

Experimental Determination of Viscosities and Densities of Mixtures Carbon Dioxide + 1-Allyl-3-methylimidazolium chloride. Viscosity correlation

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Abstract

The effect of viscosity reduction caused by the solubilization of CO₂ is studied in order to improve the biomass processing in ionic liquids. To do so, densities and viscosities of the pure ionic liquid 1-allyl-3-methylimidazolium chloride and its mixtures with CO₂ up to molar fractions of 0.25 and temperatures between 333 and 372 K have been experimentally determined. Viscosities were correlated as a function of temperature and CO₂ molar fractions with an average relative error of 2.5%. The viscosities of other mixtures CO₂ + ionic liquids were also correlated for other ionic liquids with an average relative error between 4.4 and 13%. In general these ionic liquids present a linear decrease of viscosity with CO₂ molar fractions up to around 0.5 that is more pronounced at lower temperatures and depends of each ionic liquid, and can reach between 60-100% viscosi-

ty reduction with respect the viscosity of the pure ionic liquid, making the CO₂ a promising co-solvent for viscosity reduction in process with ionic liquids.

Keywords: Ionic liquid; Carbon Dioxide; Viscosity; Density; Excess molar volume; 1-allyl-3-methylimidazolium chloride;

1. Introduction

There is an increasing interest in the use of ionic liquids (ILs) for processing cellulose and other biopolymers [1]. However, the high viscosity of ILs, which is greatly increased when they dissolve cellulose, is the main limitation for their use in these processes [2]. Imidazolium chlorides, acetates and alkylphosphates can dissolve high amounts of cellulose and other biopolymers, but recently acetates and alkylphosphates has been preferred due to their lower viscosities and melting points [1], while the imidazolium chlorides present higher viscosities. For these reasons, these ILs are sometimes set aside in cellulose processing, even though they are cheaper and more effective than others in cellulose reactions such as hydrolysis [3].

It is known that mixing an IL with molecular solvents allows decreasing its viscosity [4]. This is also possible when using carbon dioxide (CO₂) as a co-solvent, which has the advantages of being non-toxic, cheap, and can be easily separated of the IL by depressurization. ILs and CO₂ are considered to be a promising media for the development of “green” technology [5]. In biphasic mixtures IL-CO₂ at moderate or high pressure, CO₂ can dissolve significantly into the IL-rich liquid phase, up to concentrations as high as 75% in mol, but no ionic liquid dissolves in the gas phase [5],[6]. Nevertheless in the case of imidazolium chloride ionic liquids CO₂ solubility is reduced to values round 30-40% in mol [7].

So far, only a few viscosity data of mixtures carbon dioxide + IL can be found in literature: Tomida and coworkers determined the viscosities of CO₂ + 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) [8]; CO₂ + 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) [9]; CO₂ + 1-hexyl-3-methylimidazolium hexafluorophosphate (hmimPF₆) and CO₂ + 1-octyl-3-methylimidazolium hexafluorophosphate (omimPF₆) + CO₂ [10]; Liu et al determined the viscosities of CO₂ + 1-butyl-3-methylimidazolium tetrafluoroborate (bmimPF₆) [11] and Ahosseini et [12] al measured the viscosity of mixtures of several ionic liquids of the n-alkyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide family [-mimTf₂N] with CO₂. In general, the decrease in viscosity is between 85 and 45 % for BF₄ ILs with CO₂ solubilities between 45 and 35% CO₂ in mol [8]. For PF₆ ILs with 40-45% in mol CO₂ the decrease lies between 80 and 45% of the density of the pure IL [9],[10]. For the Tf₂N ILs which present solubilities of CO₂ sometimes as high as 90% the decrease in viscosity can reach 100% [12] at moderate pressures of 10-12 MPa, but with molar fractions as low as 10% of CO₂ decrease of 30-40% of the pure IL viscosity is already observed. In all cases the effect in viscosity reduction with CO₂ is more remarkable at lower temperatures.

