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## **Low pressure carbon dioxide solubility in lithium-ion batteries based electrolytes as a function of temperature. Measurement and prediction**

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## Accepted Manuscript

Low pressure carbon dioxide solubility in lithium-ion batteries based electrolytes as a function of temperature. Measurement and prediction

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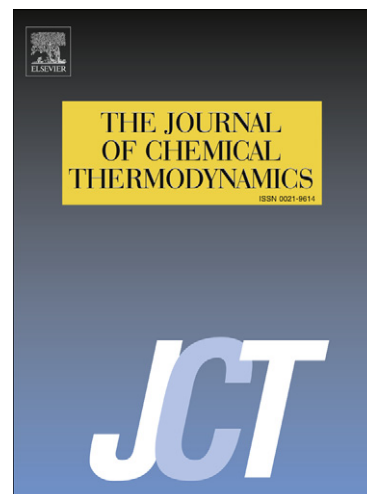
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1                   **Low pressure carbon dioxide solubility in lithium-ion**  
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6                   **Measurement and prediction**

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## Abstract

We present in this study the effect of nature and concentration of lithium salt, such as the lithium hexafluorophosphate,  $\text{LiPF}_6$ ; lithium tris(pentafluoroethane)-trifluorophosphate LiFAP; lithium bis(trifluoromethylsulfonyl)imide, LiTFSI, on the  $\text{CO}_2$  solubility in four electrolytes for lithium ion batteries based on pure solvent that include ethylene carbonate (EC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), as well as, in the EC:DMC, EC:EMC and EC:DEC (50:50) wt % binary mixtures as a function of temperature from (283 to 353) K and atmospheric pressure. Based on experimental solubility values, the Henry's law constant of the carbon dioxide in these solutions with the presence or absence of lithium salt was then deduced and compared with reported values from the literature, as well as with those predicted by using COSMO-RS methodology within COSMOthermX software. From this study, it appears that the addition of  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiPF}_6$  salt in alkylcarbonate solvents decreases their  $\text{CO}_2$  capture capacity. By using the same experimental conditions, an opposite  $\text{CO}_2$  solubility trend was generally observed in the case of the addition of LiFAP or LiTFSI salts in these solutions. Additionally, in all solutions investigated during this work, the  $\text{CO}_2$  solubility is greater in electrolytes containing the LiFAP salt, followed by those based on the LiTFSI case. The precision and accuracy of the experimental data reported therein, which are close to (1 and 15) %, respectively. From the variation of the Henry's law constant with temperature, the partial molar thermodynamic functions of dissolution such as the standard Gibbs energy, the enthalpy, and the entropy, as well as the mixing enthalpy of the solvent with  $\text{CO}_2$  in its hypothetical liquid state were calculated. Finally, a quantitative analysis of the  $\text{CO}_2$  solubility evolution was carried out in the EC:DMC (50:50) wt % binary mixture as the function of the  $\text{LiPF}_6$  or LiTFSI concentration in solution to elucidate how ionic species modify the  $\text{CO}_2$  solubility in alkylcarbonates-based Li-ion electrolytes by investigating the salting effects at  $T = 298.15$  K and atmospheric pressure.

## Keywords

Solubility,  $\text{CO}_2$ ,  $\text{LiPF}_6$ , LiTFSI, LiFAP, alkylcarbonate, lithium-ion batteries

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ACCEPTED MANUSCRIPT

## 1. Introduction

Most liquid electrolytes used in commercial lithium-ion batteries are obtained by dissolving a lithium salt in a specific alkylcarbonate mixture. Currently, the most suitable electrolytes for lithium ion battery remain the mixture of the lithium hexafluorophosphate,  $\text{LiPF}_6$  with cyclic carbonates like ethylene carbonate (EC) or propylene carbonate (PC) and linear carbonates such as dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) [1]. However, it is well described into the literature that  $\text{LiPF}_6$  is thermally unstable and decomposes in  $\text{LiF}$  and  $\text{PF}_5$ , as well as, that  $\text{LiPF}_6$  and  $\text{PF}_5$  can react with residual water to form  $\text{HF}$  [2-4]. Despite these technological issues,  $\text{LiPF}_6$  is still used as the reference salt in Li-ion batteries for more than a decade because of its unique properties in Li-ion devices providing good ionic conductivity of the electrolyte, as well as, based-on its ability to passivate an aluminium current collector, and to participate to the passivation layer on the negative electrode [5-7]. Furthermore, the selection of another safer lithium salt to be dissolved in alkylcarbonates is of great importance, but this change influences the physical, thermal and transport properties of the electrolyte [8,9]. According to the structure similarity between the hexafluorophosphate and tris(pentafluoroethane)trifluorophosphate anions, the lithium tris(pentafluoroethane)trifluorophosphate  $\text{LiFAP}$ , is currently investigated by several groups to limit potentially these property changes [6]. Lithium imide salts are also potentially a good alternative to  $\text{LiPF}_6$  since these salts could both improve the chemical and thermal stability of the electrolyte. Particularly, the lithium bis(trifluoromethylsulfonyl)imide,  $\text{LiTFSI}$  salt, which is well known to be more stable and safer than  $\text{LiPF}_6$  [10], even if it were clearly pointed-out in the literature that  $\text{LiTFSI}$  salt is more corrosive than  $\text{LiPF}_6$  towards the aluminium collector [11-14]. Additionally, the performance of a lithium ion battery depends also to a great extent on the stability of electrolyte solution, because the high voltage of the battery may cause the decomposition of lithium salt or organic solvents [15-17]. This decomposition of the electrolyte limits the battery lifetime [18,19]. For example, it is reported in the literature that the oxidation reaction of the Li-ion electrolyte at high potentials leads to the formation of  $\text{CO}_2$  when high potentials are applied to the electrode, which increases the pressure inside the sealed cell [19-21]. Furthermore, the carbon dioxide formation also

1 changes the composition of the electrolyte driven by the solubility of the carbon dioxide  
2 in this solution. These effects caused by the formation of the carbon dioxide can be  
3 evaluated with the prior knowledge of the CO<sub>2</sub> solubility in electrolyte solutions.  
4 Furthermore, the salt selection and effects on the CO<sub>2</sub> solubility in electrolytes can be  
5 analysed in detail by comparing the CO<sub>2</sub> solubility in solutions with or without a lithium  
6 salt. Many authors have reported in the literature the CO<sub>2</sub> solubility in classical  
7 alkylcarbonate solvents [22-38], but generally, these studies are basically focused on  
8 pure alkylcarbonate solvents and on their mixtures without the presence of lithium salt.  
9 However, the CO<sub>2</sub> solubility in classical Li-ion electrolytes depends not only on the  
10 pressure and temperature, but also on the salt structure and its concentration in solution.  
11 The salting effect in solvents containing a specific salt needs to be investigated,  
12 nevertheless, to date very few CO<sub>2</sub> solubility data in alkylcarbonate are available in the  
13 literature, especially for solutions containing lithium salts.

14 Herein, we report first, the solubility of carbon dioxide in eight lithium ion batteries  
15 based electrolytes containing 1 mol·dm<sup>-3</sup> lithium salt, LiPF<sub>6</sub> or LiTFSI, dissolved in a  
16 pure alkylcarbonate solvent, EC, DMC, EMC, DEC, as a function of temperature from  
17 (283 to 353) K and atmospheric pressure. The comparison of these experimental results  
18 along with those reported previously by our group in the case of the CO<sub>2</sub> solubility in  
19 pure carbonate solvents [22,23] permits the quantification of the effect of the presence  
20 of lithium salt on the carbon dioxide absorption by the pure carbonate solvent.  
21 Secondly, by using the same methodology, we report in this paper the effect of the  
22 presence or the absence of 1 mol·dm<sup>-3</sup> lithium salt (LiPF<sub>6</sub>, LiTFSI or LiFAP) on the CO<sub>2</sub>  
23 solubility in three different (50:50) wt % binary mixtures of alkylcarbonate solvents  
24 such as EC:DMC, EC:EMC and EC:DEC as a function of temperature. From these  
25 results, Henry's law constants and dissolution properties to include the Gibbs energy,  
26 the standard enthalpy and entropy of dissolution, as well as the mixing enthalpy of the  
27 solvent with CO<sub>2</sub> in its hypothetical liquid state were then deduced. Thirdly, we present  
28 a quantitative analysis of the CO<sub>2</sub> solubility evolution with the salting effects in the  
29 EC:DMC (50:50) wt % binary mixture as the function of the LiPF<sub>6</sub> or LiTFSI  
30 concentration in solution. Finally, the CO<sub>2</sub> solubility in these electrolytes has been then  
31 calculated by the COSMO-RS methodology by using directly the COSMOthermX  
32 chemical engineering software. These calculated values are then compared with  
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1 experimental values to evaluate the predictive capability of the CO<sub>2</sub> solubility in  
2 electrolytes for Li-ion batteries applications.  
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## 4 5 6 **2. Experimental**

### 7 8 9 *2.1 Materials and mixtures preparations*

10 Highly pure (GC grade, mass fraction purity > 0.9999) ethylene carbonate (EC),  
11 dimethylcarbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC)  
12 were obtained from Aldrich and were used as received. The highly pure (mass fraction  
13 0.9999 lithium salts such as: lithium hexafluorophosphate (LiPF<sub>6</sub>) and lithium  
14 bis(trifluoromethylsulfonyl)imide (LiTFSI) purchased from Sigma Aldrich and from  
15 Solvionic, respectively, were kept and used under a dry atmosphere in a glove box. All  
16 electrolytes containing the LiFAP salt were purchased from Merck with mass fraction  
17 purity greater than 0.9999. All LiFAP electrolytes were kept and used under a dry  
18 atmosphere in a glove box and then were used as received from the manufacturer.  
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30 Studied solvents mixtures were prepared by mass with an accuracy of  $\pm 1 \times 10^{-4}$  g using a  
31 Sartorius 1602 MP balance under a dry atmosphere in a glove box, and kept inside the  
32 glove box before further analyses. Alkylcarbonate mixtures studied into this work have  
33 been prepared by mass at 25 °C and are denoted in mass fraction as follow: EC:DMC  
34 (50:50) wt %, EC:EMC (50:50) wt %, and EC:DEC (50:50) wt %. Based on these  
35 mixtures, electrolytes based on lithium salts, LiX (with X = PF<sub>6</sub><sup>-</sup>, or TFSI), were then  
36 prepared by dissolving a salt into the solvent and the concentrations of lithium salts in  
37 solutions are reported in mol·dm<sup>-3</sup>.  
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46 As the experimental setup used to determine the amount of CO<sub>2</sub> dissolved in solutions is  
47 based on a chemical titration methodology, NaOH (0.5 mol·dm<sup>-3</sup>) and HCl (1 mol·dm<sup>-3</sup>)  
48 solutions, were used as received from Sigma Aldrich (Riedel-de Haen). Prior to any  
49 measurement, HCl (0.2 mol·dm<sup>-3</sup>) solutions, which were prepared using double distilled  
50 water and the HCl (1 mol·dm<sup>-3</sup>) commercial solution, were standardized from the NaOH  
51 commercial solution using potentiometric titration. Additionally, prior to any solubility  
52 measurement, solvents and electrolytes were analyzed for water content using  
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1 coulometric Karl-Fischer (Coulometer 831 - Metrohm) titration. The water content of  
2 selected solvents and electrolytes, measured before and after their preparations, is close  
3 to  $(10 \pm 1) 10^{-6}$ .  
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8 The gases used (AGA/Linde Gaz) have the following specifications: carbon dioxide,  
9 mole fraction purity of 0.99995; and argon, mole fraction purity of 0.999997. All gases  
10 were used as received from the manufacturer. Information (*i.e.* source, abbreviation,  
11 purity, and water content) for each chemical sample studied in this paper are  
12 summarized in table 1.  
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## 17 18 19 2.2 Experimental Methods

