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Solubilities of carbon dioxide in the eutectic mixture of levulinic acid (or furfuryl alcohol) and choline chloride

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ABSTRACT

The solubilities of carbon dioxide (CO_2) in the renewable deep eutectic solvents (DESs) containing levulinic acid (or furfuryl alcohol) and choline chloride were determined at temperatures (303.15, 313.15, 323.15, and 333.15) K and pressures up to 600.0 kPa using an isochoric saturation method. The mole ratios of levulinic acid (or furfuryl alcohol) to choline chloride were fixed at 3:1, 4:1 and 5:1. Standard Gibbs free energy, dissolution enthalpy and dissolution entropy were calculated from Henry's law constant of CO_2 in the DESs. Results indicated that levulinic acid based DESs are more effective to capture CO_2 than furfuryl alcohol based ones. The solubility of CO_2 in the DESs increased with increasing mole ratio of levulinic acid (or furfuryl alcohol) to choline chloride as well as pressure and decreased with increasing temperature.

1. Introduction

Serious greenhouse effect and resulting environmental problems has raised public attention worldwide [1,2]. CO_2, identified as the main greenhouse gas, is inevitably produced in large qualities from the burning of fossil fuels. Therefore, carbon capture and sequestration (CCS) have been the focus of many researches in recent years [3]. The principal technologies for CO_2 capture include absorption, adsorption, membrane separation, and cryogenic separation [4]. Currently, the industrial and commercial amine-based absorbents for carbon capture at post-combustion conditions have several inherent drawbacks, including the solvent loss, equipment corrosion, and high energy requirements for regeneration [4–8]. Thus, the development of economic and environmentally-friendly absorbents for CO_2 capture has always been desirable.

Ionic liquids (ILs) are extensively reported as a kind of new and "promising" absorbent for CO_2 in the past two decades due to their unique properties, such as high thermal stability, extremely low volatility, diversity, and tuneable properties [9–11]. However, ionic liquids still have several shortcomings including high price, complicated technology for production and purification, uncertain toxicity and poor biodegradability [12]. Hopefully, the emerging deep eutectic solvents (DESs), known as an advanced generation of ILs, seem to be good candidates [13]. The DESs were found to have many interesting solvent properties that are similar to conventional ILs. Moreover, DESs have the advantages such as acceptable cost, good biodegradability, renewability, and low-toxicity [14]. DES is easy to prepare by directly mixing hydrogen bond donor (HBD) and hydrogen bond acceptor (HBA), which form a eutectic mixture with lower melting point than its original precursors through hydrogen-bond network [15,16]. Since Abbott adopted the term of "deep eutectic solvents" (DESs) in 2003 [17], DESs have attracted increasing attentions over the past ten years. The scope of HBD has been expanded to include alcohols [18], sugars [19], organic acids [20], and amides [21], while HBA merely focuses on quaternary ammonium salts [22,23] and quaternary phosphium salts [24]. DESs were also widely used as media in chemical reaction [25–27], electro-deposition [28,29] and extraction separation [30–33] with encouraging results. Recent works explored the possibility of DESs as the absorbents for CO_2 capture. For example, Li's group [34–36] have measured the solubility of CO_2 in 1:2 mol choline chloride–urea DES (commercial name: reline), aqueous DES (choline chloride/ethylene glycol, choline chloride/glycerol, choline chloride/malonic acid) systems, aqueous blends of (reline + monoethanolamine). Francisco *et al.* [12] reported the CO_2 capture using natural 1:2 mol (choline chloride + lactic acid) DES. Li *et al.* [37] reported the solubility data of CO_2 in the eutectic mixture of choline chloride and urea at temperatures (313.15, 323.15, and 333.15) K under pressures up to 13 MPa. In our previous works [38,39], the solubility of CO_2 in the DESs composed of choline chloride and HBDs like phenol, 1,4-butanediol, 2,3-butanediol,

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1,2-propanediol, diethylene glycol, and triethylene glycol were determined. As a continuation of our study, we will present new measurements on the solubility of CO_2 in the renewable DESs containing levulinic acid (or furfuryl alcohol) and choline chloride at temperatures (303.15, 313.15, 323.15, and 333.15) K and pressures up to 600 kPa by the isochoric saturation method. The mole ratios of levulinic acid (or furfuryl alcohol) and choline chloride were fixed at 3:1, 4:1 and 5:1. For the better understand of dissolution behaviour of CO_2 in the DESs, Henry's law constant, standard Gibbs free energy, dissolution enthalpy, and dissolution entropy were further calculated from the solubility of CO_2 in the DESs.

2. Experimental

2.1. Chemicals

The CO_2 (mass fraction purity >0.9995) was supplied by Jingong Special Gas Co., Ltd. Choline chloride (mass fraction purity >0.985) was supplied by Jinan Hualing Pharmaceutical Co., Ltd. Levulinic acid (mass fraction purity $\geqslant$0.985) and furfuryl alcohol (mass fraction purity $\geqslant$0.982) were obtained from Shanghai Aladdin Chemical Reagent Co., Ltd. The summary of the chemicals used, their purities, and sources are listed in table 1. The DESs were prepared by directly mixing choline chloride and levulinic acid (or furfuryl alcohol). The water mass fraction of each DES was determined by Karl Fischer analysis (SF-3 Karl-Fischer Titration, Zibo Zifen Instrument Co. Ltd.) with the result of less than $9.6 \cdot 10^{-4}$ in all cases. The density of the DESs was carefully measured at temperatures (303.15, 313.15, 323.15, and 333.15) K under 101.3 kPa using pycnometer (its volume was first calibrated with double-distilled water at each experimental temperature) immersed in a thermostatic oil-bath. The mass of the DESs was weighed by electronic balance (Mettler-Toledo AL204) with an estimated uncertainty of $\pm 2 \cdot 10^{-4}$ g. A DSC (differential scanning calorimeter, NETZSCH 200 F3) was used to measure the melting points of present DESs. In the DSC experiment, the samples were continuously purged with 50 mL · min^{-1} of dried nitrogen. The temperature was calibrated using indium (mass fraction purity >0.99999, T_m = 429.76 K). About (10 to 25) mg of the DES were crimped in an aluminium standard sample pan and analysed under a nitrogen atmosphere by cooling-heating (2 K · min^{-1}) cycles between T = (173.15 and 283.15) K. The temperature-dependent thermal curves were recorded (figures S1 and S2). The first curve transition temperature was selected as the melting point, which corresponded to the solidus of the DES (beginning of melting). The melting points of DESs are listed in table 2.