There are much more data of densities of mixtures CO₂ + ILs, including the systems: CO₂ + methylimidazolium hexafluorophosphates ionic liquids [9], [10]; CO₂ + 1-ethyl-3-methylimidazolium ethylsulphate [13]; CO₂ + imidazolium bis[(trifluoromethyl)sulfonyl]imide and triflate ILs [14] ; CO₂ + 1-ethyl-3-methylimidazolium diethyl phosphate, CO₂ + 1-ethyl-3-methylimidazolium hydrogen sulfate [15], to mention only a few of them. In general densities present little change with increasing CO₂ concentration in the ionic liquid, meaning that these systems present considerable lower volume expansions than those of common organic solvents [

13], [14], [16]. This has been interpreted as a consequence of the CO₂ is dissolving in the ionic liquid by occupying the bulk free space in the molecule, as confirmed by atomistic simulation [17], [18] and through Raman spectroscopy [19]. As a consequence, large negative molecular volumes are found, due to the lack of expansion of the ionic liquids and the big difference in molecular mass between the ILs and the CO₂[13].

In this work the viscosities and densities of pure 1-Allyl-3-methylimidazolium chloride (AmimCl) and several CO₂ + AmimCl mixtures were experimentally determined at temperatures between 333 and 372 K and pressures between 1 and 7 MPa, comprising CO₂ concentrations between 5 and 25% in mol. Using density data, excess molar volumes were calculated. Viscosity data were correlated and, in order to test the correlation, viscosity data of other CO₂ + ILs mixtures from literature were correlated showing average deviations from 2 to 13%.

2.Experimental Section

2.1 Materials

The ionic liquid used in this work was 1-allyl-3-methylimidazolium chloride, [Amim][Cl], purchased from Iolitec (Germany), with a purity higher than 98%. The water contents were determined by Karl-Fischer volumetric titration (Metrohm 870 KF Titrino Plus) obtaining 0.59% ww in water. Carbon dioxide (99.9% purity) was supplied by Yara and was used without further purification.

2.2 Apparatus

To determine the densities and viscosities a tuning fork vibration viscosimeter was used (Solartron Viscosimeter 7827). In the ranges of viscosities determined the precision was

± 1 mPa·s in the range 1-100 mPa·s and of ± 10 mPa·s in the range 100-1000 mPa·s. Density was determined with a precision of ± 1 kg·m⁻³. The viscosimeter worked inside of a 1.7 L pressure vessel able to stand 200°C and 20 MPa. Temperature in the gas phase was determined with a thermocouple type K and in the liquid phase (where the tuning fork was situated) with a Pt100. A signal converter Solartron 7946 able to work in the T range (-200-200°C) was used with a resolution of 0.1°C and a maximum error of ± 0.3 °C. Temperature was kept constant by using a circulating bath Lauda Proline P5. Pressure was determined with WIKA type S-11 pressure transmitter with an accuracy of 1 bar (0.25% of the span (0-400 bar)).

2.3 Experimental procedure

The ionic liquid was charged in the pressure vessel and kept at 90°C at vacuum in order to reduce the water content for 8 h. In these conditions the density and viscosities of the pure ionic liquids were determined. After that CO₂ was charged in the pressure vessel and the system was equilibrated before determining the viscosity and density. Then the temperature and pressure were changed in order to determine new experimental points. After finishing all the measurements the water content was determined by Karl Fischer titration.

3. Results and Discussion

3.1 Density and viscosity of the pure ionic liquid

Densities and viscosities of the pure ionic liquid as a function of temperature are listed in Table 1. In Figure 1 data were plotted together with literature data [20], [21], [22]. It is observed that both, density and viscosity decrease with increasing temperature and that the data determined in this work were consistent with literature data .

Table 1. Densities and viscosities of 1-allyl-3methylimidazolium chloride determined under vacuum.

T/K	Viscosity/mPa·s	Density/kgm ⁻³
307.0	790	1141
311.7	530	1138
319.9	280	1133
330.0	150	1127
337.1	100	1123
347.3	61	1118
361.1	35	1110
373.2	24	

Viscosity precision ± 1 mPa·s in the range 1-100 mPa·s and ± 10 mPa·s in the range 100-1000 mPa·s. Density was determined with a precision of ± 1 kg·m⁻³. Temperature maximum error of $\pm 0.3^\circ\text{C}$. Water molar fraction of AmimCl ($x_{\text{H}_2\text{O}}=0.497$)