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21 The density of pure liquids, binary liquid mixtures and investigated electrolytes were  
22 measured by using a pycnometer ( $5 \text{ cm}^3$ ) immersed in a water bath at  $T = 298.15 \text{ K}$ .  
23 The temperature control is ensured within  $\pm 0.01 \text{ K}$  by means of a JULABO  
24 thermostated bath. The pycnometer was firstly calibrated at  $T = 298.15 \text{ K}$  with degassed  
25 water at atmospheric pressure using reference data from Wagner and Pruss [39]. More  
26 than three measurements were performed for each density measurement reported  
27 therein. The accuracy of the reported density values is better than  $\pm 5 \times 10^{-2} \text{ g}\cdot\text{cm}^{-3}$ .  
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31 The experimental apparatus used during the  $\text{CO}_2$  solubility measurements reported in  
32 this present work is based on a chemical titration technique, which was already  
33 described by our group elsewhere [22,23], and schematically represented herein in  
34 figure 1. Under a dry atmosphere in a glove box, a known quantity of electrolyte,  
35 determined gravimetrically with an accuracy of  $\pm 1 \times 10^{-4} \text{ g}$  using a Sartorius 1602 MP  
36 balance, was first placed into equilibrium cell (EqC) equipped with a septum to avoid  
37 air and moisture contaminations during measurements. The EqC was then immersed in  
38 a water bath maintained at constant temperature,  $T_{\text{exp}}$ , using a PID temperature  
39 controller and accurately measured with a calibrated  $100 \Omega$  platinum resistance  
40 thermometer within accuracy better than  $\pm 0.1 \text{ K}$ . The electrolyte was then saturated  
41 with  $\text{CO}_2$  at atmospheric pressure by dissolving the gas in the liquid phase at constant  
42 temperature during 1 hour to reach the equilibrium. Furthermore, different equilibrium  
43 times were also examined to ensure that the saturation had been reached in each case.  
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dissolved CO<sub>2</sub> in the solvent from the equilibrium cell to the titration cell, which contains a known concentration of NaOH aqueous solution. To ensure that a solvent-free (Ar + CO<sub>2</sub>) gas mixture was introduced in the NaOH titration cell, the gas mixture was first passed through an ethanol bath at  $T = 193$  K, which retains the solvent from the gas stream. The displaced quantity of dissolved CO<sub>2</sub> then reacts with NaOH solution by forming sodium carbonate (*e.g.* Na<sub>2</sub>CO<sub>3</sub>). The aqueous solution containing the sodium carbonate as well as the non-reacted NaOH was finally titrated by a known concentration of HCl solution,  $C_{\text{HCl}}$  as described in figure S1 of the supporting information, where, the first and second peaks correspond to the titrations of non-reacted NaOH and sodium carbonate, respectively. The difference of volumes between these two peaks,  $\Delta V_{\text{HCl}}$ , calculated by using the derivative method of the pH with the respect to the HCl volume added, is directly link to the amount of dissolved CO<sub>2</sub> in the solution,  $n_2^{\text{liq}}$ :

$$n_2^{\text{liq}} = \Delta V_{\text{HCl}} \cdot C_{\text{HCl}} \quad (1)$$

### 2.3 Data analysis

The solubility of the CO<sub>2</sub> in studied solvent can be expressed in mole fraction of CO<sub>2</sub> in solution,  $x_2$ :

$$x_2 = \frac{n_2^{\text{liq}}}{n_{\text{solv}}^{\text{liq}} + n_2^{\text{liq}}} \quad (2)$$

where  $n_2^{\text{liq}}$  is the amount of CO<sub>2</sub> dissolved in the liquid solution and  $n_{\text{solv}}^{\text{liq}} = n_1^{\text{liq}} + n_3^{\text{liq}}$  is the amount of solvent in the liquid phase introduced in the equilibrium cell, with  $n_1^{\text{liq}}$  being the amount of alkylcarbonate solvents and  $n_3^{\text{liq}}$  the amount of lithium salt in the liquid solution.

Henry's law constants can be then calculated from the CO<sub>2</sub> mole fraction solubility as:

$$K_H = \lim_{x_2 \rightarrow 0} \frac{f_2(p, T, x_2)}{x_2} \approx \frac{\phi_2(p_{\text{exp.}}, T_{\text{exp.}}) p_{\text{exp.}}}{x_2} \quad (3)$$

where  $f_2$  is the fugacity of the  $\text{CO}_2$  and  $\phi_2$  its fugacity coefficient calculated from the compilation of Dymond and Smith [40] at atmospheric pressure,  $p_{\text{exp.}}$  and fixed temperature,  $T_{\text{exp.}}$ .

The determination of the solubility at different temperatures from (283 to 353) K is simply done by changing the water bath set point and by repeating the same saturation and titration procedures. Each measurement was run in triplicate to avoid any experimental error. To represent the  $\text{CO}_2$  solubility in selected solutions as a function of temperature, experimental data were then correlated in the whole temperature range by using the following empirical equation:

$$\ln\left(\frac{K_H(T)}{p^0}\right) = \sum_{i=0}^n A_i (T/\text{K})^{-i} \quad (4)$$

The coefficients  $A_i$  obtained in the fit are reported in the whole manuscript together with the relative absolute average deviation, *RAAD* obtained for each solute calculated as:

$$RAAD = \frac{1}{N} \left| \frac{Y_{\text{exptl.}} - Y_{\text{calcd.}}}{Y_{\text{calcd.}}} \right| = \frac{1}{N} |\delta| \quad (5)$$

where  $N$  is the total number of data points,  $Y_{\text{exptl.}}$  and  $Y_{\text{calcd.}}$  are the experimental and calculated data for the studied property, respectively.  $\delta$  is the relative deviation between experimental and calculated data.

By using the equation 4, it is then possible to calculate the dissolution properties of the standard Gibbs energy, enthalpy and entropy of the dissolution of the  $\text{CO}_2$  in the solutions studied [41]:

$$\Delta_{\text{dis}} G^0 = RT \ln\left(\frac{K_H}{p^0}\right) \quad (6)$$

$$\Delta_{\text{dis}}H^0 = -T^2 \partial/\partial T \left( \frac{\Delta_{\text{dis}}G^0}{T} \right) = -RT^2 \partial/\partial T \left[ \ln \left( \frac{K_H}{p} \right) \right] \quad (7)$$

$$\Delta_{\text{dis}}S^0 = \frac{(\Delta_{\text{dis}}H^0 - \Delta_{\text{dis}}G^0)}{T} \quad (8)$$

where  $p^0$  is the standard state pressure.

Furthermore, the CO<sub>2</sub> dissolution in solvents can be viewed as a two-step process involving an intermediate step, in which the CO<sub>2</sub> is considered in its hypothetical liquid state driven by its standard enthalpy of liquefaction,  $\Delta_{\text{liq}}H^0$ . [22,41] Based on which, the enthalpy of mixing of the CO<sub>2</sub> with solvent,  $\Delta_{\text{mix}}H^0$ , can be calculated as:

$$\Delta_{\text{dis}}H^0 = \Delta_{\text{liq}}H^0 + \Delta_{\text{mix}}H^0 \quad (9)$$

where  $\Delta_{\text{liq}}H^0 = -16.90 \text{ kJ}\cdot\text{mol}^{-1}$  at  $T = 298.15 \text{ K}$ . [41]

#### 2.4 COSMOThermX calculations

The COSMOThermX software is based on the well known COSMO-RS (Conductor-like Screening Model for Real Solvent) methodology, which combines statistical thermodynamics methodology with the electrostatic theory of locally interacting molecular surface descriptors [42]. During this work, the same methodology as already presented previously by our group [22,43] was used firstly to optimize each structure and then to calculate the CO<sub>2</sub> solubility in selected solvents and mixtures, as well as in solutions containing additive salts like LiPF<sub>6</sub>, LiFAP or LiTFSI. Except, in the case of the calculations of the CO<sub>2</sub> solubility in LiTFSI-based electrolytes as function of the lithium salt concentration - where different methodologies to define the sigma profile of the salt have been used, like ion pair, metafile or individual ions. All COSMOThermX calculations reported during this work were done by using the ion pair sigma profile generated for each lithium salt. The gas solubility calculations were realized by using the gas solubility option within the COSMOThermX program (version 2.1, release 01.06). In this method, the partial vapor pressure, and thus gas solubility, is estimated using the following equation:

$$p_{(i)} = p_o^{vap}{}_{(i)} x_{(i)} \gamma_{(i)} \quad (10)$$

where  $p_{(i)}$ ,  $p_o^{vap}{}_{(i)}$ ,  $x_{(i)}$ ,  $\gamma_{(i)}$  are the partial and pure vapour pressures, mole fraction and activity coefficient of a selected gaseous species  $i$  in a particular solvent.[22]

During this investigation, each reported liquid composition describes the liquid phase used in the COSMOThermX software. Based on which, simulations were performed for each gas/liquid system under exactly the same conditions of temperature and pressure that were used in generating each experimental gas solubility data point. Each predicted value was determined from the simulation results as the mol fraction of gas in the liquid phase.

### 3. Results and discussion

#### 3.1 Effect on the presence of Lithium salt on density and CO<sub>2</sub> gas solubility in pure carbonate solvents.

Prior to determining the carbon dioxide solubility in electrolyte, the density of each solution was determined at  $T = 298.15$  K. Effect of the presence of  $1 \text{ mol}\cdot\text{dm}^{-3}$  of LiPF<sub>6</sub> or LiTFSI on the density values of investigated pure solvents is reported in table 2. As expected, the density of each solution containing a linear carbonate, such as DMC, EMC or DEC, decreases by increasing its alkyl chain length. Furthermore, each EC solution is denser than those containing a linear carbonate. Such conclusions are in agreement with those already reported into the literature.[44] The presence of  $1 \text{ mol}\cdot\text{dm}^{-3}$  LiPF<sub>6</sub> or LiTFSI dissolved into a pure solvent affects strongly the density of the solution. In each case, LiPF<sub>6</sub> or LiTFSI electrolytes are denser than pure solvents. For examples, deviations up to (8.4 or 13.5) % on the density are observed by comparing the electrolyte density of (DEC +  $1 \text{ mol}\cdot\text{dm}^{-3}$  LiPF<sub>6</sub> or LiTFSI) with that observed for the pure DEC solvent at  $T = 298.15$  K. It appears also that each electrolyte containing the LiTFSI salt is denser than that based on the LiPF<sub>6</sub> salt. This conclusion is in agreement with that expected by comparing the effective molar volumes at  $T = 298.15$  K of PF<sub>6</sub><sup>-</sup> ( $73.71 \text{ cm}^3\cdot\text{mol}^{-1}$ ) and TFSI<sup>-</sup> ( $157.6 \text{ cm}^3\cdot\text{mol}^{-1}$ ) anions [45]. Furthermore, non-aqueous solvents containing the TFSI anion are generally denser than those based on the PF<sub>6</sub><sup>-</sup> [46]. Finally, from table 2, it appears also that calculated deviations between pure solvent and electrolyte density values are more important in the case of linear carbonates than those observed for cyclic compounds. Additionally, such deviations seem to increase with the alkyl chain length on the linear carbonate.

The experimental carbon dioxide solubility values among the eight selected electrolyte solutions containing  $1 \text{ mol}\cdot\text{dm}^{-3}$  LiPF<sub>6</sub> or LiTFSI dissolved into a pure solvent (such as EC, DMC, EMC or DEC) are listed in table 3, where the solubility values are reported in terms of their CO<sub>2</sub> mole fractions and Henry's law constants at atmospheric pressure. For each electrolyte studied, experimental data points were obtained within the temperature interval between (283 and 353) K, except in the case of the EC solutions

