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Choline-based deep eutectic solvents for CO_2 separation: Review and thermodynamic analysis

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ABSTRACT

CO_2 separation plays an important role in energy saving and CO_2 emission reduction, both of which are necessary to address the issue of global warming. Ionic liquids (ILs) have been proposed to be "green" solvents for CO_2 separation. Unfortunately, the high cost, toxicity, and poor biodegradability of these compounds limit their large-scale application. Deep eutectic solvents (DESs) were recently considered a new type of IL with additional advantages in terms of cost, environmental impact, and synthesis. DESs based on choline salts (i.e., choline-based DESs) are promising candidates for CO_2 separation. In this work, the microstructures, physicochemical properties, and water effect of choline-based DESs are surveyed and compared with those of conventional ILs. The properties of choline-based DESs are similar to those of conventional ILs, but research on the latter remains limited. Further study on the microstructures, properties, and separation performance of choline-based DESs considering dynamic factors must be carried out through experimental measurements and model development. Thermodynamic analysis based on Gibbs free energy change is conducted to investigate the performances of choline-based-DESs during CO_2 separation from biogas. Choline-based-DESs are screened on the basis of energy use and amount of absorbent needed. The performances of the screened choline-based-DESs are further compared with those of conventional ILs screened in our previous work, as well as commercial CO_2 absorbents. Comparisons indicate that the screened DES-based absorbents show great application potential due to their nonvolatility, low energy use, or low amount required. The performances of physical choline-based-DES and 30 wt% MEA for CO_2 separation from other gas streams (e.g., flue gas, lime kiln gas, and bio-syngas) are discussed. Considering the high amounts of physical absorbents required to enable separation, further study with techno-economic analysis needs to be carried out.

1. Introduction

Global warming is a critical issue mainly attributed to increased concentrations of greenhouse gases, especially anthropogenic CO_2 [1]. CO_2 emissions are mainly produced from combustion of fossil fuels, transportation, and other industries (e.g., lime industry). In efforts to mitigate anthropogenic CO_2 emissions from large point sources (e.g., flue gas from fossil-fuelled power station and lime kiln gas from lime industry), carbon capture and storage (CCS) has been proposed to be an effective way to prevent the release of large quantities of CO_2 into the atmosphere, e.g., 28.7–32.3 Gton CO_2 in 2014 [2]. Carbon-neutral transportation fuels (e.g., methanol, hydrogen and synthetic hydrocarbons) have also been produced from biomass gasification, and biogas has been generated from biomass fermentation. These options can reduce CO_2 emissions from the transportation sector. A CO_2 removal step is generally required to produce these biofuels to increase their production yield, enhance process efficiency, and purify products. CO_2 separation can further contribute to mitigating CO_2 emissions and, thus, plays an important role in both CCS and biofuel production.

CO_2 separation is an energy-intensive process. Several technologies have been developed and commercialized for CO_2 separation, such as amine scrubbing, organic solvent scrubbing, water scrubbing, adsorption, and membrane technologies [3]. However, intensive energy use, volatility, corrosion, and degradation are deficiencies of amine scrubbing, while volatility and large-scale operations are the drawbacks of organic solvent scrubbing. High water use and low selectivity are other challenges of water scrubbing. Adsorption is limited by intensive energy-use, and low selectivity and CO_2 permeability restrict the applications of membrane technology. Thus, new technologies must be developed for CO_2 separation to optimize energy use and amounts of CO_2

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absorbents/adsorbents applied to a specific process.

Ionic liquids (ILs) have been proposed as potential "green solvents" for CO_2 separation due to their unique characteristics, which include negligible vapor pressure, nonflammability, thermal stability, and tunable physicochemical characters, among others [4]. The properties and applications of ILs for CCS have been well reviewed [5–9]. Anderson et al. [5], for example, investigated the solubilities of different gases in [Hmim][NTf_2] and compared the properties observed with those of commercial CO_2 absorbents. Bates et al. [7] reviewed the application of task-specific ILs in CO_2 capture. Ramdin et al. [9] reviewed the properties of ILs, such as their CO_2 solubility, gas selectivity, and diffusivity, as well as the effect of ions and functional groups on CO_2 solubility. The degradability and toxicity of ILs have also been studied, and toxicity (LC50:1–580 mg·L^{-1}), poor biodegradability, and high price (e.g., 783–26 120 US$·$kg^{-1}$ of imidazolium-based or pyridinium-based ILs) have been determined to limit the large-scale application of ILs for CO_2 capture and separation [10].

Deep eutectic solvents (DESs) have recently emerged as a new type of ILs. An increasing number of publications on DESs show that these solvents are becoming a popular research topic [11]. In particular, DESs based on choline salt (i.e., choline-based DESs) have been studied intensively. For example, Abbott's group [12–18] developed a series of DESs and systematically investigated their properties and applications in electrochemistry, extraction, and lubrication. Wong's and Li's groups [19–26] studied the properties and applications of choline-based DESs, including their aqueous solutions, in CO_2 separation and catalysis. Han's group [27–29] investigated the properties of choline-based DESs as CO_2 absorbents.

