and P_{IL} are the gas permeability in the amorphous phase CTA and in IL, respectively. The fittings are generally good, despite the fact that the CTA/[emim][BF₄] blends exhibit phase separation at higher [emim][BF₄] contents. This also corroborates that the phase with the lower T_g value is dominant in the blends with phase separation.

Fig. 6. Effect of the IL loading ($\phi_{am,IL}$) in the amorphous phase of the CTA/IL blends on the amorphous phase gas permeability in the CTA doped with (a) [emim][BF₄] and (b) [emim][dca] at 35 °C and 4.4 atm. The lines are best fitting based on eq. 11.

Fig. 7 shows the effect of the IL volume fraction in the amorphous phase ($\phi_{am,IL}$) on the pure-gas selectivity in the amorphous phase blends. The doping of CTA with [emim][dca] decreases CO₂/CH₄ selectivity, while the doping with [emim][BF₄] decreases CO₂/CH₄ selectivity and then increases. Adding these two ILs in CTA leads to a trade-off between an increase in CO₂/CH₄ solubility selectivity and a decrease in CO₂/CH₄ diffusivity selectivity

derived from the more flexible chains and weaker size-sieving ability. The different behavior in these two series of CTA/IL blends is caused by the more significant increase in solubility selectivity by the [emim][BF₄] doping than the [emim][dca] doping, which will be described later. On the other hand, the CO₂/N₂ selectivity generally increases with increasing the IL content, presumably because the increase in CO₂/N₂ solubility selectivity is much more dominant than the decrease in diffusivity selectivity for both series of blends.

Fig. 7. (a) Effect of the IL volume fraction in the amorphous phase of the CTA/IL blends ($\phi_{am,IL}$) on (a) pure-gas CO₂/CH₄ selectivity and (b) CO₂/N₂ selectivity at 35 °C and 4.4 atm.

3.3. Gas solubility in the CTA/IL blends

Gas sorption in glassy polymers is usually described using a dual mode model, and gas concentration, C_A (cm³ (STP)/cm³ polymer), is given by eq. 12 below [6, 67, 68]:

$$C_A = k_{D,A} p_A + \frac{C'_H b p_A}{1 + b p_A} \quad (12)$$

where $k_{D,A}$ (cm³(STP)/cm³ polymer atm) is Henry's sorption coefficient, C'_H (cm³(STP)/cm³ polymer) is the Langmuir capacity constant indicating the maximum sorption capacity of the

non-equilibrium excess volume, and b (atm^{-1}) is the Langmuir affinity of the gas. Rubbery polymers do not have Langmuir sorption sites and thus C_H' has a value of 0 [67].

Fig. 8 shows the pure-gas CH_4 and CO_2 sorption isotherms for CTA doped with the ILs at 35 °C. The gas sorption has a uncertainty of $\pm 10\%$ based on the error propagation analysis, which is also confirmed by the measurement using different samples. The sorption isotherms for pure CTA are in good agreement with those reported in the literature [6]. For the blends containing less than 50 wt% IL, the gas sorption isotherms are concave, which is typical for glassy polymers and can be described by the dual-mode sorption model [6, 67, 69]. The curves are the best fits by adjusting the sorption parameters in eq. 12. As the IL loading increases to 50%, the blends transition from glassy state to rubbery state and the isotherms become linear, which follows the Henry's sorption model for rubbery polymers [70].

Fig. 8. Pure-gas sorption isotherms at 35 °C: (a) CH₄ in CTA/[emim][BF₄] blends; (b) CH₄ in the CTA/[emim][dca] blends; (c) CO₂ in the CTA/[emim][BF₄] blends; (d) CO₂ in the CTA/[emim][dca] blends. The curves are best fits using eq. 12. The numbers by the curves indicate the IL weight percentage in the blends.

Table 3 summarizes the sorption parameters modelled using the dual-mode sorption model (*cf.*, eq. 12). The amorphous phase parameters $k_{D,am}$ and $C'_{H,am}$ are calculated with an expression similar to eq. 8. In general, the $C'_{H,am}$ value decreases with increasing the IL loading and

becomes zero when the IL loading is 40% or higher. This behavior is consistent with the gradual change from a glassy polymer containing Langmuir-type sorption sites to a rubbery polymer without Langmuir sorption sites (*i.e.*, $C'_{H,am}=0$). As the IL loading increases, the $k_{D,am}$ values slightly increase for CO₂ and decrease for CH₄, suggesting that the ILs exhibit more favorable CO₂/CH₄ solubility selectivity than CTA.

