# Solubility and Diffusivity of $CO_2$ in Ionic Polyimides with $[C(CN)_3]_x[oAc]_{1-x}$ Anion Composition

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## Abstract

Recently, mixtures of ionic liquids (ILs) containing acetate [$oAc^-$] and tricyanomethanide [$C(CN)_3^-$] anions have demonstrated promising characteristics as solvents and as $CO_2$ adsorbents. The anion composition can be optimized to obtain a significant improvement in the diffusivity while only slightly decreasing the solubility. Here, we explore a similar investigation applied to an ionic polyimide (i-PI) material in order to understand the molecular-level kinetic and thermodynamic characteristics that emerge when a polymeric material is used instead. The i-PI systems studied are part of an emerging class of "high-performance" ionene polymers that hold significant potential for applications in gas separation membranes. Here, neat i-PI systems with the two counter anions, [$oAc^-$] and [$C(CN)_3^-$], at varying concentrations are modeled by a combination of molecular dynamics (MD) and grand canonical Monte Carlo (GCMC) simulations. Higher concentrations of [$C(CN)_3^-$] are predicted to improve $CO_2$ diffusion, similar to the pure IL performance, while solubility remains relatively unchanged. The structural characteristics of the i-PI systems provide detailed insight into the effect that the anions have on the adsorption properties. The solubility is weakly related to the theoretical surface area, and the diffusivity is moderately correlated to the fractional free volume (FFV). Overall, the combination of different anions is predicted to be a viable strategy for improving the diffusivity throughout i-PI materials, but the behavior of pure ILs cannot be simply extrapolated to ion behavior in membranes.

Keywords: separations; ionic liquids; molecular simulation; membrane; carbon dioxide

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## 1. Introduction

Over the past 20 years, there have been many reports on the fundamental behavior of ionic liquids (ILs), as well as their applications in emerging technologies (electrical energy storage, industrial gas processing, biomass processing, etc.).[1-5] ILs are salts with low melting points (often liquid near room temperature), and they tend to have very low vapor pressures,[6] high thermal stability,[7] and low flammability.[8] Moreover, their specific physical and chemical properties can be tuned to achieve a wide variety of values, depending upon the combination of different cations and anions. The tunable nature of ILs provides a route for designing highly selective solvents for use in industrial applications.

One of the most thoroughly explored applications of ILs is in industrial gas processing, mainly in the separation of $CO_2$ from $N_2$ or $CH_4$. However, the relatively high $CO_2$ selectivity and solubility are compromised by high IL viscosity and high cost (compared to traditional bulk solvents, such as methanol or aqueous monoethanolamine). Thus, a variety of alternative approaches are being explored, such as adsorption and membranes formed from polymerized ILs (poly(ILs)) and supported ILs (SILMs).[2, 9-16] Past studies have indicated that the anion choice plays a dominant role in the $CO_2$ solubility performance,[17-20] and different functional groups (alkyl, hydroxyl, ether, fluoroalkyl, etc.) can be used to tune the behavior.[21-27] Recent studies have mostly focused on ILs containing anions which are more nucleophilic toward $CO_2$, such as acetate [oAc$^-$] [28, 29] or imidazolide or pyrrolide. [30]

Mixtures of the ILs 1-butyl-3-methylimidazolium acetate, [$C_4$mim][oAc], and 1-butyl-3-methylimidazolium tricyanomethanide, [$C_4$mim][$C(CN)_3$], have been previously investigated in the literature.[31, 32] [$C_4$mim][oAc] has demonstrated favorable solvation properties and has been used for $CO_2$ adsorption[33, 34] and dissolution of lignocellulose materials.[4, 5, 35, 36] Although the $CO_2$ absorption performance is good, its high viscosity (932.3 Pa·s at 293.15 K)[33] limits mass transport, which compromises its industrial utility. On the other hand, pure [$C_4$mim][$C(CN)_3$] has an unusually low viscosity,[37] but its $CO_2$ solubility is 10 times lower than in [$C_4$mim][oAc]. Due to the general tradeoff in performance, ILs containing these two anions have been used to obtain IL mixtures with the desired balance of thermophysical properties. For instance, there is a decrease of the viscosity and a significant increase of ion self-diffusion coefficients with increasing [$C(CN)_3^-$] content,[32] as well as the diffusivity of the gas molecules in the mixture.[38] Likewise, the absorption of $CO_2$ decreases with increasing [$C(CN)_3^-$] concentration.[31]

