



## Review

# Exploring the thermophysical properties of natural deep eutectic solvents for gas capture applications: a comprehensive review



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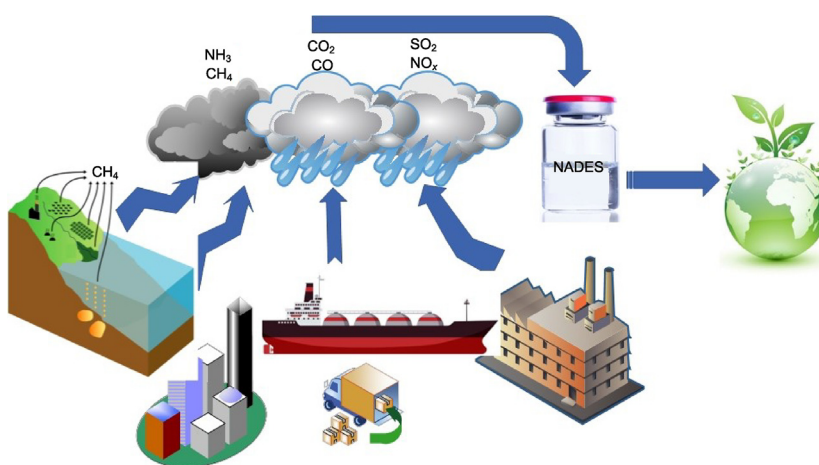
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## HIGHLIGHTS

- Comprehensive analysis of the latest DES-based methods for greenhouse gas capture.
- Curation and study of relevant thermophysical properties for gas sorption applications.
- In-depth analysis of the impact of DES structure on gas solubilities.
- Insights into the mechanism of gas solubility in DES from a molecular simulation perspective.
- Proposed future research pathways for designing DES for specific applications, potentially advancing the field.

## GRAPHICAL ABSTRACT



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## ABSTRACT

With the intensifying challenge of global warming driven largely by anthropogenic activities, effective greenhouse gas capture techniques are critical. This paper focuses on the role of deep eutectic solvents (DES) as promising agents for such capture at the source. We review the key DES-based methods for greenhouse gas capture, drawing conclusions from a thorough analysis of the existing literature. In particular, we examine the effect of DES structure on gas solubilities and explore the mechanism of gas solubility in DES through molecular simulation. We present a synthesis of state-of-the-art results in this area, assessing the potential of DES as an alternative to current industrial gas capture methods. Furthermore, we propose future research directions for the design of novel DES tailored to more specific applications.

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## 1. Introduction

In chemical engineering processes design, gas solubility data plays a crucial role in establishing phase equilibrium properties and exploring the suitability of the solvents for environmental applications. Furthermore, it is essential to have a deep insight about the solvent's microscopic structure and interactions between the molecules in the solution in order to design task specific solvents for targeted applications [1].

Since the mid of previous century, the world has been facing serious environmental problems that are escalating every year due to excessive utilization of natural resources such as water or fossil based fuels. Especially, disproportionate use of fossil based fuels is believed to be major cause on global warming. Due to combustion of oil and gas, greenhouse gases, methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), and nitrous oxide ( $\text{N}_2\text{O}$ ), are released to atmosphere leading to increase in their atmospheric concentrations [2–8]. The adapted data from the previous references were used to plot the measured concentrations of  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  over the years in the atmosphere (Fig. 1).

Emissions of  $\text{CO}_2$  have an effective role in the global warming [9]. Combustion of fossil fuel for different uses such as transportation, production of electricity and other purposes is the main emission source of  $\text{CO}_2$  [10].  $\text{CO}_2$  contributes in the global warming effect by 60% [11]. In addition to that, the content of  $\text{CO}_2$  in biogas and in the natural gas decreases the thermal content of them. That amount of  $\text{CO}_2$  in the bio and natural gases must be less than 2%, then the bio and natural gases can be transported safely by the pipelines [12].

