

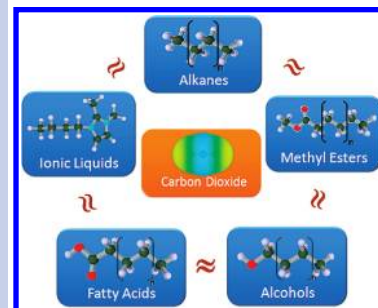
# On the Nonideality of CO<sub>2</sub> Solutions in Ionic Liquids and Other Low Volatile Solvents

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**ABSTRACT** The nonideality of CO<sub>2</sub> solutions in ionic liquids and other low volatile solvents, with which CO<sub>2</sub> is known to form electron donor–acceptor (EDA) complexes, is here investigated. It is shown that the deviations from the ideality observed are not related with the stability of the EDA complex formed, and in most cases these deviations are small and dominated by entropic effects. For this reason, when the CO<sub>2</sub> concentration is expressed in molality, the pressure versus concentration phase diagrams of CO<sub>2</sub> in nonvolatile solvents are, within the uncertainty of the experimental data, solvent independent. Following this approach, a correlation for the solubility of CO<sub>2</sub> in nonvolatile solvents, valid for pressures up to 5 MPa and temperatures ranging from room temperature up to 363 K, is here proposed. These results are tested with success by measuring the solubility of CO<sub>2</sub> in [THTDP][Cl] to show that, in such heavy ionic liquid the solubility, although identical in molality units, if expressed in mol fractions, it is larger than that in [BMIM][NTf<sub>2</sub>].

**SECTION** Statistical Mechanics, Thermodynamics, Medium Effects



The solubility of CO<sub>2</sub> in solvents of low volatility or nonvolatile is highly relevant for many technological applications. Enhanced oil recovery (EOR) requires the knowledge of the CO<sub>2</sub> solubility in heavy hydrocarbons;<sup>1</sup> purification of vegetable or animal oils or the extraction of value-added compounds from them using supercritical technologies is related with the CO<sub>2</sub> solubility in these oils, and their fatty acids and esters;<sup>2–5</sup> and the Selexol process uses a mixture of dimethyl ethers of polyethylene glycol (PEG) for the removal of acid gases from feed gas streams.<sup>6</sup> Recently, a great deal of works have addressed the use of ionic liquids (ILs) for CO<sub>2</sub> capture and gas separation purposes.<sup>7–31</sup> In all these cases, the understanding and description of the absorption of CO<sub>2</sub> in solvents of low volatility is of importance for the design and operation of processes or the design of new and enhanced sorbents for CO<sub>2</sub>.

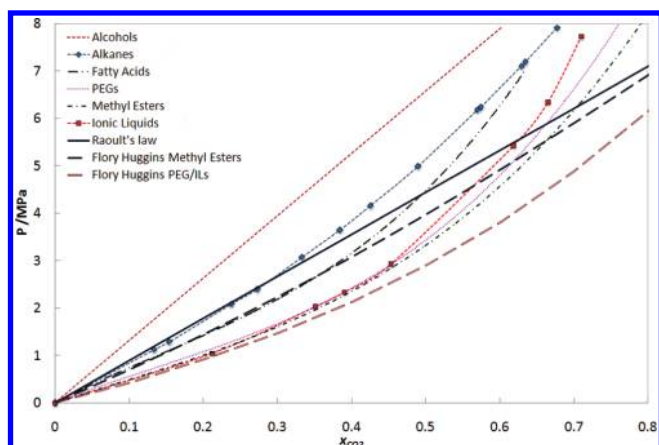
Equations of state (EoSs) are useful to correlate the experimental data available and extrapolate the data into conditions for which no experimental data is available. A number of EoSs have been used to describe the experimental data for the systems mentioned above.<sup>22,32–48</sup> The EoSs available have however a number of shortcomings. They have a very limited predictive ability for systems not previously studied. Moreover, given that empirical binary parameters are required to fit the experimental data for the most complex systems, the understanding of the solubility at a molecular level is quickly lost.