Beyond varying the composition of the bulk ILs, reports of closely-related polymeric materials have been rapidly growing in the literature. This includes examples of SILMs, poly(ILs), and other composite membranes. These materials can circumvent some of the common challenges (cost, energy consumption, solvent recovery, high viscosities, etc.) associated with the use of IL solvents in conventional absorber-stripper/flash gas processing.[39] Furthermore, poly(ILs) and related composite materials allow for a broader design space, as the underlying polymer structure and the IL chemistry can be individually tailored to a specific application.[40-46] For instance, an IL immobilized on mesoporous silica has been shown to increase the $CO_2/CH_4$ selectivity by up to 35%, as compared to unmodified silica.[40] Studies of 1-ethyl-3-methylimidazolium bistriflimide ($[C_2mim][Tf_2N]$) incorporated in Matrimid (a polyimide used in commercial membrane processes) have shown an increase in the $CO_2$ permeability coefficient from 6.5 to 38 barrer and the $CO_2/CH_4$ permselectivity from 32 to 63.[41] Bara, et al.[47] has investigated the polymerized room-temperature ionic liquids, poly(RTIL) and polymerized room-temperature ionic liquid -room temperature ionic liquid, poly(RTIL)-RTIL, composite membrane. Incorporation of just 20 mol% free RTIL in the polymer membrane yields a stable material with a $CO_2$ permeability increase of around 400% and a 33% improvement in $CO_2/N_2$ selectivity, as compared to the neat poly(RTIL). Li, et al.[42] have also reported the advantages of adding ILs to polymerized ILs with respect to $CO_2$ separation in their experimental studies. An increase in 1-butyl-3-methylimidazolium bistriflimide, $[C_4mim][Tf_2N]$, content up to 60 wt% within a poly(1-vinyl-3-butylimidazolium bistriflimide - 1-butyl-3-methylimidazolium bistriflimide, poly($[vbim][Tf_2N]$)–$[C_4mim][Tf_2N]$, composite membrane resulted in an increase in solubility of $CO_2$ from $15.1\cdot10^{-3}$ to $23.3\cdot10^{-3}$ $cm^3$(gas STP)/($cm^3$(RTIL) cmHg) and $N_2$ from $0.61\cdot10^{-3}$ to $0.95\cdot10^{-3}$ $cm^3$(gas STP)/($cm^3$(RTIL) cmHg). Also, the diffusivity of $CO_2$ increased from $0.67\cdot10^{-6}$ cm $s^{-1}$ to $2.4\cdot10^{-6}$ cm $s^{-1}$ and that of $N_2$ increased from $0.75\cdot10^{-6}$ cm $s^{-1}$ to $2.27\cdot10^{-6}$ cm $s^{-1}$. Overall, the permeability of $CO_2$ increased from 101.4 barrer to 559.5 barrer, and $N_2$ permeability increased from 4.55 barrer to 21.6 barrer. However, the IL addition does not change the corresponding $CO_2/N_2$ selectivity values, which are ~22 in all systems.

Tome, et al.[48] explored the properties of SILMs with mixtures of ILs for $CO_2$ separation, focusing on ILs with $[C_2mim^+]$ cations paired with different cyano-functionalized anions (due to their high $CO_2$ permeabilities and selectivities[49-51] and low viscosities[52]). Improved $CO_2$ solubility selectivity was obtained by mixing acetate or lactate with $[Tf_2N^-]$, but the presence of the carboxylate anions decreased the gas permeability through the SILMs due to the high viscosity. Higher $CO_2$ separation performance was found for IL mixtures containing anions like $[N(CN)_2^-]$ and $[SCN^-]$, which are inherently less viscous. Cyano-functionalized anions can have a significant impact on the gas permeation properties of SILM membranes, and depending on the number of cyano groups present, the gas permeabilities, diffusivities and solubilities can be been tuned.[48] In general, SILMs prepared with these IL mixtures approach the Robeson upper bound[53] for $CO_2/N_2$ separation.[48] Similar to bulk ILs, the SILM results demonstrate that a proper balance between $CO_2$ selectivity and viscosity is crucial to achieve improved $CO_2$ separation performance.[48]

