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Turning the solubility and lubricity of ionic liquids by absorbing CO_2

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ABSTRACT

Ionic liquids (ILs) attract high interest as lubricants or lubricant additives due to their special physicochemical characteristics. CO_2 is a widely distributed gas. In many situations, its influence on lubricants cannot be avoided. In this work, three ILs are synthesized from choline and amino acids of glycine, L-proline and lysine, respectively. The influence of CO_2 absorption on their solubility and lubricity is investigated. In general, it is interesting to find that the solubility is decreased and their lubricity is obviously improved after absorbing CO_2, which is strongly related to their functional group (amino group) interactions with CO_2. The formation of carbamate groups greatly increases the viscosity resulting in less solid contacts, and strengthens the interfacial adhesion between ILs and solids.

1. Introduction

Carbon dioxide (CO_2) is a widely distributed gas, which can be dissolved in many liquids through physical or chemical action. For physical absorption, *e.g.* by water and Polyalkylene glycol (PAG), the absorption is very low at ambient pressure but increases substantially with the increasing pressure of CO_2. For chemical absorption, the liquids with functionalized groups, *e.g.* amino group, can absorb CO_2 by relatively large amount at low pressure. Since room temperature ionic liquids (ILs) were found with high solubility of CO_2 [1], on-going efforts have been paid to evaluate new ILs and their solutions as potential absorbents for CO_2 capture [2–4]. After absorbing CO_2 through chemical action, physical and chemical properties of ILs are significantly changed, *e.g.* the viscosity is remarkably increased. The properties change of typical liquids after absorbing CO_2 is listed in Table 1.

ILs have generated great interests in fields including lubrication, chemical transformations, electrochemical applications, extractions, *etc.* due to their special physicochemical characteristics, such as high polarity, negligible vapor pressure, and nonflammability [5–8]. Since ILs have high stability and high polarity which make them strongly adhered to solid surfaces, they can form an effective adsorption film on the rubbing surfaces working as novel lubricants. At high temperature and high vacuum which is common in the space environment, ILs retain excellent lubricating properties making them good substitutes to traditional lubricants [5,9]. In addition, ILs can also be applied as anti-wear additives to traditional base lubricants, which can stand the load and reduce solid contacts by forming a robust protective surface film [10,11]. The past years have witnessed a fast development of ILs-based lubricants. The variety of ILs satisfies them with the application for different kinds of materials, in harsh operating conditions like elevated temperatures and high vacuum, toward nanoscale lubrication, as thin films *etc.* [12–15].

It is well-known that gaseous atmospheres can affect the tribological properties of lubricants, especially when there is chemical reaction between the gas and lubricants [16–18]. A few literatures reveal that CO_2 has negative influence on wear and friction [19–21]. It is speculated that CO_2 absorption will greatly affect the lubrication behaviour of ILs, since CO_2 will significantly change their physical and chemical properties. However, such influence is little studied until now.

In this work, ILs from choline and three natural amino acids: glycine, L-proline and lysine are synthesized as base lubricants and additives in poly(ethylene glycol) 200 (PEG). The solubility and lubricating properties of ILs and IL/PEG prior to and after CO_2 absorption are studied. The influence mechanism of CO_2 absorption on ILs' solubility and lubricity is discussed.

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Table 1
CO_2 absorption in typical liquids and the resulting properties change.

Liquid	Condition	CO_2 absorption ($mol_{CO2}/mol_{absorbent}$)	Properties change after absorbing CO_2
Water [45]	293.15 K, 1-10 bar	7.2×10^{-4}~6.8×10^{-3}	CO_2 reacts with water to form CO_2(aq), H_2CO_3, HCO_3^-, and CO_3^{2-}.
30%MEA/water [46]	293.15–353.15 K, 1 bar	0.5	Viscosity increases by 50% at 298.15 K
PAG [16,47]	295.15 K, 14 bar	~0.89[a]	CO_3^{2-} were formed, which improved the scuffing resistance
[EMIm][Tf_2N] [48]	298.15 K, 1-13 bar	0 (negligible)~0.28	Viscosity decreased, worse antifriction and anti-wear performance
[BMPyrr][DBP] [48]	313 K, 5 bar	The ability is close to [EMIm][Tf_2N]	Viscosity decreased, a little better antifriction but worse anti-wear performance
[H_2N-PBIm][BF_4] [49]	~295 K, 1 bar	0.449	Ammonium carbamate salt was formed
25% [Choline][Proline]/PEG200 [29]	308.15 K, 0.832 bar	0.611	Carbamate salt with strong strength was formed

MEA: monoethanolamine, POE: Polyol ester, PAG: Polyalkylene glycol, [EMIm][Tf_2N]: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMPyrr][DBP]: 1,1-Butyl-methylpyrrolidinium dibutyl phosphate, [H_2N-PBIm][BF_4]: 1-butyl-(3-aminopropyl) imidazolium tetrafluoroborateExperimental section.
[a] The value was taken from PAG0, the molecular weight of which was estimated as 659 g/mol [47].

