CO₂ Absorption Property of Ionic Liquid and CO₂ Permeability for Ionic Liquid Membrane

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The aim of this review is to provide some information on the CO₂ absorption property of ionic liquids and the CO₂ permeability for the separation membranes using ionic liquids. Ionic liquids are a unique solvent, of which the characteristics are non-volatile, non-flammable, miscible with various chemicals, and so on. The CO₂ capture using ionic liquids is a promising technology, and a variety of studies have been reported on the natures of the ionic liquid absorbents and membranes. This review presents some fundamental data on the following three topics: (1) the CO₂ solubility in the ionic liquid physical absorbents; (2) the high-pressure CO₂ absorption behavior for the ionic liquid chemical absorbents; (3) the CO₂ permeability for the inclusion membranes with ionic liquids and polymers. The first two topics describe the effects of the chemical structures of ionic liquids on the CO₂ solubility, in particular, in terms of the oxygen containing groups and the interionic interactions. The second topic also contains how amino acid anions affect the physical and chemical absorptions under high CO₂ pressure conditions. The last topic reported that the CO₂ and N₂ permeations in the inclusion membranes depend on the composition and kind of polymers.

Keywords
Ionic liquid, Carbon dioxide, Physical absorption, Chemical absorption, Membrane separation

1. Introduction

CO₂ separation is an important process for petrochemical industry, like the purification of syngas, the production of energy resources, and so on. There are some options for the CO₂ capture, absorption, adsorption, and membrane separation, depending on throughput, composition, pressure, and temperature for gas mixture sources. Absorption process is applicable to a variety of separation targets, and many kinds of absorbents have been investigated. Ionic liquids (ILs) also have attracted much attention as a promising CO₂ absorbent because they can overcome some critical issues of conventional absorbents composed of molecular liquids: the high energy-consumption for absorption/desorption and the loss and flammability of absorbent itself. ILs are a salt, of which the melting point is at or below the ambient temperature. They have some unique characteristics as absorbents: negligible vapor pressure, non-flammability, and low heat capacity. Some ILs can selectively absorb acidic gases like CO₂, SO₂, and NOₓ, while they do not dissolve in gas phase even at high pressures as demonstrated elsewhere. Because of these features, ILs have drawn much attention as an energy-efficient and environmentally-friendly CO₂ absorbent.

It is also expected that ILs are a promising material for the gas separation membrane. The membrane separation can generally reduce the operation energy and the footprint of equipment compared to other separation technologies. Supported ionic liquid membranes (SILMs), composed of porous organic or inorganic materials filled with IL, have been studied well. SILMs are stable for a much longer time than the supported liquid membranes using organic solvents because of their non-volatile nature. Furthermore, it is reported that some SILMs of ILs with the fluorinated anions show the comparable or higher CO₂ permeability and selectivity than the conventional polymer membranes.

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are essential for each technology to absorb, desorb, and transport CO₂ rapidly. The physicochemical and gas absorption properties can be tuned for individual applications by the chemical modification and the combination of cation and anion. A great number of studies have been performed to understand the effects of chemical modifications, so far.

Our research group has investigated the density, viscosity, electrical conductivity, and heat capacity of neat ILs and the CO₂ solubilities in various ILs over the wide ranges of temperature and pressure. In particular, we measured not only the mole fraction based solubility but also the molarity based solubility. A lot of experimental data on two-phase equilibria for CO₂ + IL systems have been reported at various temperatures and pressures, however, the mole fraction scaled solubilities or Henry constants were only reported in many cases. These parameters are a measure of the CO₂ absorption property in ILs, but they exclude the molecular volume/weight of ILs themselves. More important information for the engineering design in the CO₂ separation is the CO₂ capacity, i.e. the molarity or molality scaled solubilities of CO₂. Pressure-volume-temperature-composition (pVTx) relations for the binary systems are required to obtain the molarities/molalities of CO₂, however, there have been a small number of experimental data on the pVTx relations, compared to the pTx behaviors. Very limited information is available for the effect of chemical modifications on the CO₂ capacities in ILs.