In addition to above gases, there are other industrial gases such as ammonia ( $\text{NH}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), nitrogen dioxide ( $\text{NO}_2$ ), and

hydrogen sulfide ( $\text{H}_2\text{S}$ ) have a negative and toxic effect on the environment [13]. Waste gas that comes from the urea synthesis is the major source that releases the alkali  $\text{NH}_3$ . This product forms particulates and is a pollutant for the air and is a reason of pharyngitis and rhinitis [14]. Also,  $\text{NH}_3$  is a corrosive gas to the piping systems and equipment [15]. Volcanoes, waste gases of industry and fossil fuels burning produce acidic  $\text{SO}_2$ . If the atmosphere has a high concentration of  $\text{SO}_2$ , then this would be a reason of tumors, haze, acidic rain, and air pollution. Combustion process of coal is considered as a main producer of nitrogen oxides ( $\text{NO}$ ,  $\text{NO}_2$ ). These oxides cause the ozone layer damage, acidic mist, and acidic rain [16].  $\text{H}_2\text{S}$  is produced by different ways such as the industrial refineries and the production of natural gas. This gas is very corrosive, acidic, and toxic [17].

Natural gas is consisted mainly up to 90% of  $\text{CH}_4$  [18]. A small leakage from the systems of the natural gas can cause environmental worries. That is because of the high potential of  $\text{CH}_4$  to contribute to global warming. The global warming potential of  $\text{CH}_4$  was estimated over 20 and 100 years bases to be around 86 and 34 times of the  $\text{CO}_2$  potential [19]. The U.S. Environmental Protection Agency (EPA) considers the emitted  $\text{CH}_4$  by the industry of the natural gas as one of the greenhouse gases. Because of that EPA covers the emissions and the sinks volumes of methane in its inventory [20].  $\text{CH}_4$  has a main contribution in the climate change, and it has a dominant role in the climate warming pace [21]. Despite that, it is expected in the future to grow significantly as an energy source. That is because natural gas is able to provide sustainable supplies of energy and can reduce the harmful influences on the environment and the global climate [22]. Also, the natural gas clean burning properties increased its use as transportation fuel and for electricity production in