The performance trends summarized above serve as motivation to extend this concept to the design of ionic polyimide (i-PI) materials. An i-PI is a type of ionene[54] polymer with imidazolium cations in the backbone separated by an diimide linker, which is pyromellitic dianhydride, PMDA in this study (see Figure 1). Unbound counter ions maintain system neutrality, and additional ILs can be absorbed by / added to these polymers to create composite materials.[46] Here, we focus on the influence of different anion concentrations, since the anions tend to form stronger associations with $CO_2$ molecules[2] and have a stronger influence on $CO_2$ solubility.[20] We have modeled $[oAc^-]$:$[C(CN)_3^-]$ anion compositions of 100%:0%, 75%:25%, 50%:50%, 25%:75% and 0%:100%, including their interactions with $CO_2$ and corresponding molecular-level structural characteristics. The simulation results obtained indicate that the anion composition can be used to tune the gas separation properties of the i-PI polymer, but the general performance trends diverge from those observed in the corresponding bulk IL mixtures.

## 2. Simulation details

The structure of the i-PI monomer units is presented in Figure 1, along with key sites labeled. In total, 200 monomers were used to build the i-PI polymers. Ionic polyimide monomers were inserted into the simulation box followed by energy minimization using a steepest-descent algorithm. The system was then relaxed with MD simulation using alternating cycles of canonical (NVT) simulation and isothermal-isobaric (NPT) simulation, followed by a slow quench to 294 K and 1 bar. The monomer units were polymerized using a nearest-neighbor algorithm by connecting the head and tail groups. This step was followed by additional relaxation with MD. A detailed description of the polymerization procedure can be found in our previous works.[55-57] The resulting system is a dispersion of i-PI polymer chains, ranging in length from 6 to 80 repeat units and a number average molecular weight of 36.6 kDa with a dispersity of 6.0. The i-PI systems were studied with two different counter ions, [oAc$^-$] and [C(CN)$_3^-$], over a range of compositions, as summarized in Table 1. Due to the slow relaxation dynamics of the polymers, the approach used to estimate the CO$_2$ adsorption in our i-PI system is consistent with that used in our previous studies.[55-57] In summary, after several NVT and NPT molecular dynamics (MD) stages of structural relaxation, the i-PI system is brought to a final temperature of 294 K and a pressure of 1 bar. All MD simulations were performed with GROMACS 5.0.[58] In order to simulation CO$_2$ adsorption in the system, grand canonical Monte Carlo (GCMC) simulations were performed with Cassandra.[59, 60] In order to improve convergence, the GCMC and MD simulations were combined in alternating stages. During the GCMC simulations, the polymer is held rigid, while the GCMC sampling proceeds for at least 3 x $10^6$ steps (33% insertion, 33% deletion, 17% translation, and 17% rotation). After each stage of GCMC, the resulting structure (including the gas molecules) is relaxed via a 1 ns NVT MD simulation at 294 K. Following 15 cycles of GCMC/MD, the CO$_2$ adsorption was found to saturate, and the systems were then further relaxed for 20 ns. In order to study gas transport in the i-PI systems, long-time simulations are required, so an additional 100 ns of MD simulation were used for analyzing transport behavior in the systems.

**Table 1.** Summary of i-PI systems simulated. All compositions correspond to a total of 200 monomers units (with polymers of varying length).

| short name | number of [OAc$^-$] | number of [C(CN)$_3^-$] | molar ratio [OAc$^-$]:[C(CN)$_3^-$] | equilibrium density, g cm$^{-3}$ |
|---|---|---|---|---|
| oAc100 | 400 | 0 | 100:0 | 1.296 ± 0.069 |
| oAc075 | 325 | 75 | 75:25 | 1.292 ± 0.060 |
| oAc050 | 200 | 200 | 50:50 | 1.290 ± 0.062 |
| oAc025 | 75 | 325 | 25:75 | 1.284 ± 0.067 |
| oAc000 | 0 | 400 | 0:100 | 1.279 ± 0.046 |

In the above simulations, the Lennard-Jones potential and electrostatic interactions were calculated with a cutoff distance of 1.4 nm, and the smooth particle mesh Ewald sum (SPME)[61] method was used to estimate long-range electrostatic interactions, with 0.16 nm

Fourier spacing. In MD, the Nose−Hoover thermostat[62] was used to maintain the temperature, the Parrinello−Rahman[63] barostat was used to maintain the pressure, and the time step was 1 fs. Periodic boundary conditions in all three dimensions were used throughout. The i-PI was modeled using the OPLS-AA force field,[64] supplemented by partial charges estimated previously[55, 65] with electronic structure calculations. As in our previous work, the force field parameters for the anions were taken from Lopes, et al.[66-70] and the TraPPE force field was used for $CO_2$.[71-73] The Lorentz–Berthelot mixing rules were used for cross-term interactions.