This review describes some fundamental data about the effect of chemical modifications on the CO₂ absorption property based on our previous studies. There are three topics, the ionic liquid physical absorbent, the ionic liquid chemical absorbent, and the inclusion membrane of ionic liquid and polymer. Figure 1 summarizes the chemical structures and abbreviations of the ionic species presented in this review.

2. Physical Absorbent

2.1. Effects of Oxygen-containing Groups

Some research groups reported that the fluorine atom improves the CO₂ solubility in ILs. It is also pointed out that this enhancement is mainly due to the Lewis acid-base interaction between the acidic carbon atom of CO₂ and the basic fluorine atom. However, the fluorination sometimes increases the viscosity of ILs dramatically. The worse transport property causes the depression of CO₂ absorption and desorption kinetics as mentioned in introduction. We focused on the oxygen-containing groups, i.e. the ether, ester, and hydroxyl groups. It was expected that these functional groups interact strongly with CO₂ because the oxygen atom is Lewis basic as well as the fluorine atom. Actually, the similar enhancements were reported in the earlier studies on the CO₂ + polymer systems. In addition, it was demonstrated that the ether modification decreases the viscosity of ILs.

Table 1 lists the physical properties of ILs and the CO₂ solubilities with the related thermodynamic parameters of solution for physical absorbents. Since the lengths of side chain in the cations are very similar between the functionalized and analogous pairs, i.e., [N₁₁₂₂₇][Tf₂N] and [Pyr,][Tf₂N], respectively, the differences of values in Table 1 can be mainly interpreted by the effects of ester and ether functionalization. The ether group on cation slightly increased the mole fraction scaled solubility (smaller kH'), while the ester group decreased it (larger kH'). The increment of CO₂ solubility by the ether modification was also observed in the sulfates ([6SO₄]−, [1O₂SO₄]−, and [1O₂O₂SO₄]−). Although the alkyl sulfate shows the poorer CO₂ solubility than the fluorinated anions like [Tf₂N]−, the ether moiety successively improved it. The thermodynamic parameters indicate that the ether and ester modifications in ammonium cations strengthened the intermolecular interaction.

![Fig. 1 Chemical Structures and Abbreviations of the Ionic Species Presented in This Review](image-url)
between CO₂ and ILs (smaller ΔΔsolH°). They caused simultaneously the negative entropic effect (smaller TΔΔsolS°). Unlike the ether modified ammonium, the pyrrolidinium with the ether group showed the opposite trend.

According to the earlier reports, the micro phase separation occurred between the polar and apolar phases in ILs, and CO₂ dissolves preferentially in the polar phase. In addition, the carbon atom of CO₂ interacts strongly with the Lewis basic atoms. Thus, the ether and ester modifications expand the CO₂-polarizable space where CO₂ can dissolve. It is considered that these effects are related to the enthalpic term caused by the functional groups on ammoniums. The alternative interpretation of CO₂ dissolution at molecular level was proposed in the theoretical study: the rearrangement of coordination position between the cation and anion to create a “cavity” for CO₂. This means that the structure of solution changes before and after CO₂ dissolution, i.e., leading to the change of entropy. It is considered that the ester group on the ammonium makes this rearrangement more difficult compared to the ether group. On the other hand, the ether modification of the pyrrolidinium resulted in the easier change of the coordination. It is not clear what brings about the difference between the ether modified ammonium and pyrrolidinium at present. One possible reason might be the distance between the charge center (the nitrogen atom) and the oxygen atom, two carbons for the ammonium and one carbon for the pyrrolidinium.

Figure 2 presents the CO₂ solubility in molarity scale c₁ as a function of pressure p. The CO₂ capacity increased almost linearly with the pressure increment, which is a typical behavior for IL physical absorbents.