1 where measurements were performed starting from 298.15 K. Experimental results were  
2 then correlated by using the equation 4 to determine the effect of temperature on the  
3 CO<sub>2</sub> solubility in each electrolyte. Fitting parameters and *RAAD* (equation 5) are  
4 reported in each case in the table 4. According to Jacquemin *et al.* [47], the precision of  
5 the experimental values can be evaluated from the deviations between experimental  
6 values and those correlated by using equations 4 and 5, which is herein lower than 2 %  
7 except in the case of the CO<sub>2</sub> solubility in EMC electrolytes.  
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10 Figure 2 represents the CO<sub>2</sub> solubility data, expressed in mole fraction of CO<sub>2</sub> (figure  
11 2a) as well as in Henry's Law constants (figure 2b) at the atmospheric pressure, in the  
12 selected electrolyte containing 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> or LiTFSI dissolved into pure solvents  
13 as a function of temperature. It is observed that whatever the anionic structure of the  
14 lithium salt dissolved in the pure solvent, the CO<sub>2</sub> is more soluble in linear solvents than  
15 in the cyclic carbonate. That conclusion is in agreement with the variation already  
16 reported in the literature for the CO<sub>2</sub> solubility in pure solvents [22-38]. From table 2  
17 and figure 2, it can be also appreciated that, whatever the structure of the selected  
18 lithium salt dissolved in a pure solvent and whatever the temperature, the CO<sub>2</sub> solubility  
19 increases in the following order: EC < DMC < EMC ≤ DEC. For each electrolyte  
20 investigated, the CO<sub>2</sub> solubility decreases with temperature. For example the CO<sub>2</sub>  
21 solubility in EC and DEC electrolytes containing 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> are close to (0.0054  
22 and 0.0025) and to (0.0140 and 0.0055) in CO<sub>2</sub> mole fraction units at  $T = (298 \text{ and } 353)$   
23 K and atmospheric pressure, respectively. Similarly, the CO<sub>2</sub> solubility, under the same  
24 temperature and pressure conditions, in EC and DEC electrolytes containing 1 mol·dm<sup>-3</sup>  
25 LiTFSI are close to (0.0056 and 0.0027) and to (0.0172 and 0.0081) in CO<sub>2</sub> mole  
26 fraction units, respectively. In other words, the CO<sub>2</sub> is slightly more soluble in  
27 electrolyte containing 1 mol·dm<sup>-3</sup> LiTFSI than 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>. For example, at  $T =$   
28 298.15 K the Henry's law constant of the CO<sub>2</sub> in electrolyte based on the DMC and 1 f  
29 mol·dm<sup>-3</sup> LiPF<sub>6</sub> ( $K_H = 7.79 \text{ MPa}$ ) is greater than that based on DMC and 1 mol·dm<sup>-3</sup>  
30 LiTFSI ( $K_H = 6.20 \text{ MPa}$ ), which reinforces the fact that the gas solubility in electrolyte  
31 is affected by the selection of the lithium salt dissolved in the solution.  
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1 During a previous investigation, our group has reported a state-of-art experimental CO<sub>2</sub>  
2 solubility in pure carbonate solvents as a function of temperature at 0.1 MPa available  
3 in the literature [22] from which an accuracy close to 15 % could be claimed even if our  
4 previous published values should be considered with accuracy close to 2 %. In the light  
5 of this conclusion, herein, we decided to compare experimental results of CO<sub>2</sub> solubility  
6 in electrolytes presented in this work only with those previously reported by our group  
7 in the case of pure solvents (see table S1 of the supporting information), [22] in order to  
8 understand the effect of the addition of a lithium salt on the CO<sub>2</sub> solubility in carbonate  
9 solutions. We report in figure 3 a comparison of the CO<sub>2</sub> solubility in pure solvents and  
10 in different electrolytes containing 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> or 1 mol·dm<sup>-3</sup> LiTFSI at  $T =$   
11 298.15 K (figure 3a) and 353.15 K (figure 3b). Based on this information, it appears  
12 that, the CO<sub>2</sub> solubility is greater in pure solvents than in electrolytes containing 1  
13 mol·dm<sup>-3</sup> LiPF<sub>6</sub> over a temperature range from (293 to 353) K. This observation is in  
14 agreement with COSMOTermX calculations done by our group previously [22], since  
15 a salting-out effect is experimentally observed by dissolving 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> in all  
16 solvents investigated. On the other hand, the salting effect of the dissolution of 1  
17 mol·dm<sup>-3</sup> LiTFSI in each solvent is more strongly affected by the structure of the  
18 selected solvent, as well as the interaction between solvent and TFSI<sup>-</sup> anion. As reported  
19 herein by comparing data reported in tables 3 and S1 of the supporting information in  
20 the case of the CO<sub>2</sub> solubility in each solution with or without the presence of 1 mol·dm<sup>-3</sup>  
21 LiTFSI salt (or see figure 3), no salting effect is observed by adding LiTFSI in EC, *a*  
22 *contrario* of solutions based on the DMC and DEC from which salting-out and salting-  
23 in effects are, respectively, observed. Even if this effect depends mainly of both lithium  
24 salts and solvents structures and their interactions in solution, it appears also from the  
25 figure 3 that the temperature affects slightly the salting effect of each lithium salt in the  
26 solvents selected. For example, in the case of the EMC solutions salting-out and salting-  
27 in effects are observed by adding the LiTFSI at  $T =$  (298 and 353) K, respectively.  
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51 To analyze in detail these CO<sub>2</sub> solubility results, we decided then to calculate the  
52 dissolution properties as well as the mixing enthalpy of the CO<sub>2</sub> in these solutions at  $T =$   
53 298.15 K, which are reported herein in the table S2 of the supporting information and  
54 in table 5 in the case of the pure solvents and investigated electrolytes, respectively. As  
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1 expected, the standard Gibbs energies of dissolution of CO<sub>2</sub> in these solutions are  
2 positive, and follow the same order as that reported for the solubility, as the Gibbs  
3 energy is directly proportional to the logarithm of the Henry's law constants (see  
4 equation 6). Whatever the structures of the dissolved lithium salt or solvent used, the  
5 standard enthalpies and entropies of dissolution of CO<sub>2</sub> in selected electrolytes are all  
6 negative, in other words the CO<sub>2</sub> solubility in each electrolyte is entropy-driven and  
7 presents an exothermic process of dissolution. From table 5, it can be seen also that all  
8 enthalpies of mixing are positive, which clearly indicate the lack of specific interaction  
9 between selected electrolytes and CO<sub>2</sub> especially in the case of electrolytes based on the  
10 DMC, which provide the lowest energy during the dissolution process. This conclusion  
11 reinforces that reported between pure solvents and CO<sub>2</sub> [22]. Except in the case of the  
12 DEC, the difference observed between dissolution properties and mixing enthalpies of  
13 CO<sub>2</sub> with pure solvents and with electrolytes containing 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> or of LiTFSI  
14 reinforces the hypothesis that the presence of lithium salt affects the reorganization of  
15 the solution. For example, the presence of 1 mol·dm<sup>-3</sup> lithium salt in EC solution  
16 decreases the entropy of dissolution at  $T = 298.15$  K up to 20 % in comparison with that  
17 observed in pure EC (see tables 5 and S2 of the supporting information), which can be  
18 linked to a better reorganization of the liquid phase in the presence of salt. Nevertheless,  
19 in the case of the linear carbonate, the presence of salt seems to increase slightly the  
20 mixing enthalpy (or the dissolution enthalpy) as well as the entropy of dissolution in the  
21 presence of CO<sub>2</sub>, driven by an increase of interaction and in fact of requested  
22 reorganization in solutions. In other words, linear and cyclic carbonates containing a  
23 lithium salt (LiPF<sub>6</sub> or LiTFSI) are probably driven by different molecular mechanisms  
24 of dissolution. By changing the salt dissolved in solution from LiPF<sub>6</sub> to LiTFSI seems to  
25 increase the entropy of dissolution of CO<sub>2</sub> in such electrolyte, again this conclusion can  
26 be linked to the structure differences between PF<sub>6</sub><sup>-</sup> (spherical, symmetric with a charge  
27 density localized on the anion surface) and TFSI<sup>-</sup> anions (non-spherical and the charge  
28 on the anion surface is highly delocalized resulting in relatively weak cation-anion  
29 coulombic interactions) as shown in figure S2 of the supporting information.  
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1 3.2 Effect on the presence of the lithium salt on density and CO<sub>2</sub> gas solubility in binary  
2 mixture of carbonate solvents.  
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6 The density of binary mixtures of EC:DMC, EC:EMC, and EC:DEC (50:50) wt % at  $T$   
7 = 298.15 K is reported in table 6, as well as density values measured in the case of  
8 electrolytes containing 1 mol·dm<sup>-3</sup> lithium salt, *e.g.* LiPF<sub>6</sub>, LiFAP or LiTFSI. Density  
9 values from this table were then compared with those reported in table 2. As expected,  
10 each binary mixture of carbonate solvents has a density lower than that measured in the  
11 case of the pure EC and higher than those reported in the case of investigated linear  
12 carbonates. Furthermore, by increasing the alkyl chain length on the linear carbonate,  
13 the density of their mixtures with EC (50:50) wt % decreases. Such conclusions are also  
14 observed in the case of electrolytes investigated. As shown in the previous section in the  
15 case of pure solvent, the presence of salt increases the density of the binary carbonate  
16 solution. From table 6, it appears also that the density of these electrolytes is also  
17 strongly affected by the structure of the selected anion, as we found that FAP<sup>-</sup>-based  
18 electrolytes are denser than TFSI ones, which are denser than those based on the PF<sub>6</sub><sup>-</sup>  
19 anion. For example, in the case of the EC:DMC (50:50) wt % electrolytes, density  
20 values close to (1.34, 1.29 and 1.31) g·cm<sup>-3</sup> are measured in the case of electrolyte  
21 containing 1 mol·dm<sup>-3</sup> LiFAP, LiPF<sub>6</sub>, and LiTFSI salt, respectively. Again, this  
22 conclusion is in agreement with that expected by comparing the effective molar  
23 volumes at  $T = 298.15$  K of FAP<sup>-</sup>, PF<sub>6</sub><sup>-</sup> and TFSI.[45]  
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41 To evaluate the CO<sub>2</sub> solubility changes by mixing a cyclic carbonate (EC) solvent with  
42 the linear molecule, the CO<sub>2</sub> solubility in each (50:50) wt % solution without salt,  
43 reported here in the table 7, was firstly determined from  $T = (298 \text{ to } 353)$  K and  
44 compared to values obtained in the case of pure solvents (see table S1 and figure S3 of  
45 the supporting information). From this comparison, it appears that the presence of a  
46 cyclic carbonate solvent decreases strongly the CO<sub>2</sub> solubility in solution containing a  
47 linear one. For example, at  $T = 298.15$  K the CO<sub>2</sub> solubility, expressed in CO<sub>2</sub> mole  
48 fraction is close to 0.0057, 0.0098, 0.0104 and 0.0118 in pure EC, EC:DMC, EC:EMC  
49 and EC:DEC (50:50) wt % mixtures, respectively. While  $x_{\text{CO}_2}$  values close to 0.0136,  
50 0.0170, and 0.0165 are reported in the case of pure DMC, EMC and DEC, respectively  
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[22]. In other words, at  $T = 298.15$  K, the  $\text{CO}_2$  solubility in carbonate solution increases in the following order:  $\text{EC} \ll \text{EC:DMC (50:50 wt \%)} < \text{EC:EMC (50:50 wt \%)} < \text{EC:DEC (50:50 wt \%)} \ll \text{DMC} < \text{DEC} < \text{EMC}$ . For each solution, its  $\text{CO}_2$  solubility decreases as a function of temperature, and for the covered temperature range, the  $\text{CO}_2$  solubility in selected mixtures are lower than those reported in pure linear carbonate solvents. Steric effects may explain the fact that  $\text{CO}_2$  is less soluble in mixtures of (EC + linear carbonate) than in pure linear solvents, driven also by the fact that  $\text{CO}_2$  solubility is lower in cyclic than in acyclic carbonates, as shown in figure S3 of the supporting information. This experimental observation is in agreement with that reported by Gui *et al.*[35] in the case of DMC:EC, DMC:PC and DMC:DEC mixtures. However, as this group has investigated the  $\text{CO}_2$  solubility in mixture based on a (1:1) volume ration, their results in the case of the EC:DMC mixture cannot be, directly, compared with those reported in this work. Nevertheless, at  $T = 298.15$  K our group reports  $x_{\text{CO}_2} = 0.0098$  in the case of the mixture based on EC:DMC (50:50 wt %), such value is in agreement with that reported by Gui *et al.*[35],  $x_{\text{CO}_2} = 0.0104$  at  $T = 298.15$  K, in the case of the similar mixture based on a (1:1) volume ration.