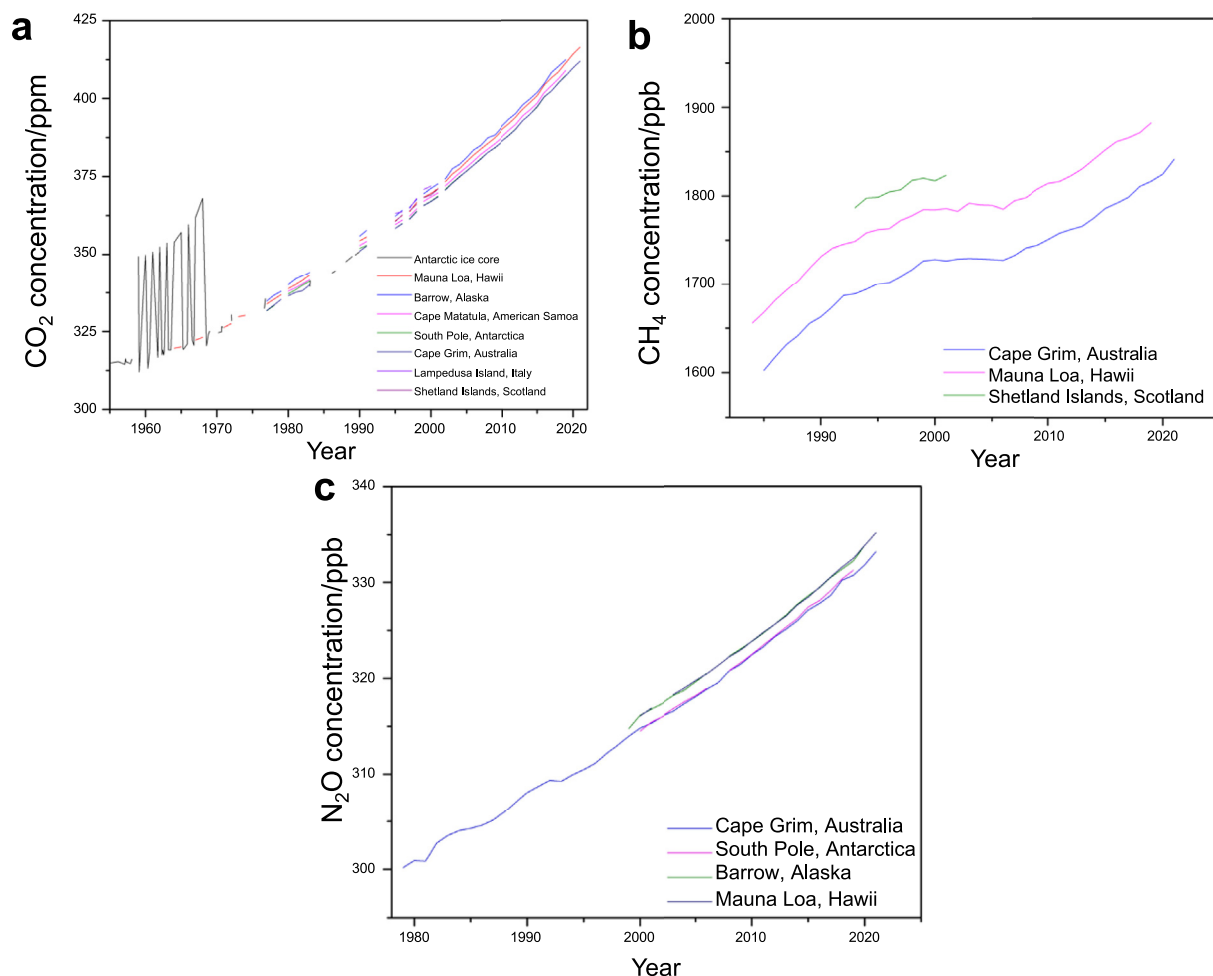


Fig. 1. Atmospheric concentration over years by different observatory stations for (a)  $\text{CO}_2$ , (b)  $\text{CH}_4$ , and (c)  $\text{N}_2\text{O}$  [2–8].

the united states [23]. Furthermore, it is the hydrogen production primary supply as it is well known that hydrogen is a clean carrier of energy [24].

Although as mentioned before,  $\text{NH}_3$  has negative effects on the environment, it is considered as an effective carrier for hydrogen. As a result, that is counted as a substitution to the hydrogen. The hydrogen density per unit volume that is offered by  $\text{NH}_3$  is higher than that by liquid hydrogen. This allows  $\text{NH}_3$  to be more reasonable alternative because the obtained amount of hydrogen will be higher [25]. Additionally, the production of  $\text{NH}_3$  on large scale is very stable [26]. Also, the storage requirements are very similar to the conventional propane. Moreover,  $\text{NH}_3$  liquifying is easier than that of pure hydrogen. That reduces the costs of the transportations and the associated costs with the developments [27]. On the other hand, the recycled  $\text{NH}_3$  could be used for the production of ammonium salt, fluids of refrigeration, fertilizers, and Nylon [28]. Also, the regenerated  $\text{SO}_2$  is favorable to be used as decolorizers, bactericides, and preservatives [29].

Due to the previously mentioned energy, environmental, and health related concerns, there is an urgent need for alternative, efficient, low-cost, and more importantly green processes of capture, storage, and separation of these gases. Over the last decade, ionic liquids (ILs) have been considered as a substitute alternative to tackle this for separation technologies [30], since ILs have distinctive properties physically and chemically such as high thermal stability, negligible vapor pressure, and tunable viscosity [31,32]. These favorable properties make ILs natural competitors to replace the classical volatile organic solvents (VOCs) [33]. Scrutinization on ILs and their potential to be used as gas capture agent over the last years have raised some concerns mostly related to their cumbersome synthesis, which generates wastes and by-products. Moreover, despite their phenomenal performance as gas solubilizing agent, their high toxicity, poor biodegradable nature, and high production cost process still remain as a major hurdle for ILs for their commercial scale deployment in industrial applications [34].