The slopes Δc₁ ≡ dc₁/dp are also summarized in Table 1. Generally, the physisorption separation is operated by pressure swing, and thus, a solvent with larger Δc₁ is a better physical absorbent. The values of Δc₁ for the ether functionalized ammonium and pyrrolidinium were

| [N₁₁₂][Tf₂N]¹¹ | 1341 | 316.4 | 3.161 | 128 | 3.12 | -12.8 | -22.4 | 0.99 |
|-----------------|------|-------|-------|-----|------|-------|-------|------|
| [N₁₁₂][Tf₂N][MePro]⁴² | 1459 | 301.9 | 3.312 | 208 | 3.38 | -13.7 | -23.6 | 0.96 |
| [P₄₄₄₄][Tf₂N]¹ⁱ | 1291 | 350.5 | 2.853 | 168 | 2.96 | -12.8 | -22.3 | 0.98 |
| [P₄₄₄₄][PF₆]¹² | 1391 | 328.1 | 3.048 | 128 | 3.35 | -14.0 | -23.9 | 1.01 |
| [P₄₄₄₄][ClO₄]¹³ | 1428 | 286.0 | 3.497 | 60.6 | 3.29 | -13.5 | -23.3 | 1.08 |
| [P₄₄₄₄][PF₆]¹³ | 1483 | 276.8 | 3.613 | 40.6 | 3.15 | -13.6 | -23.1 | 1.07 |

**Table 1** Density ρ, Molar Volume vᵣ, Concentration of Ionic Species c₁, and Viscosity η of and Henry Constant at Infinite Dilution k₀°, Enthalpy of Solution ΔΔsolH°, Entropy of Solution TΔΔsolS°, and Slope of Molarity Scaled Solubility of CO₂ Δc₁ for ILs

The values of k₀°, ΔΔsolH°, ΔΔsolS°, and Δc₁ are calculated from the experimental data using the following equations:

- **Density (kg m⁻³)**
- **Molar Volume (cm³ mol⁻¹)**
- **Concentration of Ionic Species (mol dm⁻³)**
- **Viscosity (mPa s)**
- **Henry Constant at Infinite Dilution (mol dm⁻³ MPa⁻¹)**
- **Enthalpy of Solution (kJ mol⁻¹)**
- **Entropy of Solution (kJ mol⁻¹ K⁻¹)**
- **Molarity Scaled Solubility of CO₂ (mol dm⁻³ MPa⁻¹)**

For CO₂ solubility in molarity scale c₁ as a function of pressure p, the slope Δc₁ is calculated using the following equation:

\[
\frac{\Delta c_1}{\Delta p} = \frac{dc_1}{dp}
\]

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7-11% larger than those for the non-functionalized ones, although the Henry constants for the former ILs were only ~2% better than those for the latter ones. This is due to the smaller molar volume \(v_{\text{m}}\) for the ILs with the ether group as listed in Table 1. On the other hand, the ester modified IL showed the smaller value of \(\Delta c_1\) than its analogue despite the smaller \(v_{\text{m}}\). The decrement in \(\Delta c_1\) is derived from the worse \(k_{H^*}\) for [N\(_{112,200CO}\)][Tf\(_2\)N]. The more pronounced improvement of ether group was observed in the sulfonate salts. The values of \(\Delta c_1\) for [P\(_{444,201}\)][1O2SO\(_4\)] and [P\(_{444,201}\)][1O2SO\(_4\)] were 29% and 37% larger than that for [P\(_{444,201}\)][6SO\(_4\)]. The better \(k_{H^*}\) for the ether sulfates mainly caused this enhancement. In addition, [Py\(_{1,101}\)][FSA] had the worse \(k_{H^*}\) and the higher \(c_8\) than [Py\(_{1,101}\)][Tf\(_2\)N], resulting in the same value of \(\Delta c_1\) for the two ILs. We also investigated the effect of hydroxyl group (data is not shown) and found that the functionalization caused the worse \(k_{H^*}\) and \(\Delta c_1\) as well as the higher viscosity\(^9\).

