



Short communication

## Interaction between carbon dioxide and ionic liquids: Novel electrolyte candidates for safer Li-ion batteries

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## ARTICLE INFO

## Article history:

Received 31 July 2008

Received in revised form 18 December 2008

Accepted 22 December 2008

Available online 30 December 2008

## Keywords:

RTIL

Ionic liquids

CO<sub>2</sub> absorption

Phase diagram

## ABSTRACT

Ionic liquids (ILs) are typically molten salts at temperatures lower than 100 °C. Because of their thermal and electrochemical properties, they are good candidates to replace the state-of-the-art electrolytes used in today's Li-ion batteries. These commercial batteries often suffer from hazards caused by possible misuse. Elevated voltages and high temperatures usually lead to electrolyte degradation due to parasitic reactions with the electrodes leading to gas (mainly CO<sub>2</sub>) evolution and may then eventually catch fire. Also, ILs are able to dissolve various gas molecules, making it possible to prevent a built-up of an overpressure inside the battery in case of undesired gas evolution. In this work, CO<sub>2</sub> storage in two different ionic liquids, i.e. PYR<sub>14</sub>TFSI and [BMIm][BF<sub>4</sub>] is studied with regard to their respective Li-salt. Mixtures of ILs plus different concentrations of CO<sub>2</sub> were made. Phase diagrams of the pressure vs. temperature of the systems "liquid + vapour" to liquid transitions are drawn. Data points from 1.5 bar to 70 bar are collected with a Cailletet apparatus. Both of the ILs show good CO<sub>2</sub> dissolution ability; an increase of the temperature leads to an increase of the pressure needed to dissolve similar amounts of CO<sub>2</sub>. The presence of a Li-salt hampers gas storage, particularly for PYR<sub>14</sub>TFSI. A model based on the Langmuir adsorption theory is used to describe the solubility of the CO<sub>2</sub> in [BMIm][BF<sub>4</sub>]. The PYR<sub>14</sub>TFSI IL does not obey the Langmuir-like solubility behaviour. Hence, the solubility then is described by the formation of discrete bonds between the CO<sub>2</sub> and the solvent, similarly to the concept of adspecies and surface sites.

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### 1. Introduction

Ionic liquids are attracting enormous interest due to their unique properties. ILs are typically molten salts at temperatures below 100 °C and contain ions in which charge delocalization and sterical hindrance contribute to maintain a liquid state. ILs are non-flammable, non-volatile and stable in a wide electrochemical and temperature window. Besides, they show an acceptable ionic conductivity and they have also good gas storage ability. These properties suggest ILs to be used as electrolytes for electrochemical devices [1]. Among these devices are Li-ion batteries. Today, society is more and more demanding with respect to power and capacity of a battery, and not only for portable electronic devices, but also for future (hybrid) electric vehicles. Sometimes, the use of commercial electrolytes is hampered by their high volatility and flammability. Overcharging and high temperature can make the electrolyte to react with the electrodes forming small gaseous molecules – mainly CO<sub>2</sub>. The overpressure due to the gas evolution can break the housing of the battery. Thus, the reactive components are exposed to air

and may react with oxygen and water so as to catch fire or explode [2–6]. Thanks to the properties of ILs, it is worth to investigate the CO<sub>2</sub> dissolution mechanisms in IL electrolytes with their respective Li-salt.

Interactions between gases and ILs are interesting for many reasons: ILs can be used as solvents for reactions [7], and to separate gas mixtures, even at high temperature. Besides, supercritical fluids can be used to separate species inside ILs [8–16]. Literature data are mainly related to high-pressure gas solubility, near or into the supercritical region, while low-pressure gas solubility studies are in the range from 33 bar to 59 bar [17]. In this study, the solubility of CO<sub>2</sub> in two different ILs, i.e. N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonil)imide (PYR<sub>14</sub>TFSI) and N-butyl-N-methyl-imidazolium tetrafluoroborate ([BMIm][BF<sub>4</sub>]), is studied. In that regard, imidazolium-based ILs are among the first studied ILs with respect to electrochemistry. This is mainly due to their wide voltage window stability and their acceptable conductivity [17]. The presence of acidic hydrogen in the imidazolium ring and consequently the cathode instability, may hamper their use in electrochemical devices [18,19]. Thus, another IL was studied at the same time, i.e. the room temperature IL (RTIL) PYR<sub>14</sub>TFSI. It is stressed that this particular IL has no acid hydrogen in contrast to the imidazolium-based ILs. Besides, it has a wide voltage window