In the light of ILs based research, an alternative solvent development approach has been considered since the beginning of the first decade of this millennium; a new sustainable line of absorbents named deep eutectic solvents (DES) [35] had been developed. “Eutectic” term is a Greek word origin which refers to low melting of liquid media or alloys. DES were proposed to be an alternative to ILs due to their low cost and toxicity and environmental affordability [36,37]. In addition, DES synthesis procedure is cost efficient and simple in comparison to the ILs [38].

In the context of solvents, eutectic systems indicate that the solution constituents are mixed with specific portions or molar mixing ratios that reaches to global minimum in the solvent melting point [39]. The forces between these components are neither ionic bonds nor covalent bonds, and they rather interact *via* weaker intermolecular forces established between the solvent constituents, which are called as hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD). Homogeneous mixtures formed through the combination of a HBD and HBA lead to suppression in the melting point that is lower than both HBA and HBD [40], generally, at temperatures less than a hundred Celsius DES are in liquid phase [41]. The HBAs that have been studied up to date are typically quaternary ammonium or phosphonium salts [42,43], whereas HBDs have been selected amongst the metal halides, carbohydrates, amides, alcohols, or carboxylic acids [44].

DES can be prepared commonly in an inert atmosphere by mixing and heating the HBA and HBD to form a homogeneous liquid with no further steps as purifying or solvent adding are needed. This would be favorable for the economical side. There are other methods that are used to prepare the DES such as grinding, freeze-drying, and vacuum evaporation. The grinding method simply occurs inside a glovebox or under a nitrogen atmosphere by adding the two solids to be grinded and mixed in a mill until the ground mixture is turned into a homogeneous and clear liquid. The method of freeze-drying is typically utilized by dissolving the hydrogen bond donor and the hydrogen bond acceptor in water with a

ratio of around 5 wt% to make two solutions. Then, the solutions are blended, refrigerated, and later freeze-dried to give a homogeneous and clear product. The first step of the vacuum evaporation method is to dissolve the components in water, the second step is to take off the water under vacuum pressure by heating at 323 K, finally the blend is moved in a desiccator that contains a silica gel to remove the traces of water and reach a constant reading of weight. In most cases DES are clear liquids. In some cases, a cloudy color ranged between white and yellowish-brown textures have been reported at temperature less than the eutectic temperature [45,46].

The application areas of the DES, that were recently found, are in separation of gases, aromatic-aliphatic separation, extractive distillation and desulfurization, and removal of phenol and metal from oil and water [12,47–50]. Besides, there are more promising avenues being explored for electrodeposition [51] and metallurgy [52], lithium cobalt oxide dissolution [53], gas capture and separation [10], liquid flow battery technologies and power systems [54], organic chemistry [55] and biocatalysis [56], processing of biomass [57], biomolecular stability, structure and folding [58,59], genomics/nucleic acids fundamentals [60], active pharmaceutical ingredient solubilizers [61], and synthesis of nanomaterials [62].

The urge to prepare solvents from naturally occurring components has led to a new class of DES over the last decade. First example of natural deep eutectic solvent (NADES) concept has been developed by Choi, Verpoorte, and co-authors in 2011 [63]. The newly proposed concept was done by observing the appearance of specific natural eutectic mixtures beside the observing of the superfluous metabolites in natural sources [36]. NADES have been considered similar applications as DES and have been considered mainly as a media of extraction [64], carrier media in chromatography [65], and in the biomedical applications [66].