The best approach to obtain direct molecular level interaction information for CO<sub>2</sub>-containing systems is through spectroscopic techniques. It is well-known that the CO<sub>2</sub> molecule can act both as proton acceptor or electron donor

according to the nature of the solvent, forming electron donor–acceptor (EDA) complexes.<sup>49–66</sup> A number of authors have investigated the interactions between CO<sub>2</sub> and carbonyl groups,<sup>50–55</sup> ester groups,<sup>56–58</sup> hydroxyl groups,<sup>59–64</sup> ether groups<sup>49,65,66</sup> and with ILs.<sup>67–71</sup> While these interactions observed by spectroscopic techniques are of high relevance for an understanding of the solvation of CO<sub>2</sub> in nonvolatile solvents, they are not enough to fully explain its solubility or the deviations to the ideal behavior on these systems. Although the CO<sub>2</sub> EDA complexes with sp<sup>3</sup> O-donating atoms (such as H<sub>2</sub>O and alcohols) are more stable than complexes involving sp<sup>2</sup> O-donating atoms (such as aldehydes and ketones), the solubility on the former is inferior to that observed on the latter.<sup>49</sup> Kazarian et al.<sup>68</sup> based on the solubility and spectroscopic evidence for the interactions of CO<sub>2</sub> with BF<sub>4</sub> and PF<sub>6</sub> anions were the first to recognize that “the strength of the interactions cannot be solely responsible for the solubility of CO<sub>2</sub> in ionic liquids”.<sup>68</sup> Seki et al.<sup>71</sup> in a recent work show that, although the interactions of CO<sub>2</sub> with BF<sub>4</sub> and PF<sub>6</sub> anion-based ILs are stronger than those with the NTf<sub>2</sub>, the solubility of CO<sub>2</sub> on these ILs is larger than in the former, and thus the interactions alone are not enough to provide an explanation for the CO<sub>2</sub> sorption. They recognize that “the strong Lewis acid–base interactions between the ILs and the dissolved CO<sub>2</sub> has no promotional effect on the solubility of CO<sub>2</sub>”.<sup>71</sup>

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**Figure 1.** Sketch of the pressure–CO<sub>2</sub> molar composition diagram for the systems CO<sub>2</sub> + alcohols, CO<sub>2</sub> + alkanes, CO<sub>2</sub> + fatty acids, CO<sub>2</sub> + PEGs, CO<sub>2</sub> + fatty acid esters, and CO<sub>2</sub> + ILs at 313 K.

These observations shouldn't come entirely as a surprise since the nonideality of a solution and its impact on the solubility of a given solute depends not only on the solute–solvent interactions, observed and discussed by these authors, but on a delicate balance between the solute–solute, solute–solvent, and solvent–solvent interactions. Moreover, in systems of nonvolatile solvents, these solvents present in general a large molar volume, and the solute–solvent size and shape asymmetries will generate important entropic and free volume contributions to the nonideality of the system with significant impact on the CO<sub>2</sub> solubility on these systems.

The aim of this work is to study the deviations to nonideality of solutions of CO<sub>2</sub> in nonvolatile solvents. Nonvolatile solvents are here defined as those with a vapor pressure at room temperature inferior to 100 Pa. This value was chosen because, in the systems with CO<sub>2</sub> here studied, this leads to a vapor phase composed essentially of CO<sub>2</sub>, i.e., the concentration of solvent in the vapor phase is typically inferior to 0.01 mol %. In this group of solvents are the alkanes above C<sub>12</sub>, fatty acids heavier than C<sub>5</sub>, fatty acid esters larger than octanoate, PEG with molecular weight above 400, alcohols larger than *n*-heptanol, and ILs in general. These systems will be here studied to develop a deeper understanding of the molecular mechanisms that dominate the CO<sub>2</sub> sorption on these liquids and, through it, develop a model to describe the CO<sub>2</sub> solubility in nonvolatile solvents.

*The Nonideality of CO<sub>2</sub> Solutions in Nonvolatile Solvents.* To analyze the nonideality of CO<sub>2</sub> solutions in nonvolatile solvents, experimental vapor–liquid equilibrium (VLE) data at subcritical and near critical conditions for a wide range of systems, comprising alcohols, fatty acids, fatty acid esters, PEGs, and ILs, were compared with the solubilities predicted by Raoult's law described as

$$P = x_{\text{CO}_2} \gamma_{\text{CO}_2} P_{\text{CO}_2}^{\sigma} \quad (1)$$

where  $\gamma_{\text{CO}_2} = 1$  is the CO<sub>2</sub> activity coefficient, and  $P_{\text{CO}_2}^{\sigma}$  is the vapor pressure of CO<sub>2</sub>, estimated using the correlation of the DIPPR database.<sup>72</sup> Since at high CO<sub>2</sub> concentrations most systems will exhibit a liquid–liquid region with strong positive deviations to ideality, the analysis will be restricted to the low

concentration region before the deviations related to this region appear.