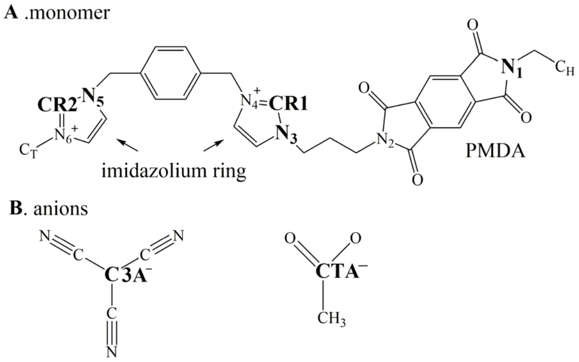

**Figure 1.** The structure of the i-PI monomer and anions with key atomic labels indicated.

The mean square displacement (MSD) of the $CO_2$ molecules (center of mass) was calculated over a time span of 100 ns to estimate the diffusion coefficient ($D^{MSD}$), obtained using the Einstein relation corresponding to the linear regime. The theoretical surface area of the i-PI system was calculated from configurations of the polymer after the MD relaxation process. The reported surface areas represent an average taken from 50 different structural configurations sampled from the trajectory every 2 ns. Additionally, the FFV of each polymer system was calculated by sampling 50 configurations, taken every 2 ns during the MD simulations. The Gelb and Gubbins approach was used for these structural analyses,[74] and additional implementation details are provided in prior works from our group.[55, 56]

## 3. Results

Densities of all i-PI compositions are presented in Table 1. The maximum density is 1.296 g cm$^{-3}$ in the oAc100 system, and it decreases with the addition of $[C(CN)_3]^-$ (reaching 1.279 g cm$^{-3}$ in oAc000). The fractional free volume (FFV), surface area, and the cavity size distribution are presented in Figures 2a-c, respectively. Regardless of the probe size, the surface area increases (values are naturally inversely proportional to the probe diameter) with respect to the $[C(CN)_3]^-$ fraction. The FFV also increases with increasing $[C(CN)_3^-]$ fraction; however, in both cases it is not a monotonic linear increase. While the FFV increases with higher concentrations of $[C(CN)_3^-]$ up to a maximum of 0.296, the impact is marginal (i.e., an FFV increase of 3.5%). This is similar to the low variability that we previously predicted with other anions, ($[PF_6^-]$, $[BF_4^-]$ and $[Tf_2N^-]$),[55-57] corresponding to slightly different FFV values of 0.297, 0.303, and 0.305, respectively. Thus, the FFV is more likely to be influenced by the organization of the polymer backbone versus the corresponding anions, which have greater structural mobility. Other i-PI monomers with increased rigidity are currently being investigated (computationally and experimentally), in order to have a more direct influence on the FFV of the polymer.