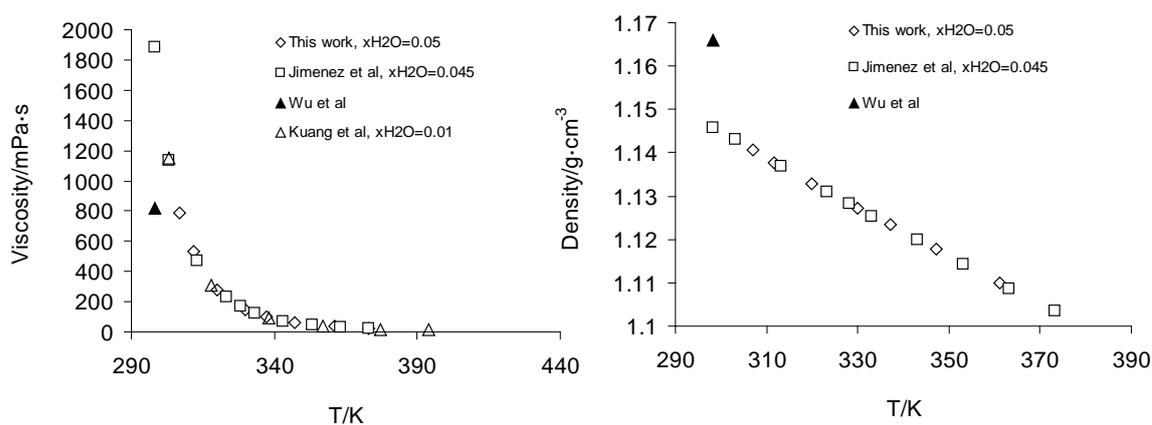


Figure 1. Comparison of viscosity and density measurement of pure 1-allyl-3-methylimidazolium chloride measured in this work and literature data [20], [21], [22]

3.2 Density and viscosity of the mixtures CO₂ + AmimCl

Experimental densities and viscosities and calculated molar values of the of the mixtures CO₂ + AmimCl were listed in Table 2. The CO₂ molar fractions were calculated with Group Contribution Equation of State developed by Skold-Jorgensen (GC-EoS) using the parameters fitted in a previous work for mixtures of CO₂ + AmimCl [23]. Densities of CO₂ at the given temperature and pressure were calculated from NIST data. [24].

Table 2. Densities and viscosities of saturated mixtures CO₂ + 1-allyl-3methylimidazolium chloride at different pressures and temperatures

T/K	P/MPa	x _{CO2}	Viscosity/mPa·s	Density/kg·m ⁻³	V ^{Ex} /cm ³ mol ⁻¹
334.7	1.0	0.054	100	1125	-143
356.6	1.0	0.039	39	1113	-111
371.5	1.0	0.032	24	1104	-95.8
368.9	4.0	0.113	24	1106	-74.0
345.3	4.0	0.148	53	1119	-87.9
368.7	5.8	0.152	22	1106	-61.8
337.3	5.0	0.194	72	1124	-80.8
349.3	4.3	0.150	44	1106	-80.7
333.6	7.2	0.251	68	1126	-58.7

Viscosity precision ± 1 mPa·s in the range 1-100 mPa·s and ± 10 mPa·s in the range 100-1000 mPa·s. Density was determined with a precision of ± 1 kg·m⁻³. Temperature maximum error of $\pm 0.3^\circ\text{C}$. Water molar fraction of AmimCl ($x_{\text{H}_2\text{O}}=0.497$). Pressure was determined with an accuracy of ± 0.1 MPa. CO₂ molar fractions calculated using GC-EoS.

It is observed that excess molar volumes present highly negative values, two orders of magnitude more negative than in the case of water + AmimCl mixtures [20]. This negative molar volumes are consistent with observed by other authors [13] in different ionic liquids indicate that the CO₂ + AmimCl mixtures present a highly packed structure, as the mixture has a molar volume much lower than this expected for an ideal mixture. This can confirm the theory that CO₂ is dissolved in the free spaces of ionic liquids and that the expansion of the ionic liquid induced by the presence of CO₂ is very small [13],[17], [18],[19]

3.3 Correlation of viscosity data

Viscosity data were correlated with an equation derived from the one used by Seddon et al [5], and that was used by Jimenez et al for correlating viscosity data of aqueous mixtures with several imidazolium chloride mixtures [20]. Even when the initial water content of the IL was low, it can strongly affect viscosity, thus, this concentration was taken into account when making the parameterization, introducing a correction of the molar concentration of both CO₂ and water, as shown in eq. 1.