In spite of the strong CO<sub>2</sub>–OH interactions observed spectroscopically,<sup>59–64,73</sup> the alcohol systems are the only with positive deviations to ideality as sketched in Figure 1 (actual data is reported as Supporting Information). This is a striking example showing that strong solute–solvent interactions are not enough to guarantee enhanced solubility if the solvent–solvent interactions destroyed during the solvation of the solute are not energetically compensated by that process.

In the analysis of the other systems, it must be recalled that the nonideality results not only from differences in the energetic interactions between the molecules, as described by the residual contribution to the Gibbs free energy, but also from entropic effects due to their size and shape differences, the combinatorial contribution, as summarized by

$$G^E = G_{\text{comb}}^E + G_{\text{residual}}^E \quad (2)$$

The entropic effects will always have a negative contribution to the nonideality that, in terms of activity coefficients, can be described by the Flory–Huggins equation:<sup>74,77</sup>

$$\ln(\gamma_{\text{CO}_2}^{\text{comb}}) = \ln \frac{\varphi_{\text{CO}_2}}{x_{\text{CO}_2}} + \left(1 - \frac{\varphi_{\text{CO}_2}}{x_{\text{CO}_2}}\right) \quad (3)$$

If the combinatorial contributions to the nonideality alone are taken into account, eq 1 will become

$$P = x_{\text{CO}_2} \exp \left( \ln \frac{\varphi_{\text{CO}_2}}{x_{\text{CO}_2}} + \left(1 - \frac{\varphi_{\text{CO}_2}}{x_{\text{CO}_2}}\right) \right) P_{\text{CO}_2}^{\sigma} \quad (4)$$

The pressure versus mol fraction plot of the CO<sub>2</sub> solubility in alkanes sketched in Figure 1 shows a behavior very close to the ideal behavior described by Raoult's law (actual data is reported as Supporting Information). Given the negative deviations to ideality predicted by the Flory–Huggins model for these systems, the near-ideal behavior must result from positive deviations in the residual (enthalpic) term. These arise from CO<sub>2</sub>–alkane interactions that must be weaker than the CO<sub>2</sub>–CO<sub>2</sub> or alkane–alkane interactions.

All the other systems studied present negative deviations to ideality. The deviations observed in ILs are intermediate between an ideal behavior and what would be predicted by the Flory–Huggins model as shown in Figure 1. This indicates that, while on the IL systems the combinatorial term is larger than the residual, thus the solubility is controlled by entropic effects, the two contributions to the Gibbs free energy still have opposite signs. This implies that there is a misfit in the solute–solvent interactions relative to the solute–solute and solvent–solvent interactions that, like in the alcohol and alkane systems, is not enough to energetically compensate for the interactions that are destroyed upon mixing.

Both fatty acids and PEGs show a nonideal behavior than can be well described by the Flory–Huggins equation while the esters display the largest deviations to the ideal behavior observed for all the systems studied, as shown in Figure 1 (see also the actual data reported as Supporting Information). This suggests that the residual contribution for the nonideality is

negligible or even negative. It results from the fact that, on these systems, the EDA complexes formed between CO<sub>2</sub> and the carbonyl group, although not more stable than those formed with the hydroxyl groups of alcohols, are favored as the CO<sub>2</sub>–carbonyl interactions seem to be energetically favorable when compared with the CO<sub>2</sub>–CO<sub>2</sub> interactions and the carbonyl–carbonyl interactions established between the ester molecules. This is in agreement with the results of Besnard et al.<sup>58</sup> that indicate that the stabilization energy of the CO<sub>2</sub>–acetone heterodimer is larger by at least a factor of 2 when compared with the CO<sub>2</sub> homodimer.

A special and extreme case of the formation of EDA complexes is the solubility of CO<sub>2</sub> in ILs with anions such as acetates and other conjugated bases of organic acids reported and discussed by Shiflett and Yokozeki<sup>29,30,78</sup> and us.<sup>31</sup> Unlike the other systems here discussed, in the low concentration range, the solubility on these systems is completely dominated by the formation of the complex and thus will not be considered in this work.