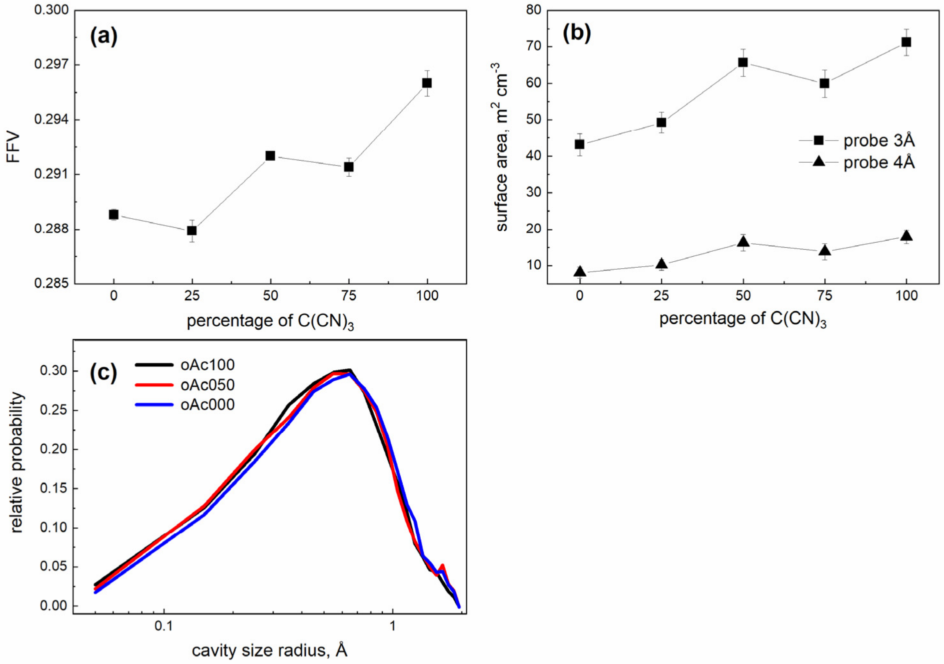

**Figure 2.** The (a) FFV and (b) surface area (using probe diameters of 3.0 and 4.0 angstroms) as a function of the anion composition. The cavity size distribution corresponding to three different systems are illustrated in (c). The lines included are a guide to the eye.

The cavity size distribution shown in part (c) of Figure 2 is very similar, regardless of anion concentration, with a peak at around 0.6 Å. However, the tail corresponding to the larger cavity sizes (1.5-2.0 Å) is more relevant to adsorption properties. Within this region, the systems that include [$C(CN)_3^-$] display elevated values, and this also corresponds to increased $CO_2$ diffusion coefficients in the materials. The solubility and diffusivity of $CO_2$ as a function of [$C(CN)_3^-$] composition are presented in Figure 3a and 3b, respectively.

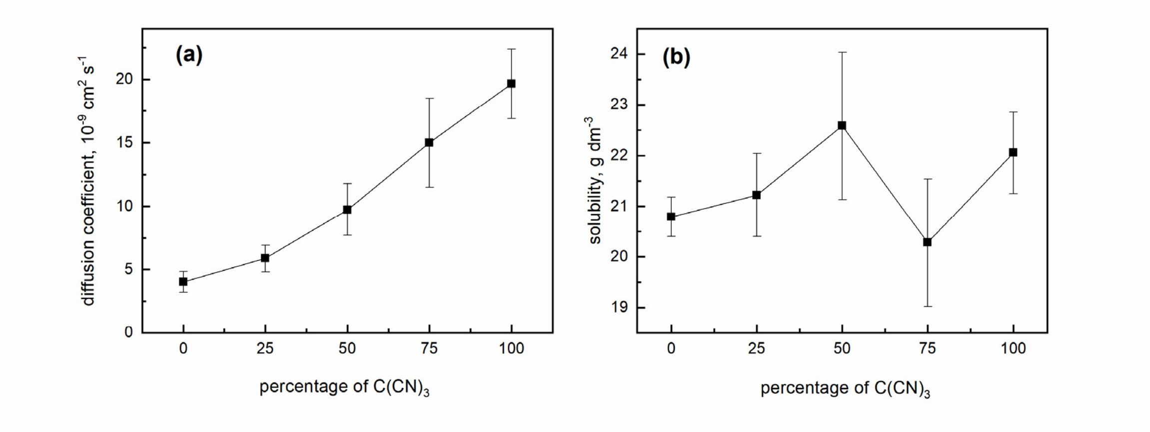

**Figure 3.** The (a) diffusion coefficient and (b) solubility of $CO_2$ as a function of the [$C(CN)_3^-$] anion concentration. The lines included are a guide to the eye.

The diffusion coefficient of $CO_2$ increases from around $5 \cdot 10^{-9}$ cm$^2$ s$^{-1}$ to $20 \cdot 10^{-9}$ cm$^2$ s$^{-1}$ as the relative amount of [$C(CN)_3^-$] anions increases from 0% to 100%. Increased $CO_2$ diffusivity was also observed in the mixtures of the pure ILs, ranging from $19.7 \cdot 10^{-7}$ cm$^2$ s$^{-1}$ in pure [$C_4$mim][oAc] to $47.6 \cdot 10^{-7}$ cm$^2$ s$^{-1}$ in [$C_4$mim][$C(CN)_3$]$_{0.75}$[oAc]$_{0.25}$.[31] The increased gas diffusivity follows the viscosity decrease observed for these mixtures.[32] However, the diffusion coefficient is two orders of magnitude higher in ILs than in our i-PI systems, likely due to the rigid polymer backbone. In our systems, we also observe that the FFV increases with respect to the [$C(CN)_3^-$] content, and this appears to be related to the diffusion coefficient, as previously suggested by others.[75, 76] Mohammad, et al.[76] found that the logarithm of the diffusion coefficient of $CO_2$ in crystalline and amorphous cellulose increases linearly with respect to the FFV. This same relationship for the i-PI systems of interest is presented in Figure 4, presenting a similar correlation.