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stability and a good ionic conductivity [17].  $\text{PYR}_{14}\text{TFSI}$ , therefore, can be a good candidate for electrochemical devices [20]. Hence, with these two basically different ILs, it is expected that a different  $\text{CO}_2$  absorption mechanisms will be found. In order to measure the  $\text{CO}_2$  solubility, a Cailletet apparatus is used operating in the pressure range from 1.5 bar until 70 bar [21]. The influence of certain Li-salts is then further analysed with the anion being the respective anion of the IL in question. Hence, these become LiTFSI and  $\text{LiBF}_4$  for  $\text{PYR}_{14}\text{TFSI}$  and  $[\text{BMIm}][\text{BF}_4]$ , respectively. Data points of the phase transition from the biphasic system liquid plus vapour ( $\text{IL} + \text{CO}_2$ ) to liquid are then recorded and discussed using reported data from Cadena et al. [22].

## 2. Experimental

The Cailletet apparatus and the operating method were already described in detail in ref [21]. In this apparatus the pressure can be varied at fixed temperature, or the temperature can be varied at a fixed pressure for a sample with a constant overall composition until a phase transition is visually observed. In general, this setup allows pressures values from 1.5 bar up to 150 in a temperature range from 250 K to 450 K. The main part of the apparatus is a thick-walled Pyrex glass tube, also referred to as the Cailletet pipe, where the sample is located. Its open lower end is connected to an autoclave from where the pressure is applied. The sample was stirred during the measurements. In order to keep the sample at the desired temperature, a water bath was used with accuracy better than 0.02 K. The Cailletet pipe was filled with a known amount of IL (or IL + salt), which was done in a glove box operating under argon in order to avoid any water and oxygen contamination of the sample. The Cailletet pipe was connected to a gas dosing system. The mixture in the tube was degassed by freezing and melting the sample under vacuum. After degassing, a known amount of carbon dioxide was added to the mixture, sealed and finally connected to the autoclave. The amount of moles of carbon dioxide in the calibrated vessel was then calculated by the ideal gas law.

$\text{PYR}_{14}\text{TFSI}$  (99%) and LiTFSI (98%) were purchased from Iolitech. The synthesis of  $[\text{BMIm}][\text{BF}_4]$  was already reported in ref [23]. According to their analysis, the IL seemed to be phase pure. Both of the ionic liquids and the respective Li-salts were stored and handled inside an argon-filled glove-box (MBraun).

## 3. Results and discussion

Figs. 1 and 2 show the  $\text{CO}_2$  dissolution in  $[\text{BMIm}][\text{BF}_4]$  without adding any salt. Fig. 1 also shows data from ref. [22] for comparison. In Fig. 2 the measured data with the Cailletet set-up are presented in an Arrhenius type plot. The energy related to the Arrhenius type equation, is assumed to agree with the solvation energy. These solvation energies  $E_s$  are  $-14.6 \text{ kJ mol}^{-1}$  and  $-16.4 \text{ kJ mol}^{-1}$  for a molar ratio of 0.2 and 0.35, respectively. Therefore, it seems that with increasing the  $\text{CO}_2$  molar ratio, the solvation energy increases. However, to maintain a similar amount of  $\text{CO}_2$  in the solution, a higher pressure is required.

The values found here are compared with the results from Cadena et al. [22]. They presented a mechanism of  $\text{CO}_2$  dissolution in imidazolium-based ILs. They suggest that there is a strong association between the  $\text{CO}_2$  and the  $\text{BF}_4^-$  anions, with the cation being a spectator ion. It has been reported that the effect of changing the anion is much greater than changing the cation [24–28]. Cadena et al. [22] further fitted the solubility curve with a quadratic polynomial function in order to calculate Henry's constant, i.e. so as to fulfil Eq. (1).

