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Gas solubility and rheological behavior study of betaine and alanine based natural deep eutectic solvents (NADES)

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Natural deep eutectic solvent (NADES) produced herein this work by mixing betaine and alanine with lactic acid and malic acid with 1:1 M mixing ratios. Thermophysical properties including water content, thermal stability, density and gas solubility of CO_2 and N_2 were experimented at different isotherms for wide pressures range up to 50 bars. Moreover, detailed rheological experiments were conducted on the studied materials to obtain viscosity and deduce the dynamic flow behavior. A pressure driven physisorption mechanism was observed for the studied systems. Betaine based NADES materials showed superior carbon dioxide and nitrogen solubility when they are mixed with lactic acid. On the other hand, the rheological experimental results show shear-thinning effect in which the η is decreasing with shear rate at all temperatures. Low viscosity profiles NADES assure the less mass transfer resistance for lactic acid based NADES systems and it also confirmed that the high CO_2 and N_2 solubility for lactic acid based NADES samples.

1. Introduction

Increasing anthropogenic carbon dioxide (CO_2) levels in the atmosphere and in the oceans have become one of the grand challenge of the mankind in recent years [1]. Unprecedented amounts of CO_2 in the atmosphere are mainly due to the uncontrolled usage of fossil based fuels and its consequent emissions of greenhouse gases to the atmosphere [2]; and such emissions are mostly come from the power generation plants and other chemical processing processes [3]. Thus; these industries are more aggressive means of gas sorption technologies in order to reduce the toxic gaseous emissions and meet the global agreements for low carbon emissions. An amine-based absorption process has been utilized in chemical process industries since the 1950s due to its high sorption capability, selectivity and stable nature. Moreover, most of the existing chemical processes utilized amine based sorption systems as current state of the art for CO_2 capture and mitigation [4]. However, due to problems such as high corrosion [5,6], solvent degradation [7], and high regeneration costs [8], amine based CO_2 capture processes lead to large increases in operating costs of the processes and eventually lead to large increase in the cost of electricity production. Although there are ongoing efforts for improving the current state-of-the-art sorption systems by retrofitting the already established CO_2 capture processes via the application of advanced process systems and engineering tools (e.g. heat and mass integration) [9], above mentioned drawbacks for the amine systems urge chemical industries to seek for sustainable solutions both economically and technologically in order to manage toxic emissions in the last few decades. Ionic liquids (ILs), molten salts consist of cation and anion and typically exist in liquid state at room temperatures, have been seriously considered for such purpose since their nature that allows to achieve tailor made thermophysical properties. Hence, some ILs (e.g. imidazolium based ILs) have gained attention in the recent years due to since they have shown abilities to provide acceptable level of CO_2 solubilization and adoptability at wide process conditions that includes both pre- and post-combustion CO_2 removal [10]. Moreover, ILs have been used in wide range of other applications such as chemical or enzymatic reactions [10–12], biocatalytic process [13], extraction solvent [13,14], electrochemical applications [15], olefin paraffin separation [16] and

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biomedical applications [17]. Despite its advantages, due to limited biodegradability, poor biocompatibility, high viscosity [18] and high production cost at bulk quantities [19,20] other alternatives have been on the rise.

Deep Eutectic Solvents (DES) is one of the alternatives to ILs that has the similar features of ILs. DES are obtained with the mixture of two or more components with a melting point lower than either of its individual constituents [19,21]. They are typically obtained by mixing a quaternary ammonium halide salt, which act as a hydrogen bond acceptor (HBA), with a hydrogen bond donor (HBD) molecule, which forms a complex with the halide. Combination of HBD and HBA forms the solvent that is called DES, and this combination leads to a significant depression in the freezing point [22,23].

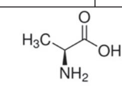
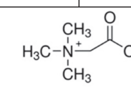
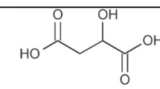
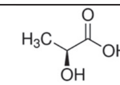
Due to the availability of many HBA and HBD, there are abundant amount of possible DES could be foreseen. The advantage of working DES is the capability of the materials and preparation process that allows us to adjust the thermophysical properties of the DES by choosing the desired combination of the DES formers. DES systems can be tailor made and used for applications such as organic reactions, extractions and synthesis [24–28], electrochemistry [29–31], enzymatic reactions [32–35], biotransformations [36], biodiesel production [37], polymer synthesis and applications [38], and potential transdermal drug delivery applications [39]. When the HBD and HBA formers of the DES are produced from naturally available chemicals, then the new solvent is called as natural deep eutectic solvents (NADES). Typical examples of NADES include eutectic mixtures of amino acids and/or sugars with organic acids [40,41]. Main advantage of NADES over DES (also ILs) is that the ability to prepare NADES at very low toxicity levels. Some recent studies hypothesizes that there are some examples of NADES in living organisms and it is believed to lead the biosynthesis of poorly water-soluble metabolites and macromolecules in the aqueous environments [24,41]. NADES are considered as viable alternatives, since they have very low vapor pressure that prevents the solvent losses [42]. Moreover they are much cheaper to produce when compared with exotic solvents as well as ILs, they are biodegradable and biocompatible, which makes their disposal straightforward and inexpensive [21,43].