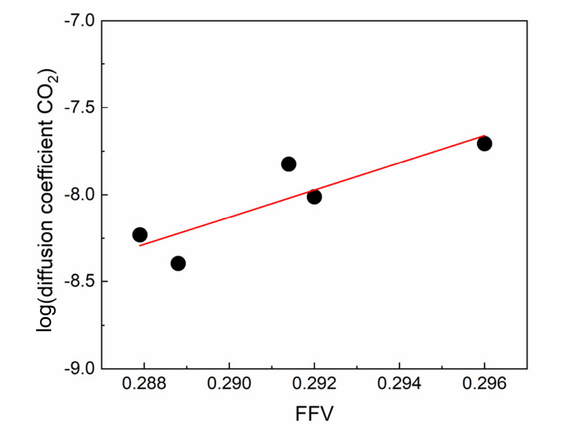

**Figure 4.** Correlation between the $CO_2$ diffusion coefficient and the FFV of the i-PI systems of interest. The line is a least-squares fit of the data, with $R^2 = 0.76$.

Solubility of $CO_2$ in the mixtures of $[C_4mim][C(CN)_3]_x[oAc]_{1-x}$ in i-PIs showed a small increase with the increase of the $[C(CN)_3^-]$ concentration. A clearly different trend was found from the experimental results of bulk IL mixtures,[31] as the absorption was much lower in $[C_4mim][C(CN)_3]$ and increased with respect to the $[C_4mim][oAc]$ concentration. This was attributed to the chemical reaction of the gas with $[C_4mim][oAc]$ through a mechanism involving the formation of a carbene $[C_4mim^+]$-$CO_2$ complex.[29, 77-79] This complex was also observed in the $[C_4mim][oAc]_x[C(CN)_3]_{x-1}$ mixture, but was not found in pure $[C_4mim][C(CN)_3]$. The presence of the carbene complex has been linked to the formation of acetic acid (HoAc) in both neat $[C_4mim][oAc]$ and $[C_4mim][oAc]_x[C(CN)_3]_{x-1}$ mixture systems.[29, 31] Although this reactive interaction is not captured with classical MD, a strong association between these groups in observed in the current simulations.

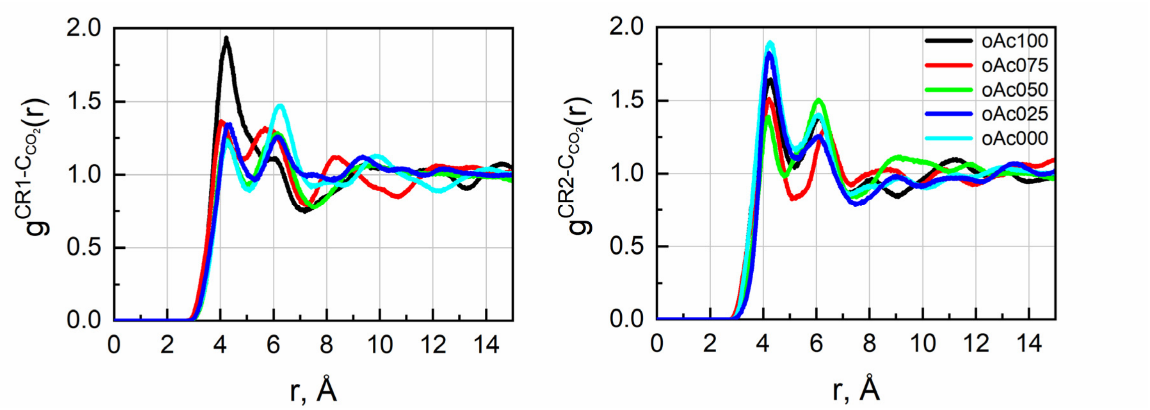

**Figure 5.** The radial distribution functions between the CR atoms in polymer backbone (as assigned in Figure 1) and the C atom of $CO_2$.