The most striking result from this analysis is that, in spite of the major differences in the chemical nature of the solvents here studied and of the interactions of their molecules in pure state, the nonideality of the CO<sub>2</sub> in solution in the composition range studied is remarkably lower than could be anticipated and, in most cases, is essentially driven by entropic effects. Moreover, as has been noticed before by other authors,<sup>68,71</sup> this analysis on the nonideality of these systems also stresses that there is no direct relationship between the stability of the EDA complex formed between the CO<sub>2</sub> and a given solvent and the nonideality of CO<sub>2</sub> on this solvent. These two observations combined suggest that, by increasing the size difference between the CO<sub>2</sub> and the solvent, the solubility must increase as the entropic contribution to the solution nonideality increases.

Since, with the exception of the alcohols, all the systems here reported present relatively small negative deviations to ideality, there should be possible to derive a comprehensive framework for the description of the solubility of CO<sub>2</sub> in nonvolatile solvents. The approach here proposed is detailed below.

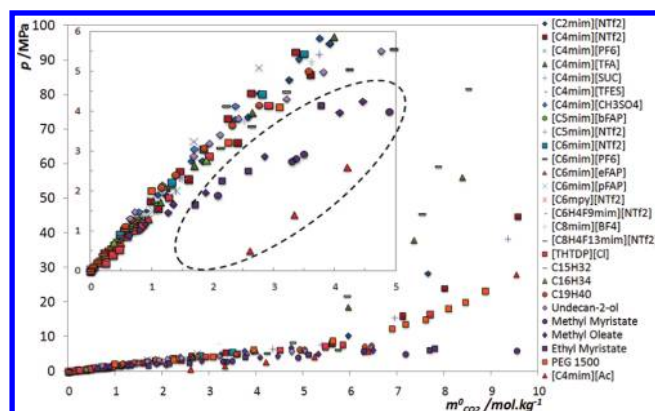
**Model development.** Adopting the approach suggested by the IUPAC for CO<sub>2</sub> solubilities in ILs<sup>75</sup> and followed in the works of Maurer and co-workers,<sup>15,18,76</sup> the solubility of a gas *i* in a liquid can be described by the extended Henry's law<sup>76,77</sup>

$$k_{H,i}^{(m)}[T,p]a_i^{(m)}[T,p,m_i] = f_i^V[T,p,y_i] \quad (5)$$

where  $k_{H,i}^{(m)}[T,p]$  is the Henry's constant of gas *i* (on the molality scale), at temperature *T* and pressure *p*, in a particular solvent. The reference state for the chemical potential of gas *i* in the liquid phase is an one molal solution of gas in the solvent, which experiences interactions as at infinite dilution in that solvent. The  $a_i^{(m)}$  is the activity of gas *i* in the liquid phase and it is described as<sup>76,77</sup>

$$a_i^{(m)}[T,p,m_i] = \frac{m_i}{m^0} \gamma_i^{(m)} = m_i^0 \gamma_i^{(m)} \quad (6)$$

where  $m^0 = 1 \text{ mol} \cdot \text{kg}^{-1}$ , and the activity coefficient  $\gamma_i^{(m)} \rightarrow 1$  as  $m_i \rightarrow 0$ .



**Figure 2.** Pressure–molality diagram of CO<sub>2</sub> + nonvolatile solvents at 313 K. Data from refs 12, 13, 16, 17, 23, 26, 31, 48, and 78–84.

For nonvolatile solvents, the gas phase is a pure gas, in this case pure CO<sub>2</sub>. For pressures up to 10 MPa, the fugacity of CO<sub>2</sub> is proportional to the pressure, and eqs 5 and 6 can thus be combined as

$$p = H_i m_i^0 \quad (7)$$

where  $H_i$  combines the Henry's constant,  $k_{H,i}^{(m)}$ , with the gas phase nonideality, proportional to pressure, and the liquid phase nonideality, proportional to concentration.

Since, as discussed above, the deviation to Raoult's law for the systems investigated is not large, eq 7 suggests the possibility of obtaining a general correlation for the solubility of CO<sub>2</sub> in solvents of low volatility or nonvolatile. This hypothesis is tested in Figure 2, where the solubility of CO<sub>2</sub> in a large number of ILs, alkanes (pentadecane, hexadecane, and nonadecane), alcohols (undecan-2-ol), and methyl esters (methyl oleate and methyl and ethyl myristate) is plotted on a *p*–*m* diagram at 313 K. With the exception of the data represented inside the ellipse for [BMIM] acetate, because of the reasons discussed above, and the fatty acid esters that show a larger CO<sub>2</sub> solubility than that observed for the other systems, the agreement observed between the solubilities in the other solvents studied is remarkable, suggesting that a common behavior is followed by the solubility of CO<sub>2</sub> on these solvents.