2.2. Effects of Intercionic Interactions

We described in the former section that not only the enthalpic effect but also the entropic effect are important to improve the CO\(_2\) solubility in addition to the smaller molar volume. The entropic term can be related to the rearrangement of coordination, and thus, the interionic interaction between the cation and anion is of importance for the improvement of energy for solvation. It is reported that the interaction energies for a pair of ILs between [eimH]+ and different anions increased in the following order: \([\text{BF}_4^-] < [\text{PF}_6^-] < [\text{Tf}_2\text{N}^-] < [\text{TCB}^-]\) \(^{25}\). This trend is in a good agreement with the experimental CO\(_2\) solubilities for the three [bmim]+ ILs, [bmim][BF\(_4\)] < [bmim][PF\(_6\)] < [bmim][Tf\(_2\)N]\(^{26}\). Therefore, we investigated the phase equilibria for the CO\(_2\)+[eimH][TCB] system\(^{37}\).

Table 1 lists the \(k_{H^*}\) values of [eimH][TCB] and [eimH][Tf\(_2\)N], which indicates that the mole fraction based solubility in the former IL was slightly larger than that in the latter IL. The enthalpies suggest that [TCB]− interacts with CO\(_2\) as strongly as [Tf\(_2\)N]−, implying that the CN group is also presumably CO\(_2\)-philic (Lewis basic). Actually, the nitrogen atoms in [TCB] have large negative partial charges\(^{28}\). The entropies reveal that the coordination change caused by CO\(_2\) dissolution in [eimH][TCB] is similar to that in [eimH][Tf\(_2\)N]. Although ILs with smaller anions like [BF\(_4\)]− and [PF\(_6\)]− generally show more negative entropic values, the weaker interaction of [TCB]− leads to the favorable entropic effect. The \(c_1\) data for [eimH][TCB] are also plotted in Fig. 2. The \(c_1\) is almost proportional to the pressure and the slope for [eimH][TCB] is 1.41 mol dm\(^{-3}\) MPa\(^{-1}\), which is ~31% higher than that for [eimH][Tf\(_2\)N]. This increment is attributed to the higher concentration of ionic species as summarized in Table 1. The molarity of CO\(_2\) in [eimH][TCB] is the largest in the IL physical absorbents investigated previously, and the more rapid absorption and desorption are expected because of its low viscosity (see Table 1).

We also studied the effect of interionic interaction via proton in a protic ionic liquid (PIL), which is a subclass of IL\(^{29}\). PILs have an advantage over the conventional ILs in the cost of production, because PILs are synthesized by simple neutralization of an acid with a base. PILs have proton-acceptor and -donor sites in the cation and anion, which can form an extended intermolecular network\(^{30–32}\). The spectroscopic study pointed out that the intermolecular interaction between the cation and anion in PILs is generally stronger than that in ILs\(^{33}\). The stronger interaction increased both the density and viscosity for PILs. The example results for [eimH][Tf\(_2\)N] are shown in Table 1. \(k_{H^*}\) for [eimH][Tf\(_2\)N] is larger than that for the corresponding IL, [eimim][Tf\(_2\)N]. The entropic term for [eimH][Tf\(_2\)N] is smaller than for [eimim][Tf\(_2\)N]. This unfavorable effect is partially compensated by the smaller enthalpy. The stronger solution structure in [eimH][Tf\(_2\)N] makes the cavity formation more difficult. The protic nature, i.e. the electro positive and negative sites can interact with the negative oxygen and positive carbon atoms of CO\(_2\), resulting in the better enthalpic effect. Figure 2 plots the relations of \(p-c_1\) for [eimH][Tf\(_2\)N] at 298.15 K. The CO\(_2\) capacities in the PIL and the corresponding IL are almost the same. This is due to the smaller molar volume of [eimH][Tf\(_2\)N] compared to that of [eimim][Tf\(_2\)N]. The intermolecular interaction via proton makes a negative contribution to the physical properties, in particular, the transport properties, but not to the molarity scaled solubility of CO\(_2\).