The effect of the dissolution of  $1 \text{ mol}\cdot\text{dm}^{-3}$  LiFAP,  $\text{LiPF}_6$ , or LiTFSI salt in these binary carbonate mixtures on their  $\text{CO}_2$  solubility was then investigated as a function of the temperature. These experimental data are listed in the table 8, and shown in figure S4 of the supporting information. As expected, and shown in figure S4 of the supporting information, for each electrolyte investigated herein, the  $\text{CO}_2$  solubility decreases with temperature. Furthermore, a comparison of the  $\text{CO}_2$  solubility data reported in each selected mixture in absence (table 7) or in presence of a lithium salt (table 8) shows, as expected from the previous section, a strong effect of the salt on this property. As shown in figure 4, it appears that, the  $\text{CO}_2$  solubility is higher in binary carbonate mixtures than in electrolytes containing  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiPF}_6$  for a temperature range from (293 to 353) K. For example, at  $T = 298.15$  K a decrease up to (20.4, 19.8 and 25.4) % on the  $\text{CO}_2$  solubility in solution containing  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiPF}_6$  is observed in comparison with solubility values obtained in the absence of salt in the case of EC:DMC, EC:EMC and EC:DEC (50:50) wt % mixtures, respectively. Nevertheless, each solubility decrease is generally less pronounced by increasing the temperature, since the  $\text{CO}_2$

solubility in the absence of salt in the case of EC:DMC and EC:EMC (50:50) wt % mixtures are (11.9 and 15.9) % higher than in presence of  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiPF}_6$ . In other words, the temperature seems to affect differently the  $\text{CO}_2$  solubility in these electrolytes but for each investigated temperature  $\text{LiPF}_6$  salt has a salting-out effect on the  $\text{CO}_2$  solubility in carbonate mixtures. By substituting the  $\text{LiPF}_6$  by the  $\text{LiTFSI}$  salt, it appears that the  $\text{CO}_2$  solubility in each solution increases. For example, at  $T = 298.15 \text{ K}$  the  $\text{CO}_2$  solubility, expressed in  $\text{CO}_2$  mole fraction unit, in EC:DMC, EC:EMC and EC:DEC (50:50) wt % electrolytes containing  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiTFSI}$  are close to (0.0098, 0.0106 and 0.0125), and are higher than those observed in electrolytes containing  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiPF}_6$  (e.g. 0.0085, 0.0087 and 0.0088), respectively. By comparing such solubility values with those measured in the case of the absence of salt, it appears that at  $T = 298.15 \text{ K}$  no salting effect is observed by adding  $\text{LiTFSI}$  in EC:DMC (50:50) wt % mixture, while salting-in effects are observed in EC:EMC and EC:DEC (50:50) wt % mixtures. As reported in the previous section and shown in figure 4, the temperature affects slightly the salting effect of  $\text{LiTFSI}$  salt in the selected carbonate mixtures. For example, in the case of the EC:EMC and EC:DEC (50:50) wt % solutions salting-in and salting-out effects are observed by adding the  $\text{LiTFSI}$  at  $T = (298 \text{ and } 353) \text{ K}$ , respectively. At  $T = 298.15 \text{ K}$ , in the case of the  $\text{LiFAP}$  electrolytes, no salting effect is observed in EC:DMC (50:50) wt % mixture, while again, salting-in effects are observed in EC:EMC and EC:DEC (50:50) wt % mixtures. As reported in the case of the  $\text{LiTFSI}$ , these salting effects depend on the structure of solvents involved in the mixture, as well as on the temperature, as depicted from tables 7 and 8 and shown in figure 4. Nevertheless, from figure 4 and table 8, it can be also appreciated that the  $\text{CO}_2$  is, generally, slightly more soluble in electrolyte containing  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiFAP}$  than  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiTFSI}$ . For example, at  $T = 298.15 \text{ K}$  the Henry's law constant of the  $\text{CO}_2$  in electrolyte based on the EC:DEC (50:50) wt % mixture and  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiFAP}$  ( $K_{\text{H}} = 6.37 \text{ MPa}$ ) is lower than that based on EC:DEC (50:50) wt % mixture and  $1 \text{ mol}\cdot\text{dm}^{-3}$   $\text{LiTFSI}$  ( $K_{\text{H}} = 8.00 \text{ MPa}$ ), which reinforces again that the gas solubility in the electrolyte is strongly affected by the selection of the lithium salt dissolved in the solution. On the other hand, it appears from this work that the  $\text{CO}_2$  solubility in selected electrolytes increases in the following order:  $\text{LiPF}_6 < \text{LiTFSI} \leq \text{LiFAP}$ . This solubility trend can be

1 explained by the difference of their volumes and sigma profiles (charge density on each  
2 anion surface) as reported in figure S2 of the supporting information.  
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6 In order to assess the dissolution properties, as well as the mixing enthalpy of CO<sub>2</sub> with  
7 each binary carbonate mixture in the absence or in the presence of 1 mol·dm<sup>-3</sup> lithium  
8 salt (LiPF<sub>6</sub>, LiTFSI or LiFAP), the variation of their CO<sub>2</sub> solubility was then first  
9 adjusted by using the equation 4 as a function of temperature. Best fitting parameters  
10 along their RAAD with experimental data are reported in table 9. From this table, it  
11 appears that all RAAD are lower than 2 %, except for mixtures based on EC:DMC + 1  
12 mol·dm<sup>-3</sup> LiPF<sub>6</sub>, EC:EMC + 1 mol·dm<sup>-3</sup> LiFAP and EC:DEC + 1 mol·dm<sup>-3</sup> LiFAP,  
13 where RAAD close to (2.7, 3.1 and 3.3) % were observed. Based on these fitting  
14 parameters, dissolution properties and mixing enthalpy of CO<sub>2</sub> with these solutions are  
15 then calculated and reported herein in table 10 at  $T = 298.15$  K. Whatever the dissolved  
16 lithium salt or the selected mixture, the standard enthalpies and entropies of dissolution  
17 of CO<sub>2</sub> in selected binary mixtures and in electrolytes are all negative. As observed in  
18 the previous section, the CO<sub>2</sub> solubility in each solution is entropy-driven and presents  
19 an exothermic process of dissolution. From the table 10 and its comparison with table  
20 S2 of the supporting information, it appears that in the absence of salt, all (50:50) wt %  
21 carbonate binary mixtures have dissolution properties at  $T = 298.15$  K lower than those  
22 observed in the case of the pure EC, but generally higher than those expected in pure  
23 linear carbonates. For example, at  $T = 298.15$  K, the entropy of dissolution of CO<sub>2</sub> in  
24 these solutions increases following this order: DMC < EC:DMC (50:50) wt % < EMC <  
25 EC:EMC (50:50) wt % < EC:DEC (50:50) wt % < DEC < EC. The reorganization of  
26 the liquid phase in the presence of CO<sub>2</sub> is in fact affected by the nature and structure of  
27 each component that defines the liquid phase. The interactions in solution also depend  
28 on such factors, since the enthalpy of dissolution, as well as the mixing enthalpy of CO<sub>2</sub>  
29 in all (50:50) wt % carbonate binary mixtures, is lower than those observed in the case  
30 of pure EC. From table 10, it also appears that whatever mixture is selected, all mixing  
31 enthalpies are positive, which indicates the lack of specific interaction between CO<sub>2</sub> and  
32 each solution. By adding a salt, a similar conclusion can be made, even if the presence  
33 of LiPF<sub>6</sub> increases the mixing enthalpy values of CO<sub>2</sub> and solutions, *a contrario* of  
34 LiTFSI or LiFAP ones. This trend can be linked to the salting effect of these lithium  
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1 salts on the CO<sub>2</sub> solubility in solution. The entropy of dissolution of CO<sub>2</sub> and solution  
2 seems also to be slightly affected by the presence and the structure of lithium salts. For  
3 each electrolyte investigated, the presence of the salt increases the entropy of  
4 dissolution of CO<sub>2</sub> and electrolyte following this order: LiPF<sub>6</sub> < LiFAP < LiTFSI. For  
5 example at  $T = 298.15$  K, entropy values up to (-76, -78, -85 and -82) J·K<sup>-1</sup>·mol<sup>-1</sup> are  
6 observed in the case of the (50:50) wt % EC:DEC mixture with no salt or containing 1  
7 mol·dm<sup>-3</sup> LiPF<sub>6</sub>, LiTFSI and LiFAP, respectively. This increase of entropy can be  
8 associated by a better reorganization of the liquid phase in the presence of lithium salt.  
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17 As each CO<sub>2</sub> solubility process is entropy driven and as the presence of lithium salt  
18 affects this property as well as the solubility of CO<sub>2</sub> in solution, we decided to  
19 investigate in greater detail the effect of the salt concentration on the CO<sub>2</sub> solubility in  
20 the electrolyte. During this work, we selected the EC:DMC (50:50) wt % mixture as a  
21 probe to identify this effect by increasing the LiPF<sub>6</sub> or LiTFSI salt concentration in  
22 solution at  $T = 298.15$  K. The CO<sub>2</sub> solubility in both electrolytes was then investigated  
23 as a function of the lithium salt concentration at 298.15 K and then compared with that  
24 observed in the EC:DMC (50:50) wt % mixture without salt. These experimental values  
25 are listed in the table S3 of the supporting information and shown in figure 5. From this  
26 figure, it can be observed that at  $T = 298.15$  K the CO<sub>2</sub> solubility in LiPF<sub>6</sub> decreases  
27 mostly linearly with the salt concentration in solution. Furthermore, as this electrolyte  
28 has a lower CO<sub>2</sub> solubility than the EC:DMC (50:50) wt % mixture without salt, it can  
29 be concluded that whatever the salt concentration in solution, a salting-out effect is  
30 observed in the case of the dissolution of LiPF<sub>6</sub> in this solution. Nevertheless, from our  
31 investigation no trivial trend can be dressed in the case of the LiTFSI-based electrolyte  
32 (Figure 5). Surprisingly, at  $T = 298.15$  K, a minimum CO<sub>2</sub> solubility in this electrolyte  
33 is observed as a function of the salt concentration for a lithium composition close to 2  
34 mol·dm<sup>-3</sup>. The CO<sub>2</sub> solubility in this electrolyte decreases up to this lithium  
35 concentration and then seems to increase again. By comparing these solubility results  
36 with those obtained in the case of EC:DMC (50:50) wt % mixture without salt, it  
37 appears, as shown in figure 5, that for LiTFSI concentration in solution between (1 and  
38 3) mol·dm<sup>-3</sup> a salting-out effect is observed by dissolving LiTFSI in this solution.  
39 However, for the LiTFSI concentration in solution lower than 1 mol·dm<sup>-3</sup> a salting-in  
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1 effect is observed. This result demonstrates again that no-trivial conclusion about  
2 salting effects as well as solubility trends can be addressed, but reinforces the fact that  
3 the CO<sub>2</sub> solubility in electrolytes is mainly driven by the temperature, pressure, and the  
4 formulation of the electrolyte through the selection of carbonate mixture, structure and  
5 concentration of lithium salt dissolved in solution.  
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### 10 11 12 *3.3 Evaluation of the CO<sub>2</sub> solubility prediction in electrolytes using COSMOThermX.*