The radial distribution function (RDF) between $CO_2$ and the CR sites of the cation (assigned as CR1 and CR2 in Figure 1) in the i-PI backbone is illustrated in Figure 5. In the case of CR1 (carbon atom in the cation ring located closer to the PMDA linker), the affinity with $CO_2$ is significantly higher in the oAc100 system. For oAc000, the second maximum at approximately 6 Å is considerably higher than the first, suggesting a reduced probability of ultimately forming the mentioned carbene complex. In the case of the CR2 site, there are some moderate offsetting interactions observed. For instance, while oAc100 displays the smallest first peak with the CR1 site, the opposite behavior is found at the CR2 site (oAc000 corresponds to the largest peak).

The surface area shows a weak correlation to the $CO_2$ solubility, as illustrated in Figure 6. This correlation was explored previously and found to be much stronger in other i-PI systems containing [$PF_6^-$], [$BF_4^-$], and [$Tf_2N^-$] anions.[55, 56] The theoretical surface area, contrary to the FFV, changes significantly with respect to the anion used. Additionally, as shown by Brennecke, et al.,[17-20] the anions have a dominant role in $CO_2$ solubility for bulk IL systems, but in our systems the overall range of $CO_2$ solubility was relatively narrow making it difficult to establish a definitive correlation.

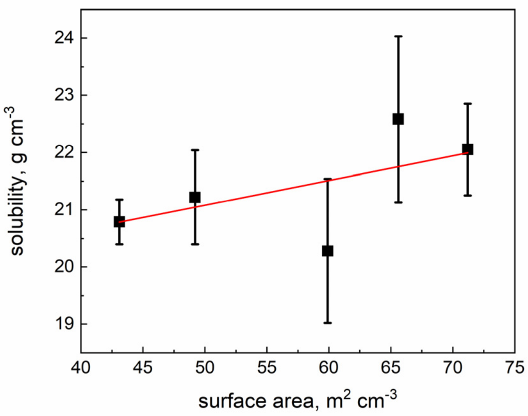

**Figure 6.** $CO_2$ solubility as a function of the surface area (corresponding to a probe diameter of 3.0 Å). The red line is a least-square fit to the data, with an $R^2$ value of 0.624.

Figure 7 shows the RDF between $CO_2$ and the different nitrogen sites of the polymer backbone, the central carbon of [$C(CN)_3^-$] anion (C3A), and the carbon atom of the carboxyl group of the [$oAc^-$] anion (CTA) in the different anion mixtures.