3. Chemical Absorbent

Unlike the physical absorbent, the chemical absorbent absorbs CO\(_2\) through the chemical reaction. Generally, the chemical absorption is saturated at lower pressures and the contribution of physical absorption becomes larger at higher pressures. Most of the earlier studies investigated the CO\(_2\) solubility at limited pressures lower than ~0.2 MPa. However, some CO\(_2\) separation processes are operated at much higher pressures of CO\(_2\). To understand whether IL chemical absorbents are applied to high CO\(_2\) pressure sources or not, it is important to investigate the CO\(_2\) solubility at high pressures and the effect of chemical modifications on both chemical and physical absorptions.

Some kinds of IL chemical absorbents have been reported so far\(^{34–41}\), and we focused on the amino acid ILs (AAILs) with tetrabutylphosphonium\(^{42}\). One of the advantages of AAILs is high CO\(_2\) solubility; one mole of AAILs absorb an equimolar amount of CO\(_2\) through a 1:1 stoichiometric reaction. In the conventional amine solutions and other amine functionalized
ILs, two moles of amines are consumed for one mole of CO$_2$ through a 2:1 reaction. Figure 3 presents the CO$_2$ solubility in mole fraction $x_1$ as a function of pressure at 333.15 K. The values of $x_1$ are 0.45-0.50 at 0.10 MPa, i.e., each AAIL absorbed 0.9-1.0 moles of CO$_2$ per mole of AAIL. $x_1$ increased steeply at pressures up to 0.15 MPa and gradually increased at higher pressures. The [P4444][Pro] + CO$_2$ solution at atmospheric pressure was analyzed using NMR, and we identified that CO$_2$ was absorbed chemically as a carbonate ([Pro-CO$_2$]$^-$). The amount of CO$_2$ absorbed chemically in [P4444][Gly] was the smallest and those in [P4444][Pro] and [P4444][MePro] are almost the same. The theoretical study revealed that the 2:1 reaction, i.e., the formation of dianion ([Pro-CO$_2$]$^{2-}$ + [Pro]$^-$ to [Pro-CO$_2$]$^-$ + [ProH]$^-$) also occurs simultaneously, although the dianion is less stable thermodynamically. It is suggested that the 1:1 reaction is promoted in [Pro]$^-$ compared to [Gly]$^-$, and the methylation of [Pro]$^-$ does not influence significantly the CO$_2$ chemisorption.

Figure 4 is the plot of the molarity scaled solubility $c_1$ against the pressure $p$. To understand the effect of the amino acid anions on high-pressure CO$_2$ solubility, $c_1$ was deconvoluted into the two contributions of physical and chemical absorptions. The molarities of physically absorbed CO$_2$ $c_{1,p}$ and chemically absorbed CO$_2$ $c_{1,c}$ are also plotted in Fig. 4. The $v_n$ value for [P4444][Pro] is larger than that for [P4444][Gly], however, the slope of $c_{1,p}$ for [P4444][Pro] is the largest in these AAILs. The proportional constant like the Henry constant was calculated based on the deconvolution result, of which the values are summarized in Table 1 with some literature values. [Pro]$^-$ is a better anion for the increment of physisorption than [Gly]$^-$; however, these anions are less effective than the typical anions like [Tf$_2$N]$^-$. The [P4444]$^+$ salt shows the smaller $k_H$ than the [emim]$^+$ salt (e.g., 2.5 MPa for [P4444][Tf$_2$N] and 3.45 MPa for [emim][Tf$_2$N] at 298.15 K). Nevertheless, $k_H$ for the amino acid ILs are larger than [emim][Tf$_2$N] at 333.15 K as summarized in Table 1.