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16 In the light of the structural and charge density differences between the FAP<sup>-</sup>, PF<sub>6</sub><sup>-</sup> and  
17 TFSI anions (see figure S2 of the supporting information) as well as in order to  
18 evaluate different tools able to predict the gas solubility in Li-ion electrolytes,  
19 experimental results presented herein were then compared with those calculated by  
20 COSMOThermX by using the same methodology reported by our group previously.[22]  
21 Additionally, we decided to investigate, herein, the accuracy of the COSMO-RS method  
22 in the case of the CO<sub>2</sub> solubility in electrolytes as a function of the temperature from  
23 (298 to 353) K by comparing the CO<sub>2</sub> solubility in electrolytes calculated by  
24 COSMOThermX with all experimental data presented during this work.  
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34 Firstly, we reported in table S1 of the supporting information the COSMOThermX  
35 calculation of the CO<sub>2</sub> solubility in pure solvents as a function of temperature from (298  
36 to 353) K, as well as their comparisons with experimental results reported previously  
37 [22]. From this table, it appears that COSMOThermX is able to predict the CO<sub>2</sub>  
38 solubility in pure solvents within accuracy up to 28 %. However, this methodology  
39 seems to be unable to predict the CO<sub>2</sub> solubility order observed experimentally. For  
40 example, COSMOThermX predicts a higher CO<sub>2</sub> solubility in DEC than in EMC.  
41 However, in each case, the CO<sub>2</sub> solubility in pure solvents is calculated with the respect  
42 of the order of magnitude giving in fact the possibility to screen the CO<sub>2</sub> solubility using  
43 COSMOThermX prior to experimental measurements, not only at  $T = 298.15$  K as  
44 reported previously by our group [22], but also as a function of temperature. Secondly,  
45 an evaluation of the CO<sub>2</sub> solubility prediction in the selected (50:50) wt % binary  
46 mixtures like EC:DMC, EC:EMC and EC:DEC using COSMOThermX has been then  
47 realized as a function of temperature as reported in table S4 of the supporting  
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1 information. From this information, it appears that the methodology is able to predict  
2 not only the order of magnitude of the reported CO<sub>2</sub> solubility in these binary mixtures  
3 but also the CO<sub>2</sub> solubility order observed experimentally: *e.g.* EC:DMC (50:50) wt %  
4 < EC:EMC (50:50) wt % < EC:DEC (50:50) wt % within an accuracy close to 35 %.  
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6 This result is in agreement with those already reported by our group [22] and by Kolar  
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8 *et al.* [44]. It appears also from the table S4 of the supporting information that CO<sub>2</sub> gas  
9 solubility in binary carbonate mixture are over estimated by COSMOTermX, but also  
10 that each difference between calculated and experimental results decreases by  
11 increasing the temperature.  
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19 After these evaluations on the COSMOTermX predictability of the CO<sub>2</sub> solubility in  
20 solution without lithium salt as a function of temperature, COSMOTermX calculations  
21 were performed to estimate the effect of the dissolution of 1 mol·dm<sup>-3</sup> lithium salt  
22 (LiPF<sub>6</sub>, LiFAP or LiTFSI) in each solution described during the experimental part, on  
23 the CO<sub>2</sub> solubility as a function of temperature as reported in the table S5 of the  
24 supporting information. As depicted from this table and shown in figure 6, excellent  
25 agreements were obtained between calculations and experimental data sets in the case of  
26 the EC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> and EC + 1 mol·dm<sup>-3</sup> LiTFSI electrolytes as a function of  
27 temperature with deviations up to (3.4 and 6.4) %, respectively. Nevertheless, for the  
28 other electrolytes investigated greater deviations between COSMOTermX calculations  
29 and experimental data sets were found as shown in the case of some LiTFSI-based  
30 electrolytes in figure 7. For example, deviations close to (45 and 30) % are obtained in  
31 the case of the DEC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub> and DEC + 1 mol·dm<sup>-3</sup> LiTFSI electrolytes,  
32 respectively. For a temperature range from (298 to 353) K, the overall accuracy of the  
33 COSMOTermX calculation is close to (40, 33 and 39) % in the case of LiPF<sub>6</sub>, LiTFSI  
34 and LiFAP electrolytes, respectively. This accuracy is in agreement with those already  
35 claimed by our group in the case of CO<sub>2</sub> solubility in pure carbonate solvents at  $T =$   
36 298.15 K [22], as well as in pure ionic liquids as a function of temperature [43].  
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54 Furthermore, as expected from the structural and charge density differences observed  
55 between each individual selected anion (see figure S2 of the supporting information),  
56 COSMOTermX calculations predict accurately that the CO<sub>2</sub> solubility in electrolyte  
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1 depends of the anion structure, as reported in the figure 8. Additionally, it appears from  
2 this work that COSMOTermX is able to reproduce accurately the experimental  
3 observation that the CO<sub>2</sub> solubility in selected electrolytes increases in the following  
4 order: LiPF<sub>6</sub> < LiTFSI ≤ LiFAP. Nevertheless, even if COSMOTermX reproduces  
5 correctly the salting-out effect in the case of the LiPF<sub>6</sub>, experimental observations in the  
6 case of the LiTFSI and LiFAP salts are not correctly predicted by using this method.  
7 For example, in the case of the EC:EMC and EC:DEC (50:50) wt % solutions salting-in  
8 and salting-out effects are experimentally observed by adding the LiTFSI at  $T = (298$   
9 and 353) K, respectively ; while COSMOTermX calculations show a salting-out effect  
10 in each case. Additionally, a salting-in effect is expected from COSMOTermX  
11 calculation by adding LiFAP salt in each solution, while salting-in and salting-out  
12 effects are experimentally observed depending of the selected carbonate mixture and  
13 temperature.  
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26 To evaluate in greater detail the CO<sub>2</sub> gas solubility prediction in electrolytes by  
27 COSMOTermX, calculations were then carried-out as a function of the lithium salt  
28 concentration in solution and then compared with experimental data sets as reported in  
29 table S6 of supporting information and shown in figure 8. In the light of the incorrect  
30 prediction of the salting effect in the case of the LiTFSI, we decided then to perform our  
31 calculations by using different “cosmo files” to define this lithium salt. During this  
32 study, three different calculation methodologies were used by defining the LiTFSI as an  
33 ion pair (*i.e.* as for the other calculations), or as two individual ions (by using two  
34 separated “cosmo files”, one per ion, by using a similar calculation approach as reported  
35 by our group previously in the case of ionic liquid [43]), or as a metafile based on a  
36 binary mixture “cosmo file” containing each ion at the 1:1 mol ratio created using the  
37 metafile editor option within COSMOTermX. From the figure 9 and the table S6 of  
38 the supporting information, it appears that COSMOTermX is able to reproduce the  
39 decrease of the CO<sub>2</sub> solubility in LiPF<sub>6</sub>-based electrolytes as a function of the salt  
40 concentration within accuracy close to 55 %. In the case of LiTFSI salt, by using the  
41 same methodology as before, *i.e.* by defining the LiTFSI as an ion-pair file during  
42 calculations, COSMOTermX predicts an increase of the CO<sub>2</sub> solubility in such  
43 electrolyte as the function of the salt concentration in solution. Furthermore, for LiTFSI  
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1 concentration lower or higher than  $1 \text{ mol}\cdot\text{dm}^{-3}$  a salting-out or salting-in effect is  
2 predicted by using this tool. Nevertheless, both observations are not in agreement with  
3 the experimental values as shown by comparing figure 5 (experimental) with the Figure  
4 9 (COSMOTermX calculations). By using metafile or individual ions “cosmo files” to  
5 define the LiTFSI salt, minima of the  $\text{CO}_2$  solubility in these electrolytes are observed  
6 for a lithium concentration close to  $(2 \text{ or } 1.5) \text{ mol}\cdot\text{dm}^{-3}$ , respectively. Even if this  
7 solubility trend as a function of the lithium salt concentration in solution is observed  
8 experimentally, both calculation methods predict a salting-out effect for this salt, as well  
9 as  $\text{CO}_2$  solubility in LiTFSI-based electrolytes lower than in the cases of  $\text{LiPF}_6$ . In other  
10 words, COSMOTermX is unable to reproduce quantitatively all observations from  
11 experimental values even by using different strategy to define the lithium salt within  
12 COSMOTermX. However this method provides qualitative answers such as the good  
13 order of magnitude of the  $\text{CO}_2$  solubility in electrolytes as a function of temperature, the  
14 correct solubility trends as a function of the solvent or lithium salt structures within an  
15 overall uncertainty close to 35 %. Finally, from our investigations by defining the  
16 lithium salt as an ion pair during the COSMOTermX calculations, a better description  
17 of experimental data is obtained while experimentally for such concentrations (e.g.  
18 lower than  $3 \text{ mol}\cdot\text{dm}^{-3}$ ) in solution we can expect a salt dissociation.  
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#### 4. Conclusions

We report firstly in this study the solubility of carbon dioxide in different electrolytes containing  $1 \text{ mol}\cdot\text{dm}^{-3}$  lithium salt,  $\text{LiPF}_6$  or  $\text{LiTFSI}$ , dissolved in a pure alkylcarbonate solvent namely EC, DMC, EMC, DEC as a function of temperature from (283 to 353) K and atmospheric pressure. We have then compared these results with those previously reported by our group in the case of pure solvents in order to understand the effect of the addition of a lithium salt on the  $\text{CO}_2$  solubility in carbonate solutions.

In the second part of this study, we present  $\text{CO}_2$  solubility in binary mixtures of EC:DMC, EC:EMC, and EC:DEC (50:50) wt % containing  $1 \text{ mol}\cdot\text{dm}^{-3}$  lithium salt, *e.g.*  $\text{LiPF}_6$ ,  $\text{LiFAP}$  or  $\text{LiTFSI}$  at  $T = 298.15 \text{ K}$  and atmospheric pressure. It appears from this work that the  $\text{CO}_2$  solubility increases in the following order:  $\text{LiPF}_6 < \text{LiTFSI} \leq \text{LiFAP}$ , which can be explained by the difference of their volumes and sigma profiles.

From these experimental values, whatever the temperature and selected carbonate solvent or mixture, a clear salting out effect is observed in the case of the dissolution of  $\text{LiPF}_6$  salt in each selected solution. In the case of  $\text{LiTFSI}$  or  $\text{LiFAP}$ , no salting, salting in or salting out effects are observed depending of the temperature, or structure of the carbonate solution. From this work, it appears that the salting effect depends mainly on both lithium salt and solvent structures and their interactions in solution. From the variation of  $\text{CO}_2$  solubility with temperature, the parameters, dissolution properties and mixing enthalpy of  $\text{CO}_2$  with these solutions are calculated showing that the  $\text{CO}_2$  solubility in each solution is entropy-driven and present an exothermic process of dissolution.

Finally, from our investigations by defining the lithium salt as an ion pair during the COSMOTermX calculations, a better description of experimental data is obtained while experimentally for investigated concentrations in solution we can expect a salt dissociation. These results and analysis presented herein can drive the formulation of safer electrolytes based on the dissolution of lithium salt in alkylcarbonates for lithium ion batteries.

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**Supplementary data**

Additional Supporting Information includes a description of the pH titration of dissolved CO<sub>2</sub> in a solvent; variation of the CO<sub>2</sub> solubility in the case of binary carbonates mixtures in absence or presence of a lithium salt as a function of temperature; sigma profile of selected anions; CO<sub>2</sub> solubility data calculated using COSMOThermX as a function of electrolyte and temperature, as well as their comparisons with experimental data reported into this work. This material is available free of charge via the Internet at <http://www.sciencedirect.com>.