In order either DES or NADES to be considered as an alternative gas sweetening solvent in larger scales by the regulatory authorities, thermophysical properties that include gas solubility performance as well as detailed rheological behavior must be investigated for various potential systems. Thus, the main purpose of this work is to contribute to such needs by focusing on selected NADES systems and study their thermophysical properties at various isotherms at wide pressure conditions up to 50 bars. In a previous work, choline chloride based NADES systems, which were prepared by mixing malic acid, lactic acid, citric acid and fructose [44]. In this work, we have selected naturally available amino acids, betaine and alanine, and studied their mixtures with lactic acid and malic acid.

2. Material and methods

Alanine (Al) with ≥98% purity (CAS Number 56-41-7) with melting point of 258 °C, betaine (Be) with ≥98% purity (CAS Number 107-43-7) with melting point of 310 °C, DL-malic acid (Ma) with 99% purity (CAS Number 6915-15-7), lactic acid (La) with 85% purity (CAS Number 50-21-5) were purchased from Sigma Aldrich. Gases that were used (CO_2 and N_2) with purities of ≥99.99% were obtained from Buzware Scientific Technical Gases, Qatar. In order to form NADES samples, (Al) and (Be) were mixed with (La) and (Ma) with 1 to 1 (1:1) molar mixing ratios by following vigorous stirring of the mixture until a clear-homogenous in a glove box in which atmosphere and humidity were controlled. All of the prepared NADES samples were observed to be liquid state at room temperature. The details of the chemical structures and physical properties of the studied NADES mixtures are given in Table 1 and the pictures of the studied NADES samples are given in Fig. 1. Prepared samples were kept at dried environment and at room temperature prior to characterization, gas solubility and rheology experiments. Considering the fact that an easy synthesis process was followed in which no solvent was added and yet no additional steps were included for purification, only heat was supplied in order to keep samples' liquid state during their preparation.

Table 1
Properties of studied NADES samples in this work.

NADES sample	[Al]:[Ma]	[Be]:[Ma]	[Al]:[La]	[Be]:[La]
Hydrogen Bond Acceptors (HBA)	 Alanine		 Betaine	
Hydrogen Bond Donors (HBD)	 Malic acid		 Lactic acid	
Molar mixing ratio	1:1	1:1	1:1	1:1
Liquid at [°C]	45	45	25	25
Experimental Density[a,b,c] [kg/m^3]	1.400	1.300	1.269	1.195
Water Content [ppm]	53,972	27,386	44,417	7,631
Water Content [%]	5.4%	2.7%	4.4%	0.7%

[a]Experimental density value at 45 °C.
[b]Standard uncertainties u are $u_r(density) = 0.003$ and $u(temperature) = 0.05$ K.
[c]Densities are reported at 0.1 MPa.

In order to observe the hygroscopic behavior of the NADESs, water content was obtained by using Karl Fischer moisture titrator (Model C20) and values are included in Table 1. Density experiments were conducted at various isotherms via Anton Paar DMA 4500 M vibrating tube densimeter. Water was used for the densimeter calibration, and reference density values for water were obtained from the fundamental equation of state by Wagner and Pruss (uncertainty lower than ± 0.003% in the full pressure and temperature ranges) [45]. Moreover, further calibration was conducted by using dimethyl sulfoxide (DMSO) at various isotherms and experimental results were compared with literature values. Further details on the calibration of the vibrating tube apparatus can be obtained elsewhere [46]. The uncertainty temperature and

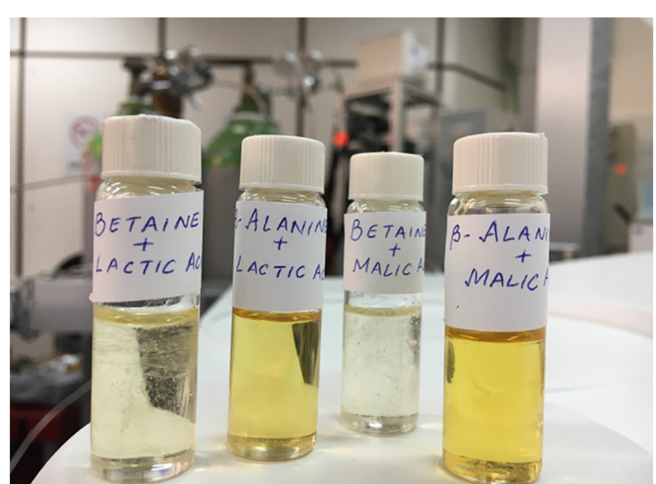


Fig. 1. Picture of the studied NADES samples in this work.