4. Ionic Liquid+Polymer Membrane

4.1. Poly(ethylene glycol) Based Polymer

SILMs can be optimized for individual application by modifying the chemical structures of ILs as described in the previous sections. However, there is a serious drawback: SILMs are not stable under pressurized conditions because ILs easily drop out from the porous material. The polymer inclusion and ion gel membranes are possible materials for overcoming this disadvantage. The rigid polymer matrices commonly restrict the gas diffusion, which leads to the lower per
meability in the inclusion membranes compared to that in SILMs. Therefore, an IL membrane with a low polymer content is more favorable for the gas separation. Some research groups reported such membranes for the CO2 separation\textsuperscript{46).}

We investigated the CO2 permselectivity and solubility for the tetra-armed poly(ethylene glycol) (Tetra-PEG) + [emim][Tf2N] ion gel\textsuperscript{51).} The previous study reported that the gel is mechanically robust (the maximum breaking strength by compression reaches 18 MPa) and thermally stable (up to 300 °C) even at 6 wt% polymer content\textsuperscript{22).} Figure 5 shows the CO2 permeability and selectivity for the Tetra-PEG + [emim][Tf2N] membrane (94 wt%-IL) and the [emim][Tf2N] SILM as a function of temperature. One important finding is that $P_{CO_2}$ for the ion gel membrane is 37-57 % higher than that for the SILM. The high permeation for the ion gel membrane might be ascribed to the larger cross sectional area where gas molecules dissolve in the IL. The porosity of the support filter is 68 %, and thus, the ideal permeability of the SILM is estimated to become 1.47 times, which agrees well with the difference in the permeabilities. The other finding is almost the same selectivities for both membranes. According to the solution-diffusion transport mechanism, an ideal selectivity of CO2 to N2 mainly depends on the solubility $c$ and diffusion coefficient $D$, $P_{CO_2)/P_{N_2}} = (c_{CO_2}/c_{N_2})(D_{CO_2}/D_{N_2})$. The present results imply that both solubilities and diffusion coefficients of CO2 and N2 in the ion gel are not so far from those in the SILM. Thus, the support polymer, Tetra-PEG, does not hinder the gas separation performance.

We also investigated the CO2 absorption behavior for the ion gel under high-pressure conditions, which is the first demonstration as far as we know. Figure 6 shows the pressure dependence of the CO2 solubility (molarity scale) and the volume expansion at 298.15 K. The ion gel expands without solvent seeping-out even at 3 MPa. The volume expansion for the ion gel is practically equal to that for the neat [emim][Tf2N]. In addition, the ion gel can absorb CO2 physically as much as the corresponding neat IL. In conclusion, the Tetra-PEG\textsuperscript{4}IL gels are promising materials applicable to the CO2 separation over the wide range of temperatures (up to 300 °C) and pressures (at least up to 3 MPa).

4.2. Poly(vinylidenfluoride) Based Polymer

In earlier studies, the polymers do not contribute to the CO2 selective permeation (in other words, the polymers are only a “container”), and the maximum performance of inclusion membrane is determined by only the property of ILs. However, if the polymers can enhance the CO2 solubility in the inclusion membranes, the CO2 permeability would be improved compared to the SILMs according to the solution-diffusion model. We investigated the effect of poly(vinylidenefluoride) (PVDF) and poly(vinilidenedifluoride-co-hexafluoropropylene) (PVDF-HFP) on the CO2 permeability\textsuperscript{53).} These conventional polymers contain the fluorine atoms, which can favorably interact with the Lewis acidic carbon atom on CO2 as mentioned before.

The Raman spectra for the inclusion membranes are summarized in Fig. 7. We observed the drastic change of Raman spectra, in particular, at 800-900 cm\textsuperscript{-1}.  

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by adding [bmim][TfO]. According to the literatures, this spectral change is interpreted as the conformational transition of polymer from non-polar α-phase to polar β-phase. The conformational transition, i.e., the plasticization was also indicated by the thermal analyses for the present membranes (the data are not shown). Commonly, the polar polymer is more CO2-philic than the non-polar polymer due to the quadrupole moment of CO2. It is expected that the plasticized (polar β-phase) PVDF and PVDF-HFP can enhance the CO2 solubility in the inclusion membrane compared to the non-plasticized polymers (non-polar α-phase).