Table 3

Dual-mode sorption model parameters for the amorphous CTA/IL blends at 35 °C

Composition		CH ₄			CO ₂		
IL	$\phi_{am,IL}$	$k_{D,am}^*$	$C'_{H,am}^\dagger$	$b \text{ (atm}^{-1}\text{)}$	$k_{D,am}^*$	$C'_{H,am}^\dagger$	$b \text{ (atm}^{-1}\text{)}$
[emim] [BF ₄]	0	0.25	4.1	0.15	1.5	22	0.22
	0.16	0.20	4.3	0.11	1.6	15	0.19
	0.25	0.18	1.9	0.075	1.6	11	0.33
	0.45	0.11	0		1.7	0	
	0.55	0.081	0		1.8	0	
[emim] [dca]	0.18	0.21	2.5	0.074	1.5	13	0.18
	0.31	0.18	0.37	0.005	1.5	9.1	0.085
	0.52	0.10	0		1.6	0	
	0.60	0.10	0		1.6	0	

* $k_{D,am} = k_D / \phi_{am} \text{ (cm}^3\text{(STP)/cm}^3 \text{ polymer atm)}$

† $C'_{H,am} = C'_H / \phi_{am} \text{ (cm}^3\text{(STP)/cm}^3 \text{ polymer)}$

Fig. 9 exhibits the effect of the IL loading on the pure-gas sorption of the amorphous polymer blends at 5.4 atm and 35 °C. Gas solubility decreases with increasing ionic liquid content in the membrane, primarily because the blends transition from the glassy state with Henry and Langmuir sorption to the rubbery state with Henry's sorption only. CTA exhibits a CO₂/CH₄ solubility selectivity of 8.2, which is very close to that of 9.0, reported in the literature [6]. As the IL loading increases, the CO₂/CH₄ solubility selectivity increases, primarily due to the higher CO₂/CH₄ solubility selectivity in the ILs than in the CTA. [Emim][dca] exhibits a

CO₂/CH₄ solubility selectivity of 18, which is close to the value of 21 reported in the literature [34]. On the other hand, [emim][BF₄] shows a CO₂/CH₄ selectivity of 41 in this study, which is much higher than that reported in the literature (20) [34], mainly because of the lower CH₄ solubility measured in this study. [Emim][BF₄] possesses the smallest molar volume among ILs known [71]. Its gas sorption behavior can be sensitively affected by the third component in the systems [71, 72], presumably because the third component (CTA in this case) may disrupt the ionic interactions in the [emim][BF₄].

The gas solubility in the CTA/IL amorphous blends can also be related to that in the individual CTA and IL components using eq. 13 as shown below [65, 66]:

$$\ln S_{am} = \phi_{am,CTA} \ln S_{am,CTA} + \phi_{am,IL} \ln S_{IL} \quad (13)$$

where $S_{am,CTA}$ and S_{IL} are the gas solubility for the amorphous phase CTA and IL, respectively.

As shown in Figs. 9a and 9b, the gas solubility can be satisfactorily described by the equation.

Fig. 9. Effect of the IL volume fraction in the amorphous phase CTA and IL ($\phi_{am,CTA}$) on CO₂ and CH₄ solubility in (a) the CTA/[emim][BF₄] blends, and (b) the CTA/[emim][dca] blends; and (c) CO₂/CH₄ solubility selectivity. All values are for the amorphous phase at 35 °C and 5.4 atm. The lines are best fits using eq. 13.

3.4. Gas diffusivity in the CTA/IL blends

Fig. 10a illustrates the effect of the IL loading on the pure-gas CO₂ diffusivity (*cf.* eq. 7) at 5.4 atm and 35 °C. In general, the diffusivity increases with increasing the IL loading in the amorphous phase polymer blends, due to the increase in the polymer chain flexibility, as

indicated by the decreasing T_g values. As shown previously in Table 2, the doping with [emim][dca] leads to more significant decrease in T_g and therefore, higher CO₂ diffusivity than that with [emim][BF₄], especially at the higher IL content.

As shown in Fig. 10b, the CO₂/CH₄ diffusivity selectivity is generally greater than 1, due to the smaller molecular size of CO₂ (3.3 Å) than CH₄ (3.8 Å) [73]. As the IL content in the amorphous phase increases, the blends become more flexible and lose size-sieving ability, resulting in the decreased CO₂/CH₄ diffusivity selectivity. For example, pure CTA shows a CO₂/CH₄ diffusivity selectivity of 3.2, while CTA doped with ~55 wt% [emim][BF₄] or [emim][dca] shows the CO₂/CH₄ diffusivity selectivity of only 1.2, signifying the largely weakened size-sieving ability due to the glass-to-rubber transition at high IL loadings in these blends.