$$\mu / mPa \cdot s = \exp\left(\frac{E}{(T / K)^2} + \frac{A}{T / K} + B\right) \cdot \exp\left(\frac{x_{H_2O}}{C + D \cdot T / K}\right) \cdot \exp\left(\frac{x_{CO_2}}{F + G \cdot T / K}\right) \quad (1)$$

Where μ is the viscosity in mPa·s, T is temperature in K, x_{H_2O} and x_{CO_2} are water and CO₂ molar fraction are expressed with relation to the ionic liquid, respectively in CO₂ and water free basis. A, B, C, D, E, F, G are empirically obtained parameters. The parameters used for the pure IL (A, B and E) and for the influence of water concentration (C and D) are the same used by Jimenez et al [20], and the parameters E and F adjusted to correct viscosity with CO₂ concentration were adjusted in this work. Parameterization

was performed by minimizing the average relative deviation (ARD %) defined as shown in eq. 2.

$$ARD\% = \Sigma \left(\frac{|\mu_{\text{exp}} - \mu_{\text{calc}}|}{\mu_{\text{exp}}} \right) \quad (2)$$

Adjusted parameters are shown in Table 3. The ARD% of the equation is of 2.5% while the maximum deviation with respect to experimental data is 5.7%

Table 3. Parameters fitted to the correlations for calculating the viscosities mixtures CO₂ + H₂O+ 1-allyl-3-methylimidazolium chloride at different . Deviations referred to viscosity.

$$\mu / mPa \cdot s = \exp\left(\frac{E}{(T/K)^2} + \frac{A}{T/K} + B\right) \cdot \exp\left(\frac{x_{H_2O}}{C + D \cdot T/K}\right) \cdot \exp\left(\frac{x_{CO_2}}{F + G \cdot T/K}\right)$$

A	-15113	Jimenez et al [20]
B	17.64	Jimenez et al [20]
C	0.784	Jimenez et al [20]
D	-3.10 · 10 ⁻³	Jimenez et al [20]
E	3636000	Jimenez et al [20]
F	3.731 ± 0.015	This work
G	-1.255 · 10 ⁻²	This work
ARD%	2.5%	
Max. Dev.	5.7%	

The predicted viscosities of several CO₂+AmimCl mixture with low water concentration and water free predicted by the correlation are plotted in Figure 2 as a function of pressure and of CO₂ molar fraction. Please note that the molar fractions in the ionic liquid corresponding to a given P,T data were calculated with the GC-EoS [23]. It is observed that CO₂ can reduce the viscosity of the AmimCl up to 43% at 60°C and 7.5 MPa and molar fractions of 0.25 of CO₂ with respect to the ionic liquid. At higher temperatures the effect of CO₂ in viscosity is lower i.e. at 95°C, the pressure necessary to have a molar fraction of 0.25 in the ionic liquid is of 13 MPa, and the viscosity is reduced only a 25% with respect the viscosity of the pure ionic liquid.