Figure 8 presents the CO2 permeability and selectivity for the [bmim][TfO] + PVDF and + PVDF-HFP membranes. The inclusion membranes with 25 wt%-IL showed the smaller $P_{CO2}$ and $P_{CO2}/P_{N2}$ than the [bmim] [TfO] SILM. This might be due to the slower diffusion and the decrement of solubility of gas components. The addition of polymer generally increases the viscosity of IL, resulting in the worse diffusivity. In addition, the non-polar polymers do not have the CO2 affinity as mentioned above. On the other hand, the values of $P_{CO2}$ and $P_{CO2}/P_{N2}$ for the inclusion membranes with 75 wt%-IL are higher than those for the SILM (e.g., $P_{CO2}$ for the inclusion membrane was 2.1 times higher than that for the SILM), although the diffusion of gas species would be slower. The cross sectional area where gas species pass through for the inclusion membrane was higher than that for the SILM, as mentioned in the section 4.1. Again, the ideal permeability of the SILM is 1.47 times as high as its experimental permeability. This value is still smaller than the ratio mentioned above (2.1 times), which suggests that the CO2 solubility in the membrane was higher than that in the IL itself. This upgrading is derived from the enhanced interaction between the polar polymer and the CO2 molecule. In conclusion, the appropriate compo-

Fig. 7 Raman Spectra for the [bmim][TfO] + PVDF and + PVDF Inclusion Membranes

Fig. 8 Temperature $T$—permeability of CO2 $P_{CO2}$ and selectivity of CO2 $P_{CO2}/P_{N2}$ for the PVDF (a) and PVDF-HFP (b) inclusion membranes.
sitions of IL and fluorinated polymer successfully improves the performance of IL membrane.

5. Conclusion and Outlook

We described the effects of chemical modifications on the CO$_2$ absorption and physical properties for ILs. The strong interactions between CO$_2$ and ILs, the weak electrostatic cation-anion interactions, and the smaller volume are required to improve the CO$_2$ physisorption in ILs. On the other hand, the information for the IL chemical absorbents is still limited. It has been reported the effective chemical structures for the improvement of CO$_2$ chemisorption at atmospheric pressure and room temperature. However, it is unclear how the chemical modifications influence other properties, such as the high pressure CO$_2$ solubility, the temperature dependence of CO$_2$ chemisorption, and so on. These properties are also essential to design various chemisorption processes. Thus, we have presented a new analytical method to evaluate both the chemical and physical sorption capacities of ILs over an extended pressure range. The bio-compatibility and -degradability for both kinds of IL absorbents must be considered for the commercial use; however, a limited number of reports is available. Although the ether group, as introduced in this review, is a possible choice to improve the biodegradability, further investigations should be performed in the future.

The modified ILs can be applied not only the absorption but also the membrane separations. The ion gels with low polymer contents are a good candidate for the gas separation membranes under various temperature and pressure conditions. The ion gel membranes have the superior permselectivity to the SILMs because of its large cross sectional areas where gas species pass through, though the manufacturing of "special" polymers is disadvantageously still cost-intensive. Another approach is the improvement of membrane performance using conventional polymers as presented in this review. In both cases, the compatibility between the polymer matrixes and the IL molecules is the key factor. In spite of some literatures available, the more deep insights should be provided for diverse combinations of polymer and IL.

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Nomenclatures

- $k_B$: Henry constant [Pa]
- $P$: permeability [Barrer]
- $p$: pressure [Pa]
- $\Delta v$: entropy of solution [J mol$^{-1}$ K$^{-1}$]
- $T$: temperature [K]
- $\nu_0$: molar volume [m$^3$ mol$^{-1}$]
- $\Delta V$: volume expansion rate [-]
- $x$: mole fraction [-]

<Greek>

- $\eta$: viscosity [Pa s]
- $\rho$: density [kg m$^{-3}$]

<Subscript>

- 1: CO$_2$ [-]
- 2: IL [-]
- c: chemical absorption [-]
- p: physical absorption [-]

<Superscript>

- o: neat IL [-]
- $\infty$: infinite dilution [-]

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