$$H = \lim_{x \rightarrow 0} \frac{p}{x} \quad (1)$$

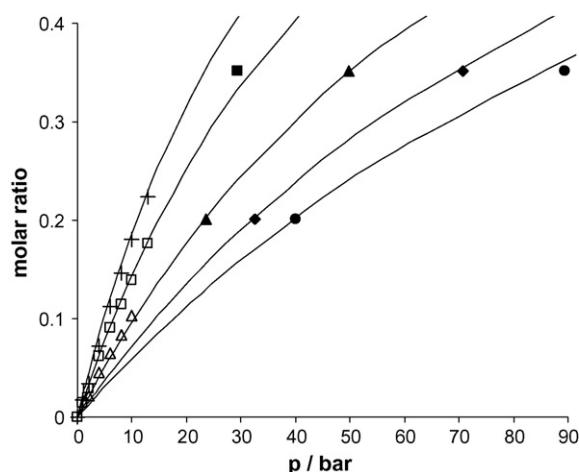


Fig. 1. Phase diagram of  $\text{CO}_2$  dissolution in  $[\text{BMIm}][\text{BF}_4]$  at 10 °C (+); 25 °C (□, ■); 50 °C (Δ, ▲); 70 °C (◆); 85 °C (●), respectively. The values from 0 bar to 20 bar (□, Δ) are taken from Cadena et al. [22], while the pressure values above 20 bar (■, ▲, ◆, ●) refer to the present experiments with the Cailletet apparatus. It is stressed that for the lower temperature data from ref. [22], a hysteresis was reported – here we took only the lowest molar ratio values.

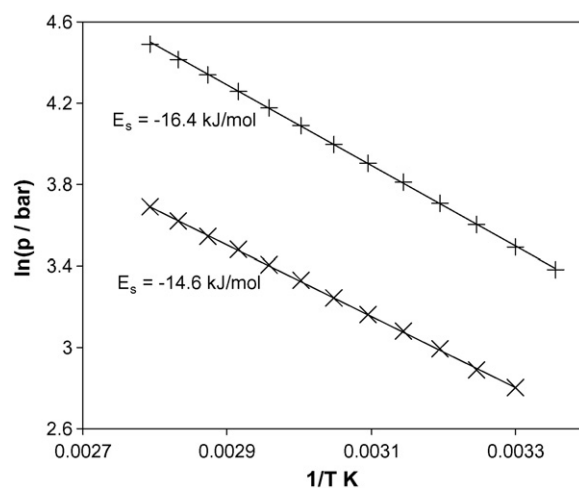


Fig. 2. Modified phase diagram of the dissolution of  $\text{CO}_2$  in  $[\text{BMIm}][\text{BF}_4]$  for two different  $\text{CO}_2$  molar ratios, i.e. 0.20 (x) and 0.35 (+). Measurements were taken from 20 °C to 95 °C. The figure further includes the solvation energy  $E_s$  calculated via an Arrhenius type relation.

Here  $x$  represents the limiting mole fraction of  $\text{CO}_2$  when dissolved into the ionic liquid at pressure  $p$ . For pressures lower than 50 bars, the gas solubility into ILs follows Henry's law. However, above 50 bars, a significant deviation was found and at a given  $P$  and  $T$  the mole fraction of the gas is given rather than concentration in  $\text{moles L}^{-1}$  [17]. Therefore, it seems that the mole fraction is a better quantity to describe the solubility of  $\text{CO}_2$  in the IL, particularly in the pressure interval under study.

Table 1 then shows the fitted data of Henry's constant together with the solvation energy calculated by the Arrhenius equation based on reported Henry's constants [22]. It is stressed that this

Table 1  
Data derived from ref. [22].

$H$ (bar)	25 °C	50 °C	$E_s$ ( $\text{kJ mol}^{-1}$ )	
10 °C	40.8 ± 2.7	56.5 ± 1.4	88.9 ± 3.2	-14.8