TABLE 1
Description of chemicals used in the study.

Chemical	Source	Mass fraction purity
Carbon dioxide	Jingong Special Gas Co., Ltd.	>0.9995
Choline chloride	Jinan Hualing Pharmaceutical Co., Ltd.	>0.985
Levulinic acid	Shanghai Aladdin Chemical Reagent Co., Ltd.	$\geqslant$0.985
Furfuryl alcohol	Shanghai Aladdin Chemical Reagent Co., Ltd.	$\geqslant$0.982

2.2. Apparatus and procedures

A stainless apparatus as illustrated in our previous work [38] was used to measure the solubility of CO_2 in the DESs. It was mainly composed of gas equilibrium cell (EC) and gas reservoir (GR) with the volumes of (141.61 and 370.99) cm^3, respectively. The temperature was carefully controlled using thermostatic water baths with a precision of ±0.05 K. The pressure was monitored by pressure transmitter (Fujian WIDEPLUS Precision Instruments Co., Ltd, WIDEPLUS-8, 0-600.0 kPa) with an accuracy of ±0.1% full-scale.

The solubility of CO_2 in the DESs was determined using an isochoric saturation method [40]. The detailed experimental procedures were described in our previous works [38,39]. In a typical run, the temperature of GR was kept at 303.15 K. After a known mass of DES (about 60 to 80 g, the accurate mass of the DES, w, was weighted by electronic balance) was added into the EC, the air in the whole system was evacuated to pressure p_0. Keeping the valve needle between GR and CO_2 cylinder open, GR was charged with CO_2 up to pressure p_1. The temperature of EC was set at T using a thermostatic water bath. Keeping the needle valve between GR and EC open, CO_2 was transferred into EC to contact with DES. (Gas + liquid) equilibrium was supposed to be reached if the pressure of EC kept unchanged within 2 h. The final pressures were recorded as p_2 for GR and p_3 for EC. Then, the partial pressure of CO_2 at equilibrium was calculated as following,

$$p_s = p_3 - p_v \quad (1)$$

where p_s is the partial pressure of CO_2 at equilibrium state. p_v represents the saturated vapour pressure of DES at the experimental temperature. In present work, the values of p_v are indirectly determined using the TGA analysis according to literature method [41]. In brief, the evaporation rates of DES and reference substance (RS) were recorded under the same conditions, respectively. Levulinic acid and furfuryl alcohol were selected as reference substances for (levulinic acid + choline chloride) and (furfuryl alcohol + choline chloride) mixtures, respectively. The saturated vapour pressures of two reference substances were taken from literatures [42,43]. The p_v of DES was calculated as the produce of following two parts, p_v of reference substance and the evaporation rate ratio of DES to RS. The values of p_v for two DESs are listed in Table 2. The absorbed CO_2 (n_{CO_2}) was calculated by the following equation,

TABLE 2
Physical properties of the deep eutectic solvents studied (DESs) (expressed by mole ratio of levulinic acid or furfuryl alcohol to choline chloride, the same below): melting points (T_m, under p = 101.3 kPa), density (ρ, under p = 101.3 kPa) and saturated vapour pressure (p_v) at different temperatures.[a]

Solutions	T_m/K	ρ/(g · cm^{-3})				p_v/Pa			
		303.15	313.15	323.15	333.15	303.15	313.15	323.15	333.15
$n_{levulinic\ acid}$: $n_{choline\ chloride}$ = 3:1	262.0	1.1346	1.1276	1.1209	1.1138				4.3
$n_{levulinic\ acid}$: $n_{choline\ chloride}$ = 4:1	263.0	1.1341	1.1273	1.1204	1.1131				5.5
$n_{levulinic\ acid}$: $n_{choline\ chloride}$ = 5:1	263.2	1.1337	1.1270	1.1202	1.1130				7.7
$n_{furfuryl\ alcohol}$: $n_{choline\ chloride}$ = 3:1	237.4	1.1318	1.1252	1.1186	1.1120	49	114	242	436
$n_{furfuryl\ alcohol}$: $n_{choline\ chloride}$ = 4:1	238.6	1.1315	1.1243	1.1171	1.1099	57	123	255	461
$n_{furfuryl\ alcohol}$: $n_{choline\ chloride}$ = 5:1	239.4	1.1309	1.1238	1.1166	1.1095	64	133	266	479

[a] Standard uncertainties u are $u(T)$ = 0.05 K, $u(T_m)$ = 0.1 K, $u(p)$ = 0.6 kPa, $u(p_v)$ = 1.0 Pa and the combined expanded uncertainty Uc is $Uc(\rho)$ = 0.0008 g · cm^{-3} (0.95 level of confidence). The standard uncertainty of mole ratio of levulinic acid or furfuryl alcohol to choline chloride is 0.001.