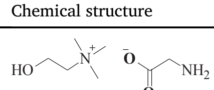
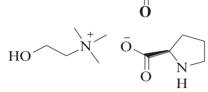
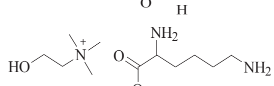
2. Material and methods

2.1. Materials and preparation of ILs-based lubricants

ILs from amino acids as green and high-performance lubricants are of interest to a big scientific community in the context that ionic liquid lubricants should be readily available and environmentally friendly [22–26]. In this work, three ILs, namely [Cho][Gly], [Cho][Pro] and [Cho][Lys] (shown in Table 2), were synthesized from choline hydroxide solution (46 wt% in water, Sigma-Aldrich, USA) and amino acids: glycine, L-proline and lysine (purity ≥ 99.99 wt%, China National Medicines Corporation Ltd.) by previous method [22].

For the description of the synthesis detail, [Cho][Lys] is taken as an example here. First, 15.349 g (0.105 mol) lysine was added into 26.343 g choline hydroxide solution with 0.1 mol choline hydroxide. The mixture was stirred for 48 h at room temperature. Then, it was washed with ethyl acetate to remove the excessive amino acids. In the end, the obtained

Table 2
Synthesized ILs in this work.

[Cho][AA]	Full name	Chemical structure
[Cho][Gly]	Cholinium glycinate	
[Cho][Pro]	Cholinium L-prolinate	
[Cho][Lys]	Cholinium lysinate	

mixture was subjected to rotary evaporation under 70 °C for 1 h, then dried in a vacuum oven at 343 K for 2 days to get the products. The synthesis of [Cho][Gly] and [Cho][Pro] was similar to that of [Cho][Lys].

In order to study the influence of CO_2 absorption on the solubility and lubricity of ILs as lubricant additives in PEG, ILs were added to PEG to get homogeneous IL/PEG mixtures as the same dissolving method described in Ref. [27]. A loading of 10 wt% IL was selected in this work, considering that the non-corrosive ILs at relatively higher loading maintain good lubricating performance through physical adsorption [22], and the influence of CO_2 absorption will be obvious at high IL loading. The PEG with an average molecular weight of 200 g/mole was procured from China National Medicines Corporation Ltd. It was dried under vacuum at 343 K for 48 h before use. The water content was measured by Karl Fischer titration (Shanghai Peiou, V100). CO_2 with high purity (≥99.99 wt%) was supplied by Nanjing Tianhong gas factory, China.

2.2. Characterizations

The structure of [Cho][Lys] was identified by ^1H NMR spectroscopy (Bruker AV-300, tested at 500 MHz, 303 K) using D_2O as solvent with tetramethylsilane as an internal standard. The synthesis of [Cho][Gly] and [Cho][Pro] was proved in our previous work [28].

The CO_2 absorbing performance of ILs and IL/PEG was evaluated under room temperature of approximately 25 °C and ambient pressure. The liquid was put in a sealed Erlenmeyer flask and kept being stirred, then the CO_2 gas was injected into the flask and exhausted from the outlet pipe. The absorbed CO_2 amount was obtained by measuring the mass gain with an analytical balance with an accuracy of 0.01 mg.

The viscosity of liquids at 25 °C and 1–100 s^{-1} shear rate was investigated with a Bohlin CVO 100 rheometer.

2.3. Solubility of ILs after CO_2 absorption

After CO_2 absorption, precipitates may be produced for the decreased solubility of ILs. To investigate CO_2 absorption influence on ILs' solubity, particle size distribution IL/PEG mixtures before and after CO_2 absorption was measured by photon correlation spectroscopy using a Zetasizer Nano ZS90 instrument (Malvern Instruments Ltd., Worcestershire, UK).

2.4. Tribological tests

Tribological properties of the lubricants were evaluated with an Optimol SRV-III oscillating friction and wear tester based on ASTM D 6425 protocol. The upper steel ball slides under reciprocating motion against a stationary steel disc at a given frequency of 50 Hz with an amplitude of 1 mm (corresponding to the sliding velocity of 0.1 m/s). The ball (100Cr6 steel, diameter 10 mm, surface roughness (Ra) 20 nm, provided by SKF, Sweden) and disc (100CR6 ESU hardened, Ø24 mm × 7.9 mm, and surface roughness (Ra) 120 nm, supplied by Optimol Instruments Prüftechnik GmbH, Germany) were cleaned with

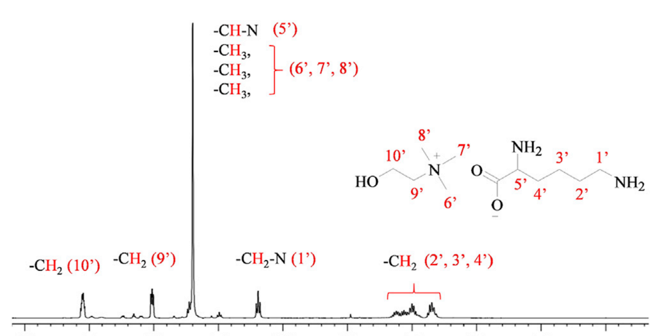


Fig. 1. ^1H NMR results of the synthesized [Cho][Lys].