Several reviews on DESs have also been published. Smith et al. [30] reviewed the properties of DESs and their applications in metal processing and synthesis. Zhang et al. [31] reviewed the syntheses, properties, and applications of DESs considering their dissolution, separation, catalysis, organic synthesis, and material preparation. García et al. [32] discussed the physicochemical properties and applications of DESs in gas separation, focusing on gas solubility. Tang et al. [33] reviewed recent developments in DESs in chemical sciences. Many other reviews [34–56] mainly focus on a specific property or application of DESs. While the contributions of past research on DESs are undoubtedly valuable, a systematic comparison of the molecular structures, properties, and water effects, between choline-based DESs and conventional ILs through experimental measurements to model development has yet to be conducted. The available research work focuses mainly on the CO_2 solubility/selectivity of choline-based DESs and their aqueous solutions. The performances of these absorbents for CO_2 separation in terms of operational conditions, amounts of absorbents needed, and their energy use have not been evaluated. Thus, judging which absorbent is preferred for CO_2 separation remains challenging.

In this work, the molecular structures and physicochemical properties of choline-based DESs, as well as the effects of water content on these structures and properties, were surveyed and compared with those of conventional ILs. Thermodynamic analysis was further conducted to evaluate the performances of choline-based-DESs for CO_2 separation, and findings were compared with those of conventional ILs and commercial CO_2 absorbents.

2. Review of choline-based-DESs

2.1. Choline-based DESs

As a unique type of IL, DESs are eutectic mixtures of a salt ($R_1R_2R_3R_4N^+ \cdot X$) and a complexing agent (CA) with a certain stoichiometric ratio. Similar to conventional ILs, most DESs are in liquid state at or near room temperature. Metal salts, metal oxides, and hydrogen bond donors (HBDs; e.g., amides, amines, alcohols, carboxylic acid) can be applied as CAs [16,17,30,53]. Choline-based DESs are those based on choline salts with a formula of ($(CH_3)_3CH_2CH_2OHN^+ \cdot X^-$).

The development of DESs, especially choline-based DESs, has a short history. In 2001, Abbott et al. [57] reported a range of moisture-stable, Lewis-acidic ILs by mixing appropriate molar ratios of quaternary ammonium salts [$Me_3NC_2H_4Y$]Cl (Y = OH, Cl, OC(O)Me, OC(O)Ph) and MCl_2 (M = Zn and/or Sn). Then, in 2003, Abbott et al. [17] synthesized eutectic mixtures of a quaternary ammonium salt ($R_1R_2R_3R_4N^+ \cdot X^-$, X^- = F^-, Cl^-, Br^-, I^-) and urea. The synthesized solutions were liquid at room temperature and presented unusual solvent properties. Thereafter, choline-based DESs were intensively studied as potential solvents in electrochemistry, CO_2 absorption, nanotechnology, and catalysis.

The components of choline-based DESs are mostly natural compounds, which means additional environmental impacts can be avoided during their development. Among the widely used choline salts, choline chloride (ChCl) is an inexpensive, biodegradable, and nontoxic material either extracted from biomass or synthesized from product or by-product from fossil reserves, i.e., petroleum [31]. HBDs can include urea, glycerol, ethylene glycol, and amino acids, to name a few. Their low price makes choline-based DESs acceptable for industrialization. For example, the costs for ChCl (50–100 wt%) and HBD (i.e., glycerol) are only in the range of 0.09–0.55 US$·$kg^{-1}$ [58] and 0.22–2.2 US$·$kg^{-1}$ [59], respectively.

2.2. Molecular structure

The molecular structures of choline-based DESs are different from those of conventional ILs. Choline-based DESs consist of a choline salt and electroneutral CA. The CA forms a complex with X^- in the choline salt, and the resulting complex is considered the whole anion [31,60]. The formation of choline-based DESs can be written as:

$$[\text{choline}]^+ + X^- + \text{complexing agent} \leftrightarrow [\text{choline}]^+ + \text{complex agent}n \cdot X^- \quad (1)$$

Inter- and intra-molecular interactions exist in choline-based DESs. Among these interactions, the hydrogen bond formed between X^- and HBD dominates the properties of choline-based DESs [61,62]. Abbott et al. [17] proved the existence of a hydrogen bond in ChCl/urea (1:2) using NMR spectroscopy. Other techniques, such as crystallographic data, FAB-MS and FT-IR [63–65], have also been used to explore the molecular structures of choline-based DESs. The molecular structure of a choline-based DES with molar ratio of choline salt to HBD of 1:2 is illustrated in Fig. 1.

By comparison, only asymmetric organic cations and anions exist in conventional ILs without any neutral molecules. Possible cations include imidazolium, pyridinium, ammonium, and phosphonium, and possible anions include simple halides (e.g., F^-, Cl^-, Br^-, I^-) or inorganic anions (BF_4^-, PF_6^-). Interactions between constituent ions include Coulomb forces, hydrogen bonds, and dispersion forces [66]. The available experimental and theoretical work [67–71] shows that, for conventional ILs: (1) Coulomb forces are the dominant interactions, (2) the hydrogen bond network induces structural directionality, and (3)

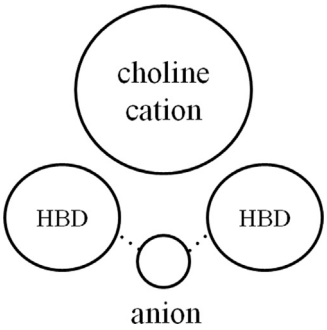

Fig. 1. Molecular structure of choline-based DES (choline salt: HBD = 1:2).