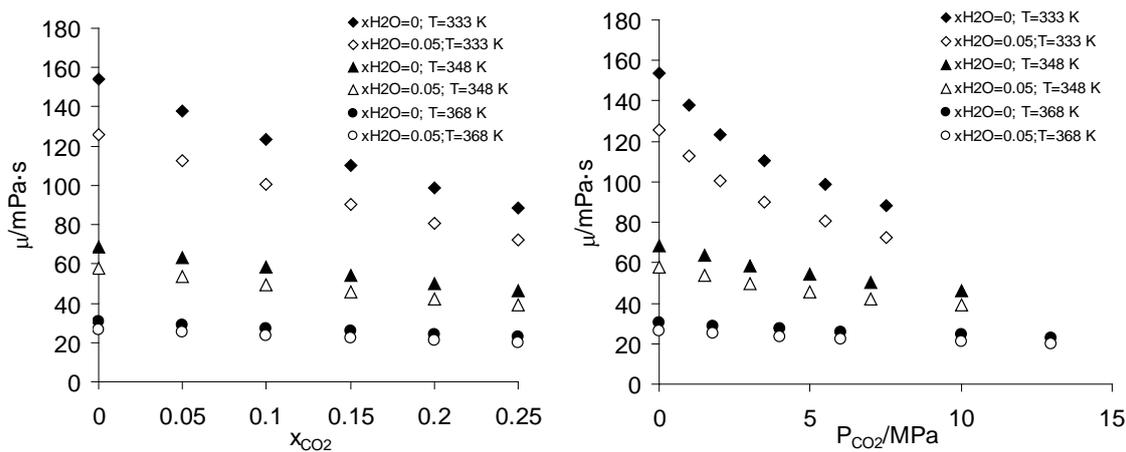


Figure 2. Viscosity predicted by the correlation as a function of CO₂ molar fraction and CO₂ pressure for different temperatures and initial water concentrations of the ionic liquid AmimCl

To test the validity of this correlation with other CO₂ + IL mixtures, literature viscosity data were correlated for several CO₂ + ionic liquids mixtures using literature data: 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF₄) [8]; : 1-butyl-3-methylimidazolium hexafluorophosphate (bmimPF₆) [9]; 1-hexyl-3-methylimidazolium

hexafluorophosphate (hmimPF₆) [10],[25], [26] ; 1-octyl-3-metylimidazolium hexafluorophosphate (omimPF₆) [10],[26],[27]; 1-ethyl-3-metylimidazolium trifluoromethylsulfonylimide (emimTf₂N) [12], [28]; 1-hexyl-3-metylimidazolium trifluoromethylsulfonylimide (hmimTf₂N) [12], [29] and 1-decyl-3-metylimidazolium trifluoromethylsulfonylimide (dmimTf₂N) [12], [30]. Parameters adjusted, ARDs and maximum deviations from experimental data are presented in Table 4. Viscosities can be predicted with average deviations from 4 to 13% and maximum deviations from 15 to 46%.

Table 4. Parameters fitted to the correlations for calculating the viscosities mixtures CO₂ + IL for the ILs: bmimBF₄ [8]; bmimPF₆ [9]; hmimPF₆ [10],[25], [26] ; omimPF₆ [10],[26],[27]; emimTf₂N [12], [28]; hmimTf₂N [12], [29] and dmimTf₂N[12], [30]

$$\mu / mPa \cdot s = \exp\left(\frac{E}{(T/K)^2} + \frac{A}{T/K} + B\right) \cdot \exp\left(\frac{x_{CO_2}}{F + G \cdot T/K}\right)$$

Parameters	bmimBF ₄	bmimPF ₆	hmimPF ₆	omimPF ₆	emimTf ₂ N	hmimTf ₂ N	dmimTf ₂ N
A	-4260	-4690	-6950	-6320	-3980	-2300	-4700
B	4.03	4.59	7.62	6.39	4.68	1.44	4.90
E	1330950	1508250	1945200	1902000	1079740	936800	1390300
F	1.17	0.698	0.7337	0.621	1.632	0.968	1.006
G	-4.74 · 10 ⁻³	-3.02 · 10 ⁻³	-3.20 · 10 ⁻³	-3.02 · 10 ⁻³	-6.65 · 10 ⁻³	-4.30 · 10 ⁻³	-4.26 · 10 ⁻³
ARD %	4.6%	4.5%	4.4%	8.3%	6.4%	13%	6.2%
Max Dev	16%	15%	26%	29%	27%	46%	35%
			[10],[25],				
Literature	[8]	[9]	[26]	[10],[26],[27]	[12], [28]	[12], [29]	[12], [30]

In figure 3 predicted viscosity of mixtures CO₂ + IL are compared to experimental data is shown. A good reproducibility of the experimental data is observed.