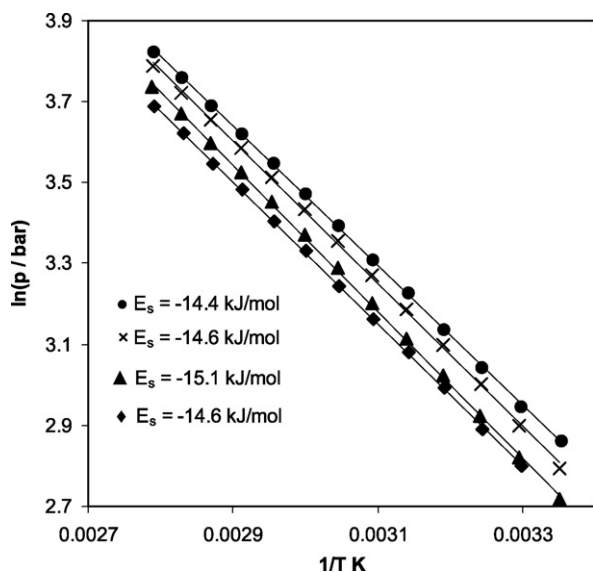


Fig. 3. Modified phase diagram of the dissolution of CO<sub>2</sub> in [BMIm][BF<sub>4</sub>] (molar ratio  $M=0.2$ ) for four different LiBF<sub>4</sub> molar ratios, i.e. 0 (◆); 0.026 (▲); 0.0512 (×) and 0.0748 (●). The figure further includes the solvation energy  $E_s$  calculated via an Arrhenius type relation.

value is not the same as the  $\Delta H$  that was reported by Cadena et al. [22], but the values do not differ much.

The solvation energy  $E_s$  derived from ref. [22], i.e.  $-14.8 \text{ kJ mol}^{-1}$  and  $E_s$  calculated for the present work are very close.  $E_s$  does not change much going from zero to a molar fraction of 0.2. Therefore, it is anticipated that the solvation mechanism does not change in this range, and a mechanism that can describe this is a Langmuir type dissolution mechanism, taking into account that at low CO<sub>2</sub> molar ratios, Henry's law can be applied. This theory is also referred to as Michaelis-Menten theory in biochemistry. It is stressed that the solubility then is described by the formation of discrete bonds between the CO<sub>2</sub> and the solvent, i.e. one CO<sub>2</sub> molecule per dissociated ion. The equation to describe the solubility is then given by:

$$M = \frac{M_{\max} k P}{1 + k P} \quad (2)$$

where  $M$  is the molar ratio of the dissolved gas,  $M_{\max}$  is the maximum molar ratio – that is theoretically taken to be one (unity),  $k$  is the dissolution constant and is equal to the inverse of Henry's constant  $H$ , and  $P$  is the pressure. Clearly, at  $P$  close to 0, Eq. (2) transfers to Henry's law. In order to calculate  $k$  and thus  $H$ , we used the Arrhenius equation with  $E_s$  obtained from our data and to scale it to the data point at 95 °C at  $M=0.35$ . In Fig. 1 several fitted curves have been plotted based on the newly calculated Henry's constant. The curves for the data from Cadena et al. [22] are given as well. The agreement with the Langmuir isotherm is very good up to a molar ratio of 0.2. Nevertheless, at higher CO<sub>2</sub> molar ratios, i.e. over 0.2, the interaction between CO<sub>2</sub> and the solvent and/or between CO<sub>2</sub> and CO<sub>2</sub> is involving other numbers of positions, as is the case in a Langmuir adsorption isotherm. This effect is clearly reflected by a shift in  $E_s$  from  $-14.6 \text{ kJ mol}^{-1}$  to  $-16.4 \text{ kJ mol}^{-1}$ . This phenomenon is still under study, and NMR results could give an answer to that.

When adding the respective Li-salt, i.e. LiBF<sub>4</sub>, the solvation energy does not change much as shown in Fig. 3. Also the pressure to maintain a similar CO<sub>2</sub> molar ratio does not change much. Clearly, the [BMIm][BF<sub>4</sub>] IL is fairly insensitive for LiBF<sub>4</sub>. The situation for the other IL, PYR<sub>14</sub>TFSI, is completely different. The data as shown in Fig. 4, do not reveal a linear relation of the Langmuir-type isotherm when plotting  $1/M$  vs.  $1/p$ . However, in order to obtain

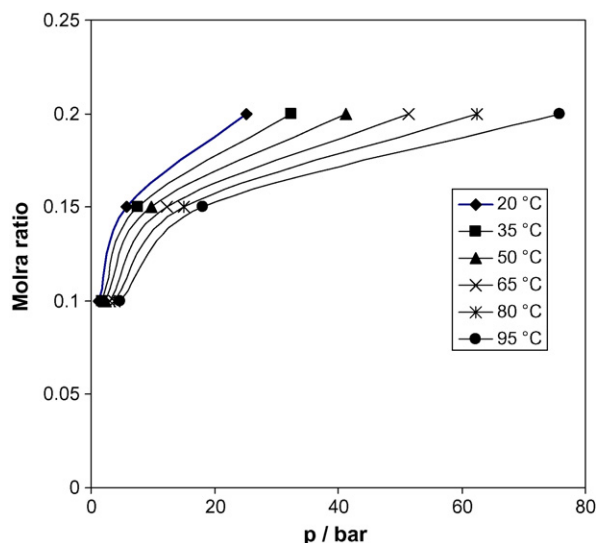


Fig. 4. phase diagram of CO<sub>2</sub> dissolution in PYR<sub>14</sub>TFSI (molar ratio  $M=0.1$ ; 0.15 and 0.2) at different temperatures.