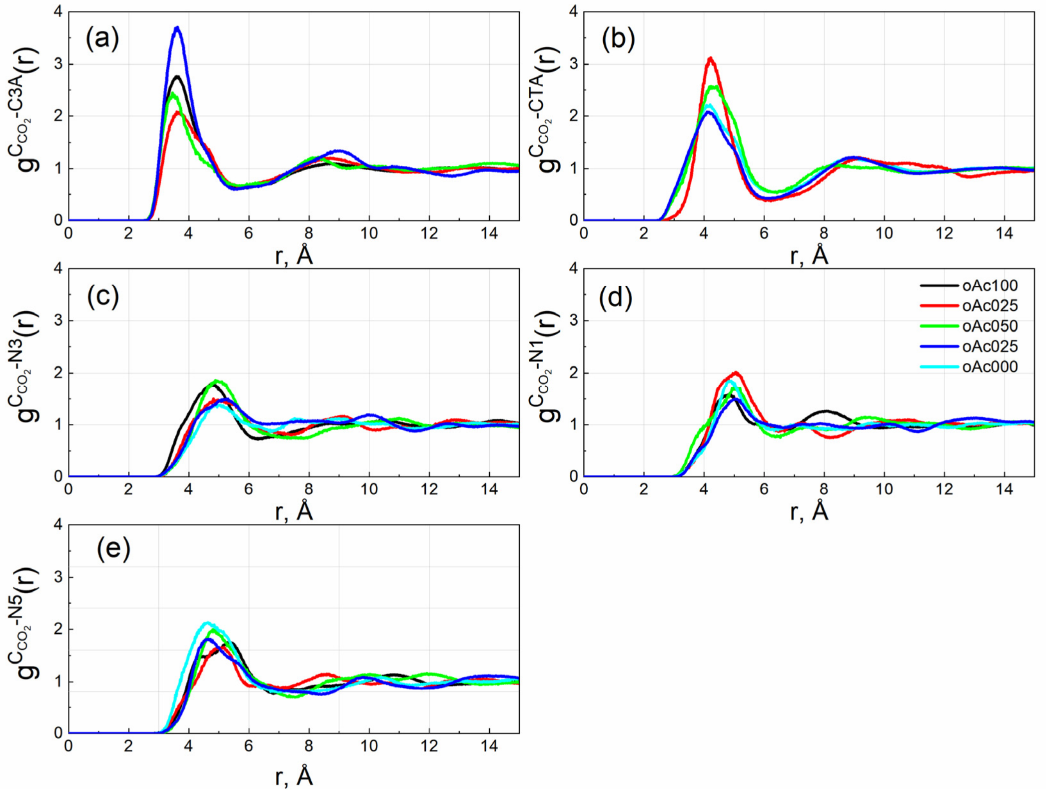

**Figure 7.** RDF between $CO_2$ (C atom) and (a) the central carbon atom of the [C(CN)$_3^-$] anion (C3A), (b) the central carbon atom the [oAc$^-$] anion (CTA), (c) N3 imidazolium site of the polymer backbone (d), N1 imide site of the polymer backbone, and (e) N5 imidazolium site of the polymer backbone. Site labels are illustrated in Figure 1.

The RDFs indicate that the $CO_2$ molecules are more often observed in the vicinity of the anions. Lepre, et al.[31] also found that $CO_2$ is mostly solvated by the anions in the bulk ILs, and the affinity between $CO_2$ and the [C(CN)$_3^-$] anions is a bit stronger than with the [oAc$^-$] anions. This is similar to findings for the i-PI systems of interest here. Regardless of the value of the peak height, the first maximum of the N3-$CO_2$ and N5-$CO_2$ plots tends to move to longer or shorter distances, respectively, with the increase of the [C(CN)$_3^-$] fraction. This is related to the weaker interaction of $CO_2$ with the CR site of the cation upon increase of the [C(CN)$_3^-$] composition. Although the RDF between the anions and the N atoms in the i-PI backbone is also calculated, no significant difference is found with respect to anion composition (data not shown).

Overall, the results for our i-PI systems cannot easily be interpreted within the context of bulk IL mixture behavior. For instance, Lepre, et al.[31] found that the absorption of $CO_2$ in mixtures of [$C_4$mim][oAc] and [$C_4$mim][C(CN)$_3$] is very close to that calculated by simply averaging the results of the pure ILs, even in the presence of coexisting chemical and physical absorption mechanisms. This linear composition-dependent behavior of $CO_2$ adsorption in bulk IL mixtures has been reported by several other authors,[34, 80-82] as well. However, this linear dependence may not be true for all bulk IL mixtures.[83] Nevertheless, we find that the properties of the bulk ILs cannot simply be translated to the trends in the i-PI based systems for predicting the $CO_2$ adsorption/diffusion properties.

## 4. Conclusion

In this study, the solubility and transport behaviors of $CO_2$ within i-PI polymers were modeled, focusing on the effects of varying ratios of two different counter anions, [oAc$^-$] and [C(CN)$_3^-$]. The structural properties of these polymers are calculated, and we observe an increase of the surface area and FFV with respect to the [C(CN)$_3^-$] concentration. The addition of [C(CN)$_3^-$] improves the diffusivity of the $CO_2$ molecules, but the solubility is only marginally affected. These findings contrast with the results for the bulk IL mixtures, as the solubility decreases with respect to the [C(CN)$_3^-$] in bulk IL mixtures. However, in both cases, the addition of [C(CN)$_3^-$] improves the diffusion. Some of the i-PI structural features can be correlated to the $CO_2$ adsorption and diffusion (surface area weakly correlates with solubility and FFV moderately correlates with diffusivity).

Our studies of similar i-PI polymer systems[55-57] have shown that the FFV does not change considerably with respect to different anions, but there can be very large changes in the theoretical surface area. The monomer structure tends to have a stronger influence on the FFV (and ultimately gas diffusivity). However, the properties of the bulk ILs cannot be easily transferred to the trends observed in the i-PI systems. Also, it should be recognized that there are experimental aspects that are not often captured in the model systems, such as the presence of water,[31] which can directly affect the $CO_2$ absorption capacity.[33]

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## Data Availability

The raw data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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