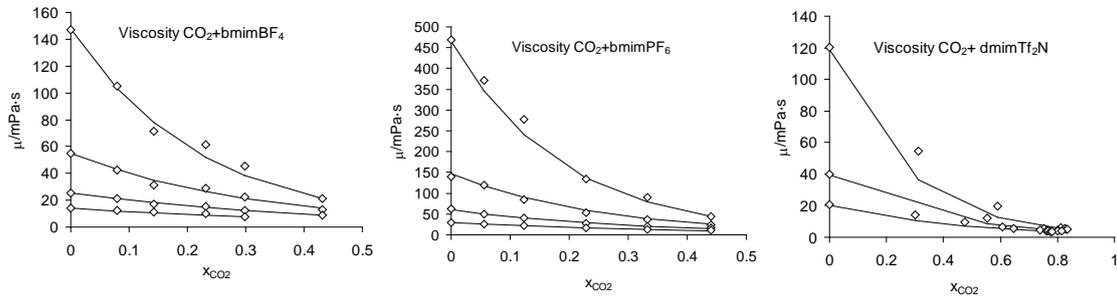


Figure 3. Comparison of the viscosity predicted by the model and the experimental data for the mixtures CO₂ +IL: bmimBF₄ [8]; : bmimPF₆ [9]; and dmimTf₂N[12], [30]. Symbols represent the experimental data and lines represent the predictions of the model.

In figure 4 the percentage of viscosity reduction vs molar fraction of CO₂ with respect to the viscosity of the pure IL at the same temperature is plotted for some ionic liquids of the different families considered in this work, at 333 and at 293 K. It is observed that viscosity reduced linearly with CO₂ molar fraction until reached a certain concentration of CO₂ beyond which the reduction of CO₂ is lower. The viscosity reduction can reach between 60-90% depending on the ionic liquid and it is more pronounced at lower temperatures.

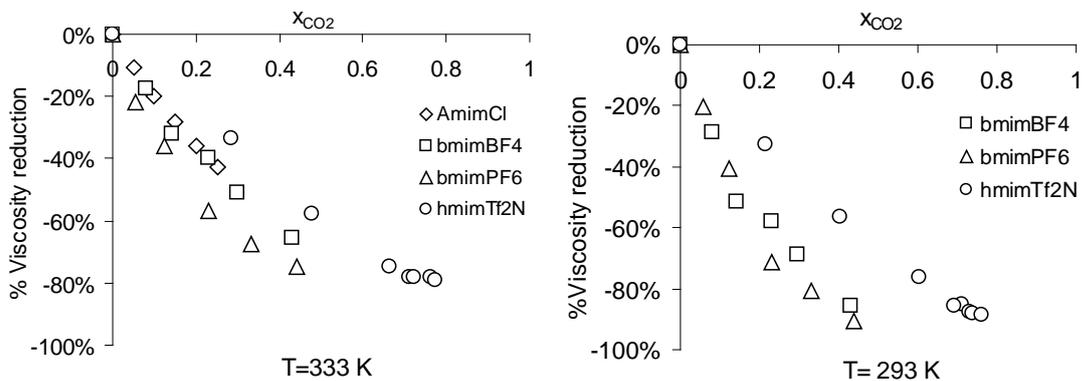


Figure 4. Percentage of viscosity reduction with CO₂ molar fraction for the ionic liquids bmimBF₄ [9], bmimPF₆ [10], hmimTf₂N [12] and AmimCl at 333 and 293 K.

4. Conclusions

The viscosities and densities of the pure ionic liquids 1-allyl-3-methylimidazolium chloride (AmimCl) have been experimentally determined as well as for mixtures CO₂ + AmimCl with molar fractions up to 0.25 and temperatures in the range 333-372 K.

Densities were used to calculate excess molar values, that resulted strongly negative with values -60 and -140 cm³/mol, being less negative at higher temperatures and CO₂ molar fractions. This indicates that the CO₂ + AmimCl mixtures present a highly packed structure and can confirm the generally accepted theory that CO₂ is dissolved in the free spaces of ionic liquids and that the expansion of the ionic liquid induced by the presence of CO₂ is very small.

Viscosities were correlated as a function of temperature and carbon dioxide molar fractions with an average relative error of 2.5%. The viscosities of other mixtures CO₂ + ionic liquids were also correlated for ionic liquids of the families imidazolium tetrafluoroborate, imidazolium hexafluorophosphate and imidazolium trifluoromethylsulfonylimide with an average error between 4.4 and 13%.

In general AmimCl and the other ionic liquids present a linear decrease of viscosity with CO₂ molar fractions up to around 0.5 mol that more pronounced at lower temperatures and depends of each ionic liquid, and can reach between 60-100% viscosity reduction with respect the viscosity of the pure ionic liquid, making the CO₂ a promising co-solvent for viscosity reduction in process with ionic liquids.

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