the CO<sub>2</sub> solubility at various temperatures for 1 atmosphere, the data are plotted as  $\log(P/\text{bar})$  vs.  $M$  (Fig. 5). Here then, straight lines can be obtained for all pressures, and by extrapolating the lines down to 1 bar ( $\sim 1 \text{ atm.}$ ) the CO<sub>2</sub> solubility can be found. The solvation energies, given in Fig. 6, are dependent on the CO<sub>2</sub> molar ratio, and changes from  $14.9 \text{ kJ mol}^{-1}$  to  $13.2 \text{ kJ mol}^{-1}$  going from  $M=0.1$  to  $M=0.2$ , respectively. This indicates a changing interaction between the dissolved CO<sub>2</sub> molecules and the solvent, and this then cannot account for a Langmuir-type of mechanism. Also, the pressure required to maintain a similar CO<sub>2</sub> molar ratio at different temperatures is significantly different. Obviously, this IL is strongly sensitive to the CO<sub>2</sub> molar ratio. The effect is also significantly different when adding the respective Li-salt (Fig. 7). A model for the understanding of this behaviour is underway. A possible model may be a Langmuir-Hinshelwood mechanism, in which a competition takes place for the active sites of the ion between the CO<sub>2</sub> molecule and other species in the solution. Eventually, the various ions, thus seen as providing the active sites, may bind to less or more CO<sub>2</sub> molecules than one, as was found for the [BMIm][BF<sub>4</sub>] ionic liquid. To understand this more complicated mechanism, NMR and Infrared spectroscopy measurements are being conducted, so as to

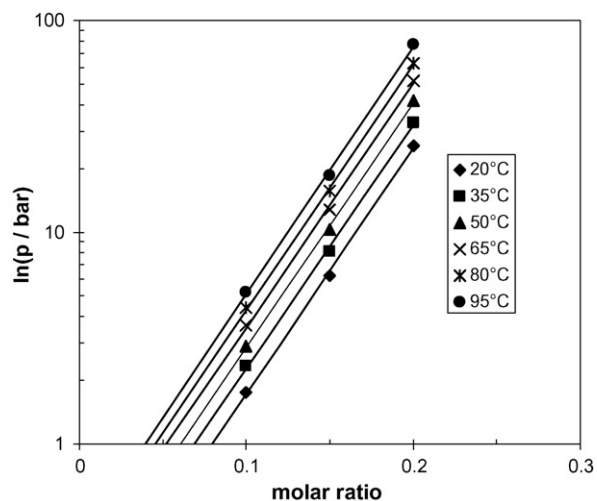
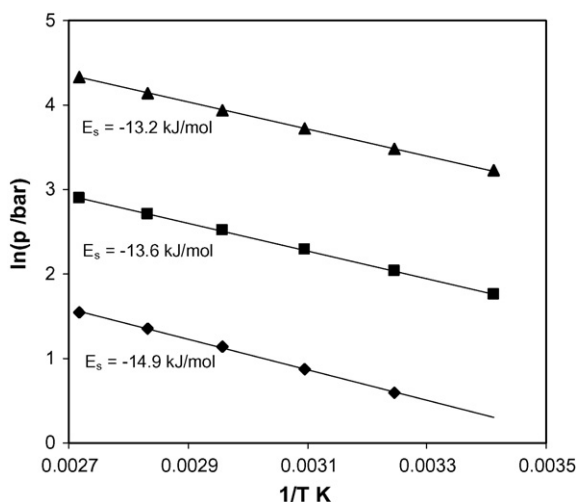
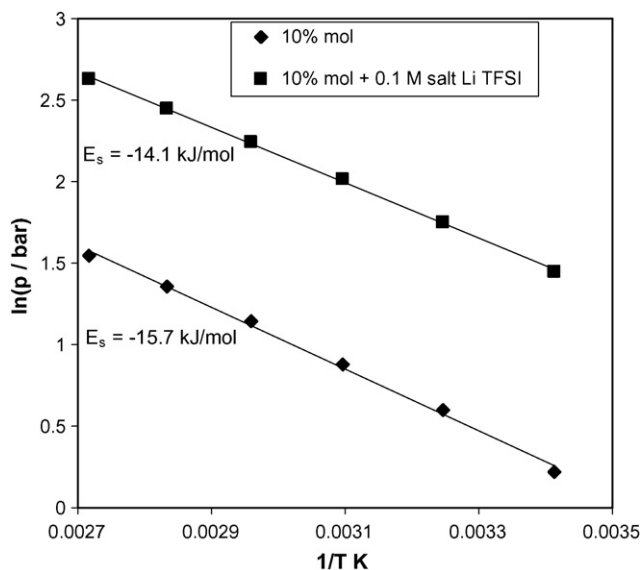