## 5. References

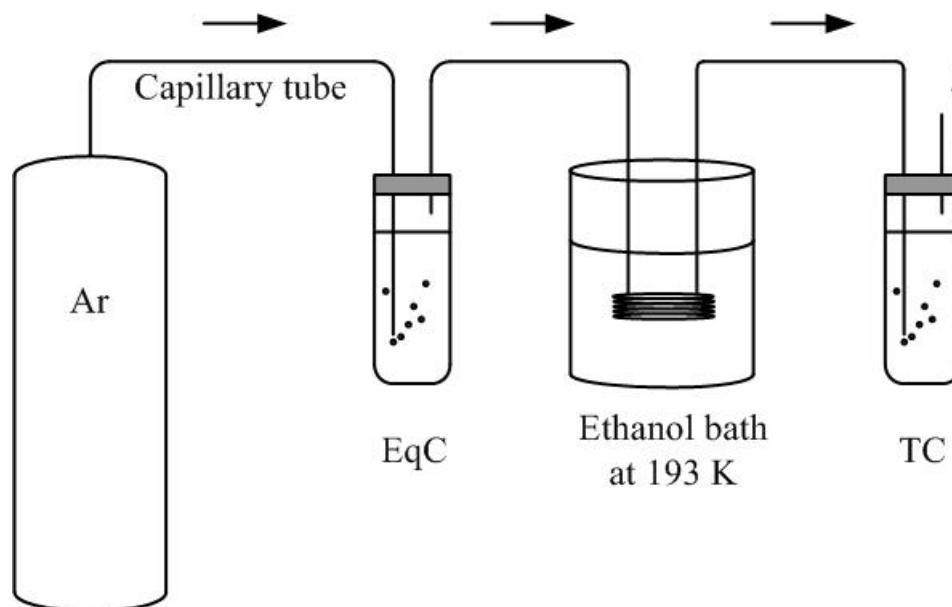
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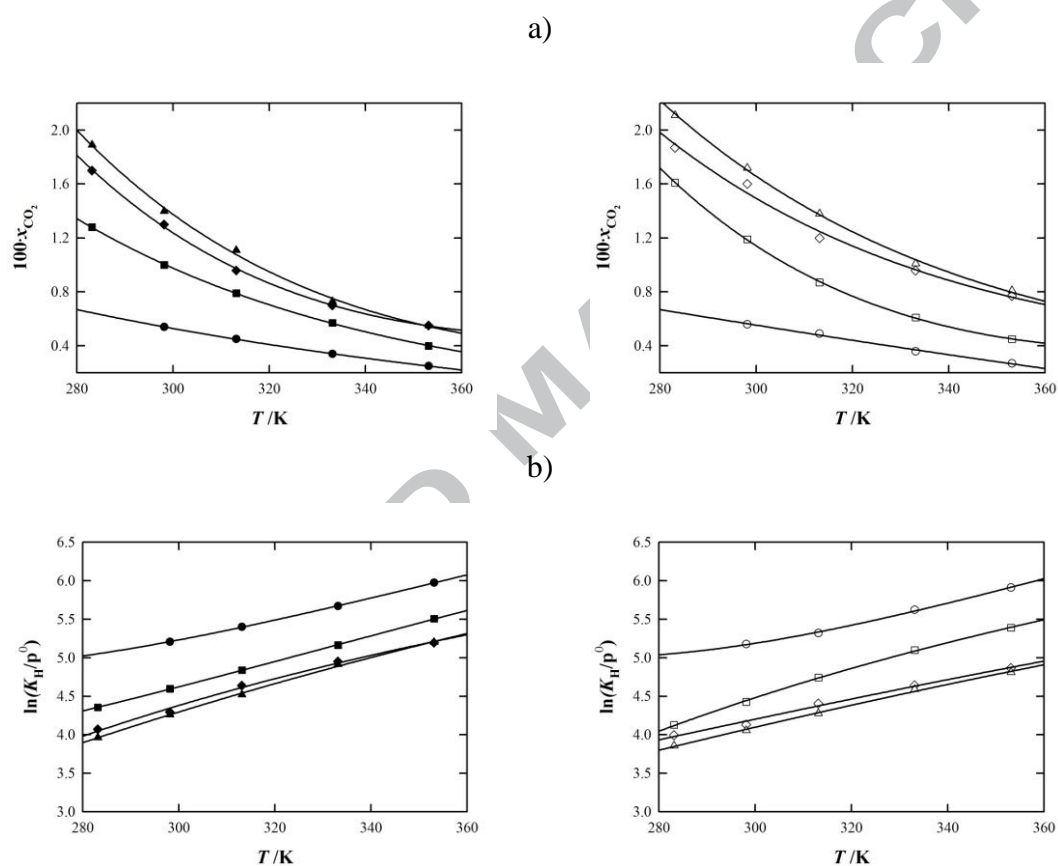
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1 **Figure 1.** Solubility equipment used in this work: EqC, equilibrium cell containing the  
2  $\text{CO}_2$  saturated solvent; TC, titration cell containing the NaOH aqueous solution.[22]  
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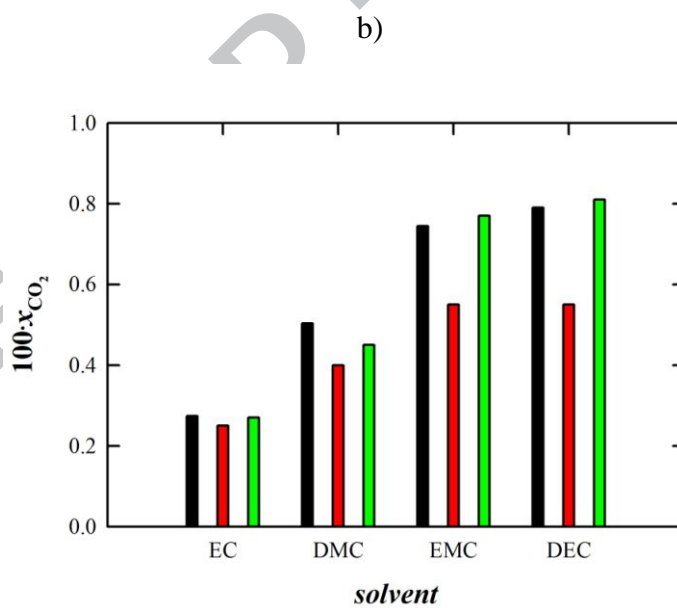
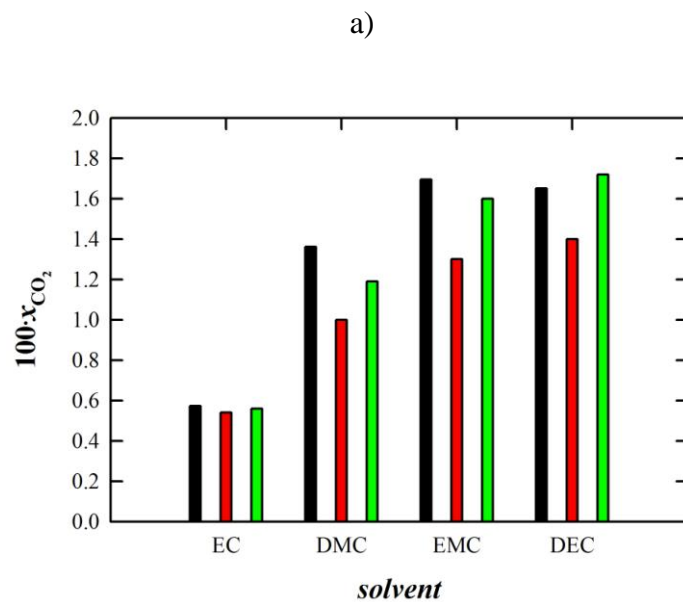




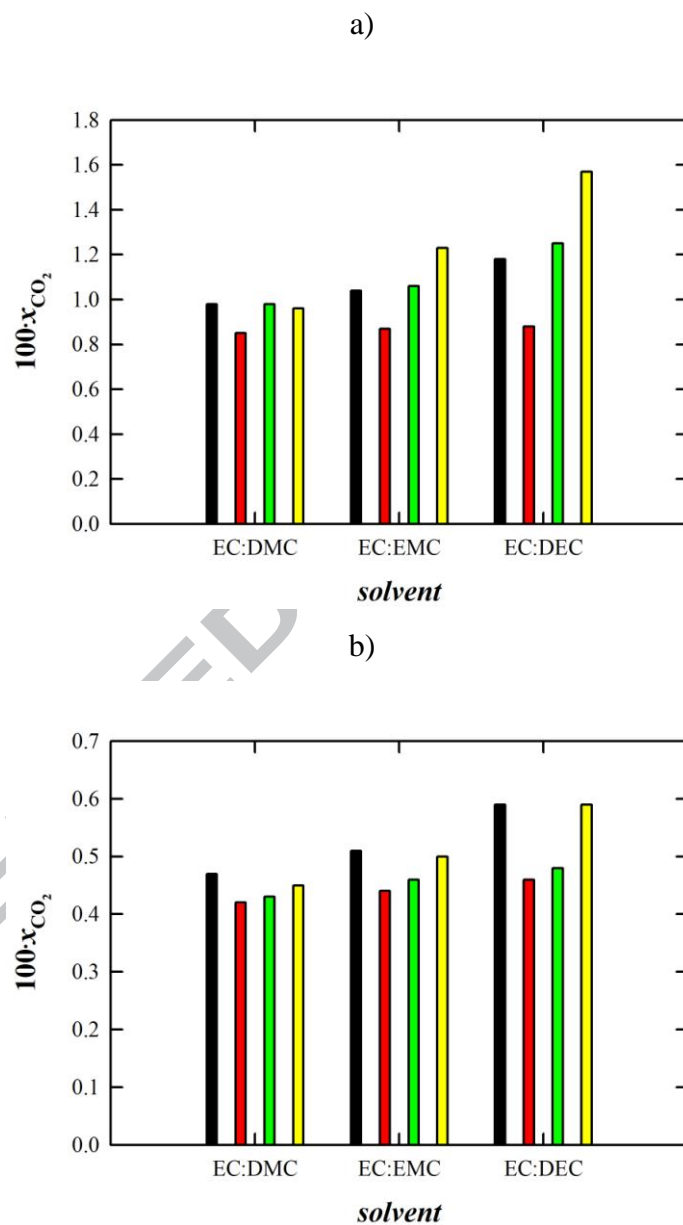
1 **Figure 2.** CO<sub>2</sub> solubility as a function of temperature in: ●, EC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; ○, EC + 1 mol·dm<sup>-3</sup> LiTFSI; ■, DMC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; □, DMC + 1 mol·dm<sup>-3</sup> LiTFSI; ◆, EMC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; ◇, EMC + 1 mol·dm<sup>-3</sup> LiTFSI; ▲, DEC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; △, DEC + 1 mol·dm<sup>-3</sup> LiTFSI; expressed: a) as CO<sub>2</sub> mole fraction, b) as  $\ln(K_H/p^0)$  and 0.1 MPa. Lines represent the smoothed data using the parameters in table 4.



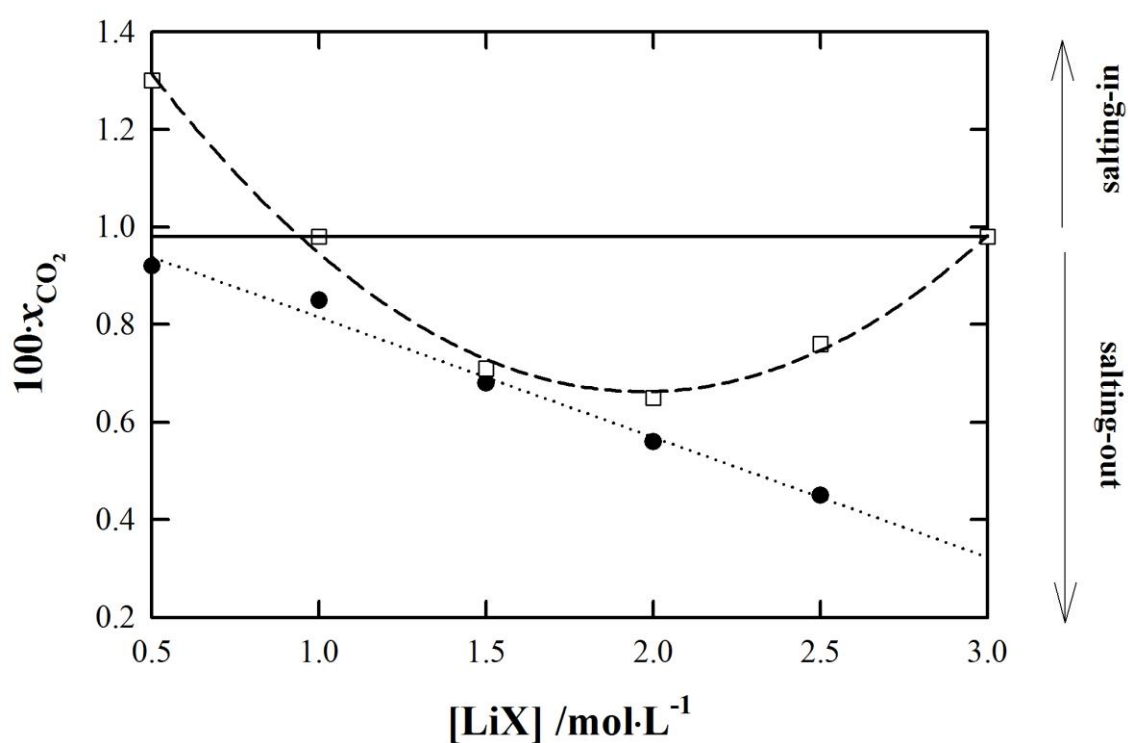
1 **Figure 3.** CO<sub>2</sub> solubility in: black bars, pure solvents; red bars, electrolytes containing  
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3 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; green bars, electrolytes containing 1 mol·L<sup>-1</sup> of LiTFSI at: a) *T* = 298  
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5 K; b) 353 K and 0.1 MPa.