To extend eq 7 to a larger temperature range, the temperature dependency of the Henry's constant proposed by Benson and Krause<sup>77</sup> was adopted. Within a temperature range of up to 100 K it can be expressed as

$$\ln H_i = \alpha + \frac{\beta}{T} \quad (8)$$

Combining eqs 7 and 8, it is possible to develop a general description for the solubility of CO<sub>2</sub> in nonvolatile solvents. For this purpose, experimental data from various authors and in various types of nonvolatile solvents was used.<sup>12,13,16,23,31,81</sup> The result is shown in Figure 3 (complete data is reported as Supporting Information) where the value of  $H_i$  at each temperature is reported. A general correlation for the solubility of CO<sub>2</sub> in nonvolatile solvents,

including ILs, expressed in molality, as a function of pressure and temperature, can thus be proposed as

$$p = m_i^0 e^{(6.8591 - \frac{2004.3}{T})} \quad (9)$$

This correlation is valid for pressures up to 5 MPa, for temperatures ranging from room temperature up to 363 K, and molalities up to 3 mol·kg<sup>-1</sup>. Note that the IUPAC reference data for CO<sub>2</sub> solubilities in ILs is expressed in molalities using an approach similar to what is here proposed.<sup>75</sup>

Equation 7 and the results presented in Figures 2 and 3 indicate that the solubility of CO<sub>2</sub> in nonvolatile solvents, expressed in molality, is within the experimental uncertainty of the data available<sup>75</sup> and, with the few exceptions discussed above, solvent independent. Solubilities in the literature are, however, generally reported in molar fractions and not molalities. For a dilute solution, the relationship between the solubility expressed in molar fraction and molality can be obtained as

$$x_{\text{solute}} \approx m_{\text{solute}} M_{\text{w,solvent}} \quad (10)$$

This means that, if, at a given pressure, two solvents present similar solubilities when expressed in molalities, their solubilities will differ when expressed in molar fractions. Moreover, it shows that the solubility value, expressed in molar fraction, will increase with the solvent molecular

weight,  $M_w$ , ILs and PEGs, because of their large molecular weights, present larger solubilities, expressed in molar fractions, than other solvents, even when their solubilities are identical when expressed in molalities. This is also a consequence of the nonideality of these solutions being dominated by the entropic effects as discussed above. The larger the solvent, the higher the solubility of CO<sub>2</sub> on this solvent due to the entropic contribution to the Gibbs free energy. This is valid, in particular, for two ILs of different molecular weight and provides a good explanation for the fact that ILs based on the bis(trifluoromethylsulfonyl)imide, [NTf<sub>2</sub>], anion present one of the largest CO<sub>2</sub> solubilities reported,<sup>12,13,31</sup> in spite of the weak interactions observed by spectroscopy,<sup>71</sup> and that the solubility of CO<sub>2</sub> in ILs increases with the alkyl chain length of the cation.<sup>12,13,31</sup>

The results here obtained indicate that any IL with a molecular weight large enough, even if it is not based on the [NTf<sub>2</sub>] anion, should present a CO<sub>2</sub> solubility larger than an imidazolium with a fluorinated anion.<sup>85</sup> To test this hypothesis, a chloride ([Cl]) based IL was chosen, along with a cation that is formed essentially by alkyl chains, to create an IL with a very large molecular weight, while at the same time minimizing the possibility of forming EDA complexes with CO<sub>2</sub> or have any type of significant intermolecular interactions besides London dispersion forces. The IL chosen for this purpose was the trihexyltetradecylphosphonium chloride, [THTDP][Cl] ( $M_w = 519.31$ ). The results for the solubility of CO<sub>2</sub> in [THTDP][Cl] measured by us, using a technique and apparatus detailed elsewhere (cf. Supporting Information for experimental details and results), are compared in Figure 4 against 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>4</sub>mim][NTf<sub>2</sub>] ( $M_w = 419.36$ ), one of the ILs with the largest CO<sub>2</sub> solubility reported,<sup>12,13,16,17,23,31,78–81</sup> at 313 and 363 K. It is here shown that the solubility of CO<sub>2</sub>, expressed in mole fraction, is indeed larger in [THTDP][Cl] than in [C<sub>4</sub>mim][NTf<sub>2</sub>] as predicted. Nevertheless, when expressed in molality, the solubilities in the two ILs overlap each other as shown in Figure 4.