Fig. 5. Modified phase diagram of CO<sub>2</sub> in PYR<sub>14</sub>TFSI (molar ratio  $M=0.1$ ; 0.15 and 0.2) at different temperatures, where  $\ln(p)$  is given as a function of the molar ratio.



**Fig. 6.** Modified phase diagram of the dissolution of CO<sub>2</sub> in PYR<sub>14</sub>TFSI for three different molar ratios, i.e. 0.1 (◆); 0.15 (■) and 0.2 (▲). The figure further includes the solvation energy  $E_s$  calculated via an Arrhenius type relation.



**Fig. 7.** Modified phase diagram of the dissolution of CO<sub>2</sub> in PYR<sub>14</sub>TFSI (molar ratio  $M=0.1$ ) for two different LiTFSI molar ratios, i.e. 0 (◆); and 0.0286 (■). The figure further includes the solvation energy  $E_s$  calculated via an Arrhenius type relation.

find out the bonds between the active sites and the CO<sub>2</sub> molecule. This then may affect the solubility of the CO<sub>2</sub> significantly when adding extra species, such as a lithium salt.

#### 4. Conclusions

Ionic liquids (ILs) are potential candidates for use as liquid solvents for electrolytes in Li-ion batteries because of their low vapour pressure, wide voltage and temperature stability. Besides, they have a high CO<sub>2</sub> storage capacity, which make them interesting for reducing the pressure build-up during parasitic reactions in the battery. Here two different ILs, i.e. [BMIm][BF<sub>4</sub>] and PYR<sub>14</sub>TFSI, have been studied in that respect. [BMIm][BF<sub>4</sub>] shows a Langmuir type isotherm of solubility with solvation energy of 14.6 kJ mol<sup>-1</sup>. The Langmuir model then allows calculating the solubilities at various temperatures and CO<sub>2</sub> pressures. The CO<sub>2</sub> storage capacity is 1.66%mol at 25 °C and 1 atmosphere (molar ratio  $M=0.0166$ ). The

model can be used to a CO<sub>2</sub> molar ratio of about 0.2. At higher molar ratios, the solvation energy increases, indicating that the CO<sub>2</sub> bonding to the solvent has changed. When adding the concordant Li-salt LiBF<sub>4</sub>, only a small change in the CO<sub>2</sub> storage capacity was found. However, the solvation energy does not change. The situation with PYR<sub>14</sub>TFSI is completely different. This IL does not obey the Langmuir-type solubility. The solvation energy is strongly dependent on the molar ratio, indicating a strong interaction between the CO<sub>2</sub> and the IL. The CO<sub>2</sub> storage capacity of PYR<sub>14</sub>TFSI is 7.6%mol ( $M=0.076$ ) at 25 °C and 1 atmosphere, which has been calculated by extrapolation. When adding the respective lithium salt, i.e. LiTFSI, a three times higher pressure of CO<sub>2</sub> is required to dissolve the same amount of CO<sub>2</sub> in the solution. Apparently, Li-ions are replacing the CO<sub>2</sub> in the solvent. The solvation energy also changes and goes to lower values.

#### Acknowledgments

This work would not be possible without the help of Louw Florusse and Eugene Straver for their training how to use the Cailletet apparatus. Thanks also to Cor Peters' group for the interesting and helpful discussions. Furthermore, the Alistore Network of Excellence is acknowledged for the fruitful discussions.

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