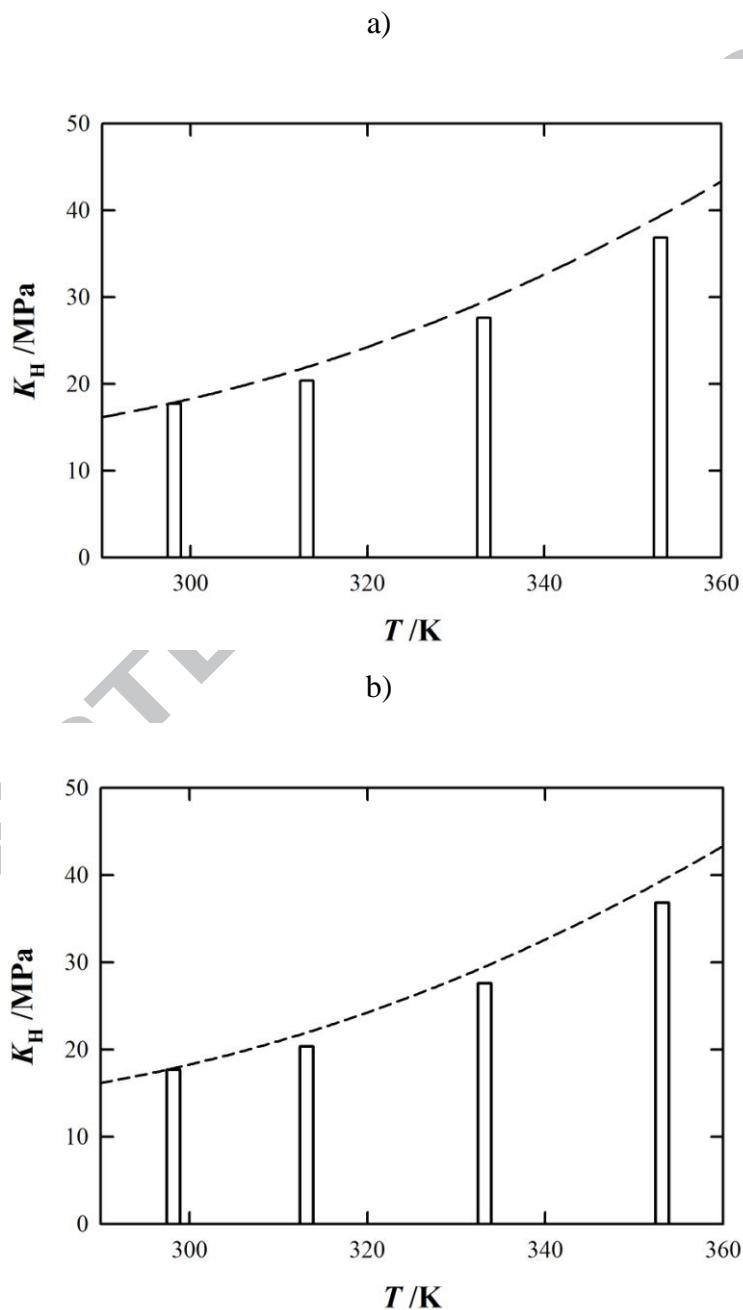
**Figure 4.** CO<sub>2</sub> solubility in: black bars, carbonate mixtures (50:50) wt %; red bars, electrolytes containing 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; green bars, electrolytes containing 1 mol·dm<sup>-3</sup> LiTFSI ; yellow bars, electrolytes containing 1 mol·dm<sup>-3</sup> LiFAP at: a)  $T = 298$  K; b) 353 K and 0.1 MPa.



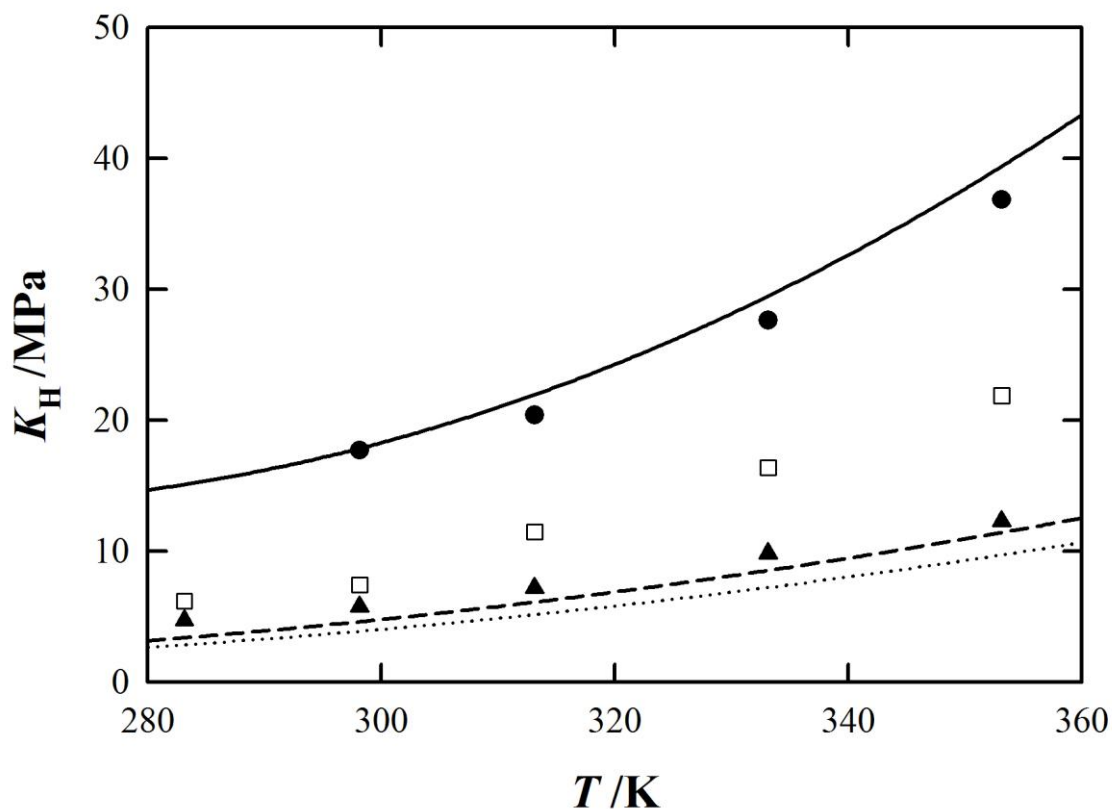
**Figure 5.** CO<sub>2</sub> solubility in (50:50) wt % EC:DMC-based electrolytes containing; ●, and dotted line: LiPF<sub>6</sub>; □, and dashed line: LiTFSI salt as a function of the lithium salt (LiX) concentration in solution expressed in mol·dm<sup>-3</sup> at  $T = 298.15$  K and 0.1 MPa. The solid line represents the CO<sub>2</sub> solubility in (50:50) wt % EC:DMC mixture without salt at  $T = 298.15$  K and 0.1 MPa.



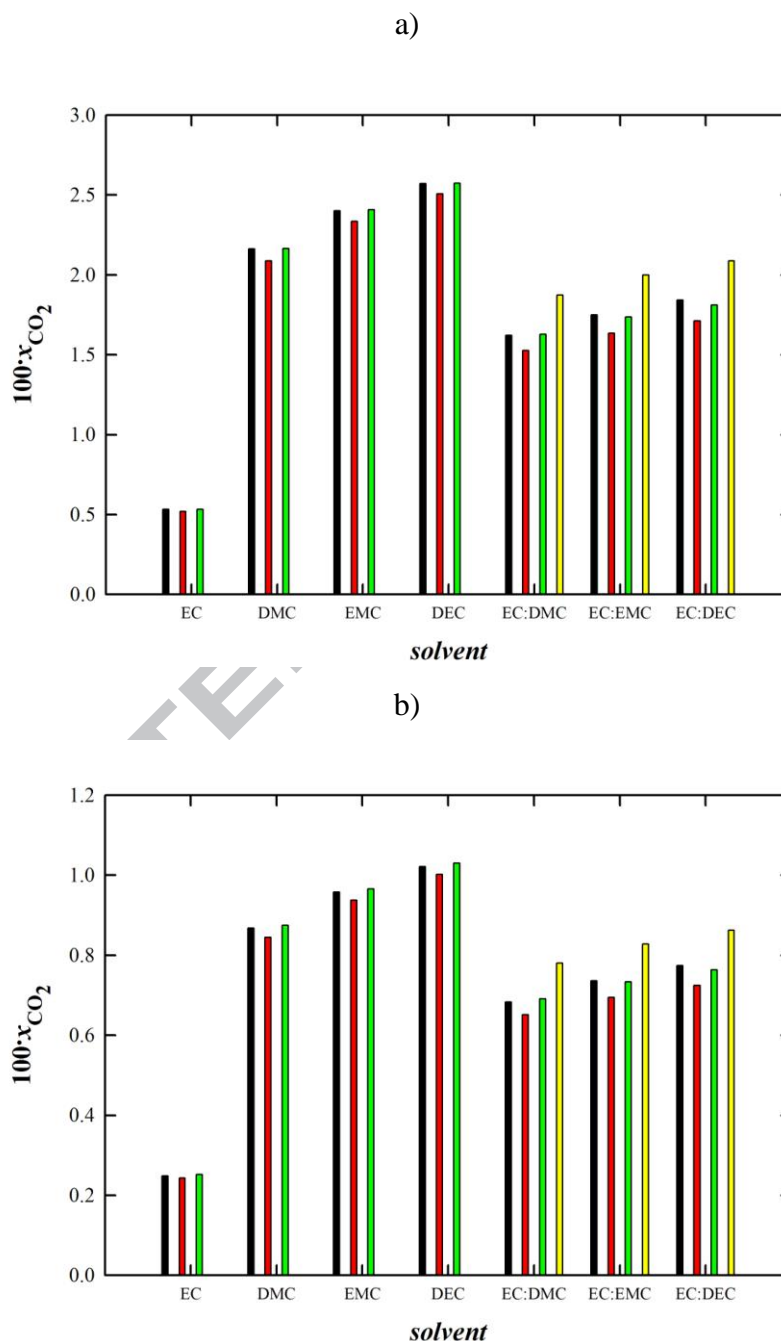
1 **Figure 6.** Comparison between experimental data (bars) of the CO<sub>2</sub> solubility,  
2 expressed in Henry's law constant, in a) EC + 1 mol·dm<sup>-3</sup> LiPF<sub>6</sub>; b) EC + 1 mol·dm<sup>-3</sup>  
3 LiTFSI from table 3 with those calculated by COSMOTermX (dashed lines) as a  
4 function of temperature and atmospheric pressure.  
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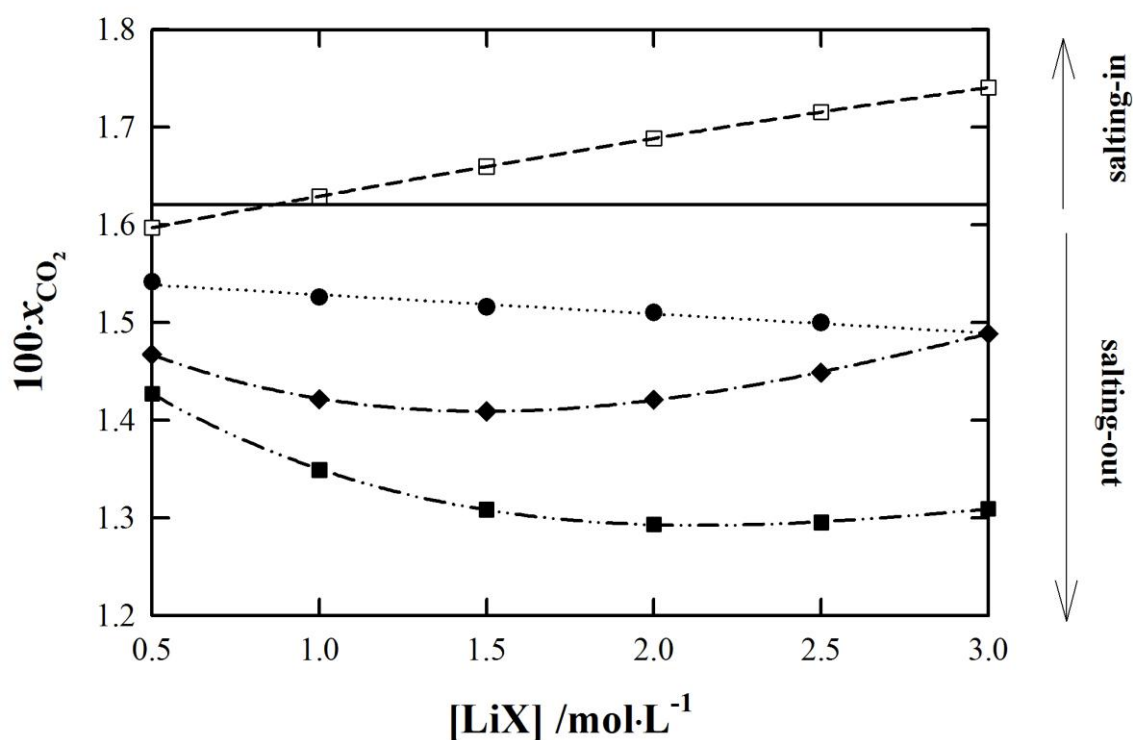
1 **Figure 7.** Comparison between experimental data of CO<sub>2</sub> solubility, expressed in  
2 Henry's law constant, in electrolytes containing 1 mol·dm<sup>-3</sup> LiTFSI dissolved in: ●, EC;  
3 □, DMC; ▲, DEC with those calculated by COSMOTermX: solid, dashed and dotted  
4 lines as a function of temperature and atmospheric pressure, respectively.  
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**Figure 8.** COSMOTermX calculations of the CO<sub>2</sub> solubility in: black bars, pure carbonate or (50:50) wt % carbonate mixtures; red bars, electrolytes containing 1 mol·dm<sup>-3</sup> of LiPF<sub>6</sub>; green bars, electrolytes containing 1 mol·dm<sup>-3</sup> LiTFSI ; yellow bars, electrolytes containing 1 mol·dm<sup>-3</sup> LiFAP at: a)  $T = 298$  K; b) 353 K and 0.1 MPa.