Fig. 10. Effect of the IL volume fraction in the amorphous phase ($\phi_{am,IL}$) on (a) pure-gas CO₂ diffusion coefficients and (b) CO₂/CH₄ diffusivity selectivity in the amorphous phase of CTA/IL blends at 5.4 atm and 35 °C. The lines are to guide the eye.

As shown in the Supplemental Information (Table S2), the fractional free volume (*FFV*) in the blends is estimated using the Bondi's group contribution method [23, 74]. There is no significant change in the *FFV* of the blends as the IL loading increases from 0 to ~50%. On the other hand, the gas diffusivity increases by almost five fold while the CO₂/CH₄ diffusivity selectivity substantially decreases, which is caused by the increased polymer chain flexibility, instead of the changes in the *FFV*. This behavior has been observed. For example, tetramethyl polycarbonate (TMPC) with an *FFV* of 0.180 has a N₂ permeability of 1.1 Barrers at 35 °C [75], while poly(dimethyl siloxane) (PDMS) has the same *FFV* value (0.180) and a N₂ permeability of 400 Barrers, presumably due to its much lower *T_g* (-120 °C) [76].

3.5. CO₂/CH₄ and CO₂/N₂ separation properties

Fig. 11 compares the CO₂/CH₄ and CO₂/N₂ separation properties of these CTA/IL films with other materials represented in a Robeson's plot [73, 77, 78]. The upper bound line in a Robeson plot provides a rough estimate of the highest selectivity possible for a given collection of pure-gas permeability in polymer-based materials and this serves as a guideline for the development of new membrane materials [73, 77, 78]. The pure-gas permeation properties in the ILs were determined at low pressures with the ILs supported in porous supports, and they are near the upper bound lines [35]. For both CO₂/CH₄ and CO₂/N₂ separation, the doping of CTA with the ILs generally moves the separation properties closer to the upper bound, which demonstrates the effectiveness of the strategy in improving the CTA-based materials for membrane gas separation. The CTA/IL blends could be further optimized by identifying ILs with higher CO₂/CH₄ and CO₂/N₂ separation performance and higher efficiency in disrupting the crystallinity in the CTA than the two ILs studied here (*i.e.*, [emim][BF₄] and [emim][dca]).

Fig. 11. Comparison of the CTA/IL blends with other materials for (a) CO_2/CH_4 separation and (b) CO_2/N_2 separation at 35 °C, as shown in Robeson plots [73, 77, 78]. The arrows indicate that the separation performance of the blends moves closer to the upper bound with adding ILs.

4. Conclusion

Although ILs have been widely explored for blending with membrane polymers to improve gas separation properties, this study for the first time aims to modify CTA, a workhorse membrane material for CO_2/CH_4 separation by doping with ILs. Doping with [emim][BF₄] and [emim][dca] has been demonstrated here to be an effective way in disrupting the CTA crystallization, increasing gas diffusivity and permeability. The IL doping also decreases the degradation temperature and glass transition temperature. The blends become rubbery at the room temperature when the IL loading is 50 wt% or above. At an IL loading higher than 40%, the CTA/[emim][BF₄] blends exhibit two T_g 's indicating a phase separation in the amorphous phase, while the CTA/[emim][dca] blends have only one single T_g , indicating that [emim][dca] is more compatible with CTA than [emim][BF₄] [79].

Doping of CTA with the two ILs improves the CO₂/CH₄ and CO₂/N₂ solubility selectivity in the blends, due to the strong affinity between the ILs and CO₂. For example, CTA exhibits a CO₂/CH₄ solubility selectivity of 9.1 at 35 °C, whereas CTA doped with 55 wt% [emim][BF₄] exhibits a CO₂/CH₄ solubility selectivity of 22, which is among the highest selectivity reported for polymeric materials. On the other hand, IL doping of CTA decreases the CO₂/CH₄ diffusivity selectivity. Nevertheless, for both CO₂/CH₄ and CO₂/N₂ separation, the doping of CTA with the ILs moves the separation properties of the resulting blends toward Robeson's upper bound lines, which demonstrates the effectiveness of the approach in improving the CO₂/light gas separation properties by IL doping.

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