In conclusion, this work shows that the solubility of CO<sub>2</sub> in nonvolatile solvents is not driven exclusively or predominantly by the favorable interactions between the gas and the solvent. The CO<sub>2</sub> displays an approximately ideal solubility in alkanes and minor negative deviations to ideality in ILs that are lower than expected from that predicted from

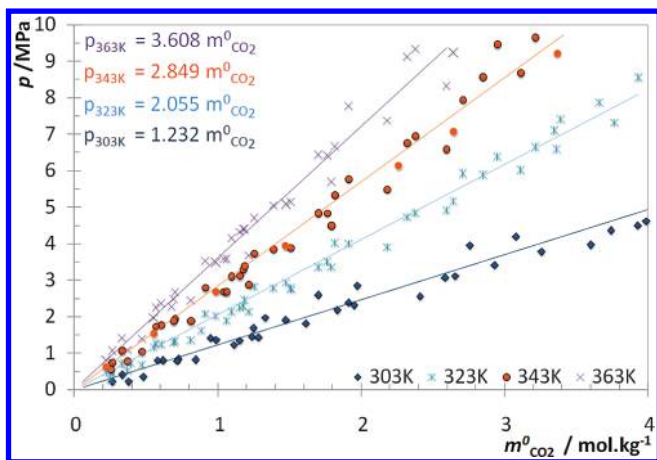


Figure 3. Pressure–molality diagram of CO<sub>2</sub> + nonvolatile solvents.<sup>12,13,16,23,31,81</sup>

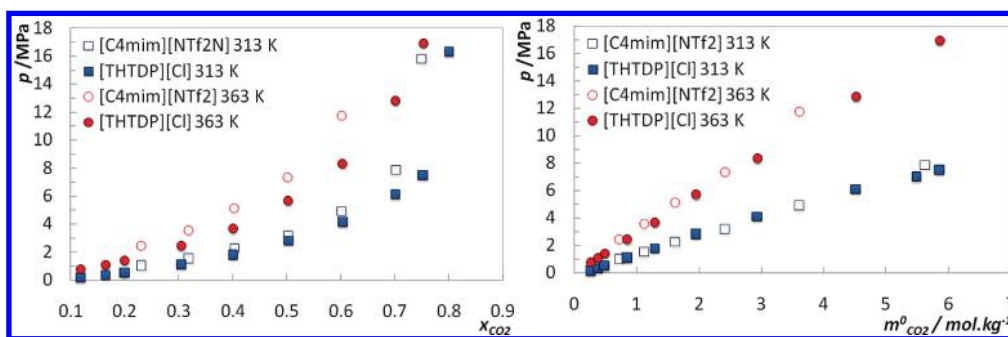


Figure 4. Pressure–mole fraction (left) and pressure–molality (right) diagrams of [THTDP][Cl] and [C<sub>4</sub>mim][NTf<sub>2</sub>] + CO<sub>2</sub> at 313 and 363 K.<sup>15</sup>

entropic factors alone as described by the Flory–Huggins equation. Negative deviations are observed for carbonyl containing systems such as fatty acid esters and, in spite of CO<sub>2</sub>–OH being the most stable EDA complex formed on the systems studied, the solubility of CO<sub>2</sub> in alcohols actually presents a positive deviation to ideality. The nonideality of these solutions, and its impact on the CO<sub>2</sub> solubility, is thus the result of a complex and delicate balance between the solute–solute, solute–solvent, and solvent–solvent interactions and cannot be inferred from the strength of solute–solvent interactions alone. This study suggests that the use of large molecular weight solvents and the introduction of sp<sup>2</sup> O-donating atoms (such as in ether and carbonyl groups) in the IL alkyl chain may have a favorable impact on the CO<sub>2</sub> solubility on these compounds.

When the molecular weight effect is removed from the analysis by comparing the solubilities in molalities instead of molar fractions, the differences in solubilities, among the various systems studied, are minimized, and the solubility of CO<sub>2</sub> on nonvolatile solvents seems to be essentially solvent independent within the uncertainty of the experimental data available. On the basis of these results, it was possible to develop a general correlation for the solubility of CO<sub>2</sub> in nonvolatile solvents.

**SUPPORTING INFORMATION AVAILABLE** Deviations from Raoult's law for the experimental data for alcohols, alkanes, fatty acids, fatty esters, PEGs, and ILs on which Figure 1 is based. Text describing the experimental measurements, list of compounds depicted in Figures 2 and 3, and graphical representation of eq 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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