1 **Figure 9.** COSMOTermX calculations of the CO<sub>2</sub> solubility in (50:50) wt %  
 2 EC:DMC-based electrolytes containing; ●, and dotted line: LiPF<sub>6</sub>; □, and dashed line:  
 3 LiTFSI salt defined as an ion-pair; ■, and dashed-dotted line: LiTFSI salt defined as  
 4 two individual ions; ◆, and dashed-dotted-dotted line: LiTFSI salt defined using a  
 5 metafile as a function of the lithium salt (LiX) concentration in solution expressed in  
 6 mol·dm<sup>-3</sup> at *T* = 298.15 K and 0.1 MPa. The solid line represents the CO<sub>2</sub> solubility in  
 7 (50:50) wt % EC:DMC mixture without salt at *T* = 298.15 K and 0.1 MPa.  
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**Table 1.** Source, abbreviation, purity, and water content for each chemical sample reported during this work.

Chemical name	Source	Abbreviation	Mole fraction	Water content
			Purity	$1 \times 10^{-6}$
ethylene carbonate	Aldrich	EC	0.9999	< 10
dimethyl carbonate	Aldrich	DMC	0.9999	< 10
ethyl methyl carbonate	Aldrich	EMC	0.9999	< 10
diethyl carbonate	Aldrich	DEC	0.9999	< 10
lithium hexafluorophosphate	Aldrich	LiPF <sub>6</sub>	0.9999	< 5
lithium bis(trifluoromethylsulfonyl)imide	Solvionic	LiTFSI	0.9999	< 5
lithium tris(pentafluoroethane)trifluorurophosphate <sup>a</sup>	Merck	LiFAP	0.9999	< 10
sodium hydroxide standard solution, 0.5 mol·dm <sup>-3</sup>	Riedel-de Haen	NaOH	-	-
hydrochloric acid standard solution, 1 mol·dm <sup>-3</sup>	Riedel-de Haen	HCl	-	-
carbon dioxide	AGA/Linde Gaz	CO <sub>2</sub>	0.99995	-
argon	AGA/Linde Gaz	Ar	0.999997	-

a, all LiFAP electrolytes were purchased from Merck in solution containing already 1 mol·dm<sup>-3</sup> of LiFAP salt dissolved in each investigated binary solvent mixture.

**Table 2.** Experimental density values of pure solvents as well as of electrolytes containing 1 mol·L<sup>-1</sup> of lithium salt (LiPF<sub>6</sub> or LiTFSI) at  $T = 298.15$  K and atmospheric pressure.

$\rho / \text{g}\cdot\text{cm}^{-3}$ at $T = 298.15$ K <sup>a</sup>					
Solvent	pure solvent	LiPF <sub>6</sub>	100· $\delta$ <sup>b</sup>	LiTFSI	100· $\delta$ <sup>b</sup>
EC	1.35 <sup>c</sup>	1.40	- 3.6	1.42	- 5.1
DMC	1.07	1.14	- 6.6	1.16	- 8.5
EMC	1.01	1.09	- 8.2	1.13	- 12.2
DEC	0.97	1.05	- 8.4	1.10	- 13.5

a, precision and accuracy of the reported experimental data are close to ( $1 \times 10^{-2}$  and  $5 \times 10^{-2}$ ) g·cm<sup>-3</sup>, respectively.

$$\text{b, } 100 \cdot \delta = \frac{\rho_{\text{puresolvent}} - \rho_{\text{electrolyte}}}{\rho_{\text{puresolvent}}}$$

c, measured in its sub-cooled liquid state after heating at  $T = 353$  K.

**Table 3.** Experimental values of CO<sub>2</sub> solubility in selected electrolytes containing 1 mol·dm<sup>-3</sup> of lithium salt (LiPF<sub>6</sub> or LiTFSI) expressed both as Henry's law constants,  $K_H$  and as CO<sub>2</sub> mole fraction,  $x_2$ , at atmospheric pressure.  $\delta$  are relative deviations calculated from each correlation reported in table 4.

<i>Electrolyte</i>	<i>T /K</i>	$10^2 \cdot x_{\text{CO}_2}^a$	$K_H / \text{MPa}^a$	$100 \cdot \delta$
EC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	298.15	0.54	18.27	-0.15
	313.15	0.45	22.15	+0.40
	333.15	0.34	29.03	-0.38
	353.15	0.25	39.27	+0.14
EC + 1 mol·dm <sup>-3</sup> LiTFSI	298.15	0.56	17.69	+0.60
	313.15	0.49	20.40	-1.63
	333.15	0.36	27.63	+1.55
	353.15	0.27	36.85	-0.56
DMC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	283.15	1.28	7.79	-0.22
	298.15	1.00	9.91	+0.38
	313.15	0.79	12.63	+0.16
	333.15	0.57	17.48	-0.61
DMC + 1 mol·dm <sup>-3</sup> LiTFSI	353.15	0.40	24.58	+0.29
	283.15	1.61	6.20	+0.80
	298.15	1.19	8.36	-1.80
	313.15	0.87	11.46	+0.44
EMC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	333.15	0.61	16.38	+1.24
	353.15	0.45	21.88	-0.71
	283.15	1.70	5.85	+2.11
	298.15	1.30	7.32	-5.42
EMC + 1 mol·dm <sup>-3</sup> LiTFSI	313.15	0.96	10.35	+2.55
	333.15	0.70	14.12	+1.91
	353.15	0.55	18.06	-1.38
	283.15	1.87	5.43	+1.74
DEC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	298.15	1.60	6.23	-4.70
	313.15	1.20	8.17	+2.72
	333.15	0.96	10.36	+0.97
	353.15	0.77	12.98	-0.92
DEC + 1 mol·dm <sup>-3</sup> LiTFSI	283.15	1.89	5.27	+0.26
	298.15	1.40	7.10	+0.24
	313.15	1.11	9.19	-2.03
	333.15	0.73	13.62	+2.46
DEC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	353.15	0.55	18.14	-0.98
	283.15	2.11	4.73	+0.87
	298.15	1.72	5.78	-1.43
	313.15	1.38	7.21	-0.93
DEC + 1 mol·dm <sup>-3</sup> LiTFSI	333.15	1.01	9.85	+2.68
	353.15	0.81	12.28	-1.26

a, precision and accuracy of the reported experimental data are close to (1 and 15) %, respectively.[22]

**Table 4.** Parameters of equation (4) used to smooth the experimental CO<sub>2</sub> solubility results from table 3 along with the relative average absolute deviation of the fit (*RAAD*).

<i>Electrolyte</i>	$A_0$	$A_1$	$A_2$	100· <i>RAAD</i>
EC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	+ 17.844	- 6.5002 × 10 <sup>3</sup>	+ 8.1492 × 10 <sup>5</sup>	0.3
DMC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	+ 16.132	- 5.4539 × 10 <sup>3</sup>	+ 6.0027 × 10 <sup>5</sup>	0.3
EMC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	+ 9.5592	- 1.4359 × 10 <sup>3</sup>	- 3.5264 × 10 <sup>4</sup>	2.7
DEC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	+ 12.266	- 3.0595 × 10 <sup>3</sup>	+ 2.0055 × 10 <sup>5</sup>	1.2
EC + 1 mol·dm <sup>-3</sup> LiTFSI	+ 20.510	- 8.3008 × 10 <sup>3</sup>	+ 1.1112 × 10 <sup>6</sup>	1.1
DMC + 1 mol·dm <sup>-3</sup> LiTFSI	+ 10.457	- 1.7591 × 10 <sup>3</sup>	- 1.0021 × 10 <sup>4</sup>	1.0
EMC + 1 mol·dm <sup>-3</sup> LiTFSI	+ 11.417	- 3.1341 × 10 <sup>3</sup>	+ 2.9089 × 10 <sup>5</sup>	2.2
DEC + 1 mol·dm <sup>-3</sup> LiTFSI	+ 11.367	- 3.0466 × 10 <sup>3</sup>	+ 2.5982 × 10 <sup>5</sup>	1.4

**Table 5.** Thermodynamic parameters of CO<sub>2</sub> with selected electrolytes based on a pure carbonate solvent and CO<sub>2</sub> solubility expressed in Henry's Law constant for electrolytes studied at  $T = 298.15$  K and 0.1 MPa.

<i>Electrolyte</i>	$K_H^a$	$\Delta_{\text{dis}}G^{0a}$	$\Delta_{\text{dis}}H^{0a}$	$\Delta_{\text{mix}}H^{0a}$	$\Delta_{\text{dis}}S^{0a}$
	MPa	kJ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>	kJ·mol <sup>-1</sup>	J·K <sup>-1</sup> ·mol <sup>-1</sup>
EC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	18.27	12.94	-12.26	4.64	-84.53
DMC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	9.91	11.42	-14.55	2.35	-87.08
EMC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	7.32	10.77	-13.64	3.26	-81.86
DEC + 1 mol·dm <sup>-3</sup> LiPF <sub>6</sub>	7.10	10.58	-11.51	5.39	-74.09
EC + 1 mol·dm <sup>-3</sup> LiTFSI	17.69	12.85	-11.84	5.06	-82.81
DMC + 1 mol·dm <sup>-3</sup> LiTFSI	8.36	10.98	-15.26	1.64	-88.04
EMC + 1 mol·dm <sup>-3</sup> LiTFSI	6.23	10.25	-10.83	6.06	-70.71
DEC + 1 mol·dm <sup>-3</sup> LiTFSI	5.78	10.07	-11.62	5.28	-72.75

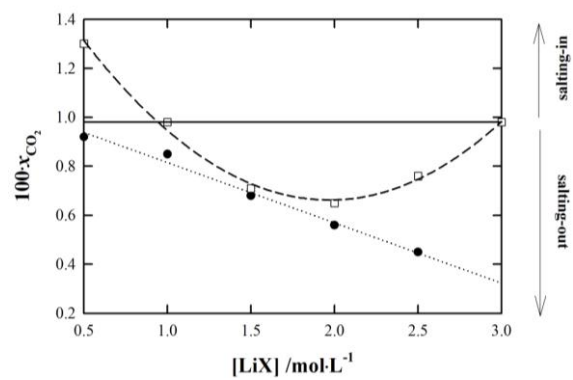
a, accuracy of the reported data are close to 15 %.

**Table 6.** Experimental density values of (50:50) wt % of carbonate binary mixtures, as well as of their solutions containing 1 mol·dm<sup>-3</sup> lithium salt (LiFAP, LiPF<sub>6</sub> or LiTFSI) at  $T = 298.15$  K and atmospheric pressure.

Solvent	$\rho / \text{g}\cdot\text{cm}^{-3}$ at $T = 298.15$ K <sup>a</sup>						
	No salt	LiFAP	100· $\delta$ <sup>b</sup>	LiPF <sub>6</sub>	100· $\delta$ <sup>b</sup>	LiTFSI	100· $\delta$ <sup>b</sup>
EC:DMC	1.23	1.34	- 8.9	1.29	- 4.9	1.31	- 6.5
EC:EMC	1.19	1.32	- 10.9	1.27	- 6.7	1.29	- 8.4
EC:DEC	1.09	1.30	- 19.3	1.25	- 14.7	1.28	- 17.4

a, precision and accuracy of the reported experimental data are close to  $(1 \times 10^{-2}$  and  $5 \times 10^{-2})$  g·cm<sup>-3</sup>, respectively.

$$\text{b, } 100 \cdot \delta = \frac{\rho_{\text{puresolvent}} - \rho_{\text{electrolyte}}}{\rho_{\text{puresolvent}}}$$



ACCEPTED MANUSCRIPT

**Highlights**

- CO<sub>2</sub> solubility is measured in pure alkylcarbonates and their binary mixtures.
- The CO<sub>2</sub> solubility varies significantly for concentration LiPF<sub>6</sub>, LiTFSI and LiFAP salt.
- The dissolution of the CO<sub>2</sub> in all solvents is entropy-driven and exothermic.
- CO<sub>2</sub> solubilities were predicted using COSMOthermX and compared to measurements.