In chemical process industries, the major source of air pollution is related to the fuel type as most widely used fossil fuels are rich in aromatics, nitrogen, and sulfur-containing aromatic substances [67]. As mentioned earlier, when these fuels are combusted, hazardous gaseous emissions are released. Despite mitigation efforts to avoid release of such toxic effluents to atmosphere, the uncaptured amounts are posing threat to climate and human health [68]. Classical approach in gas sorbent design mainly utilizes the classical organic such as ethylene glycol, N,N-dimethylformamide, sulfolane [69] with the inclusion of some synergistic compounds such as piperazine [70]. Such solvents are widely used, and they are predictable in terms of their working mechanism, which creates a comfort zone in conservative chemical industries. However, the main issue with these organic solvents is that they have relatively low boiling points and high relative volatilities in mixtures, which leads to high fresh solvent make-up requirement in processes. Furthermore, since they are mostly chemical sorbents, their regeneration is heat intensive and leads to an increase in the overall carbon footprint of the existing processes. Other than these issues, these solvents typically have a high corrosive nature, high toxicity, and high environmental impact. Therefore, there is a continuous search for replacing the classical organic solvents and in recent years the application of NADES as gas capture solvents has gained attention in academia and several works have been published focusing mostly on  $\text{CO}_2$  capture. Besides, there are recent studies [71–74] on  $\text{SO}_x$ ,  $\text{NO}_x$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{S}$ , and  $\text{N}_2$  capture *via* NADES showing the great potential of these novel solvents for future utilization in industrial scale. This paper focuses on the recent developments on the application of NADES for gas capture and implementation in toxic gas separation purposes.

In this review, we would like to address the solubility of various process gases in eutectic solvents, which are considered hazardous to the environment. The selection of the materials and gases have been selected from the open literature which is extensively studied in the past decade and should arouse a common interest in the community of chemistry and chemical engineering.

## 2. Classification and types of DES

In general, DES have been divided into five different types. The first class is the combination of a metal chloride and a quaternary salt of ammonium. Most of the prepared and investigated DES are categorized under the first type. The second class consists of a metal chloride hydrate and a quaternary salt of ammonium. The third class is formed by adding a molecular organic component as a carboxylic acid, polyol, or an amide which will act as the HBD to a quaternary salt of ammonium. The fourth class is the one which is made by a HBD and a metal chloride hydrate [75]. The fifth class is made only of nonionic compounds. This class is relatively new type of DES [76] and in this type, there is a lack of the ionic contribution but still shows the characteristics of DES melting point. Because of that, it is proposed the hydrogen bonds are predominant in this type. In addition to the previous types, there are different mixture types that showed the depressions of deep eutectic too, but it cannot be categorized under the previous five types. The situation of these mixtures, as a combination of some of the acids and bases of Brønsted and Lowry, suggests the possibility of new types discovery [46]. Table 1 shows the five types of DES with their generalized chemical formula.

There are some DES that have common names such as Ethaline (Ethylene glycol-Choline chloride). Also, some NADES have specific names that are commonly used such as Reline (Urea-Choline chloride), Glyceline (Glycerol-Choline chloride), Fructoline (Fructose-Choline chloride), Glucoline (Glucose-Choline chloride), Maline (Malonic acid-Choline chloride) [77,78], and Oxaline (Oxalic acid-Choline chloride) [79].

NADES is made by combining two or three substrates that can have self-association by three ways of interactions, which are hydrogen bonding, polar, and ionic interaction, to develop eutectic mixtures. These substrates are natural, cheap, biodegradable, and renewable. NADES generally are in the liquid phase at the range of room temperature to a hundred degrees Celsius. Natural component use in the NADES formation is the main distinction between NADES and DES. A sharp difference between DES and NADES occasionally is not easy to make; for instance, succinic acid, levulinic acid, itaconic acid, ethanol, acetic acid, ethylene glycol, and other examples can be formed from natural and petroleum processes and materials [83].

In this work, the most widely studied hydrogen bond donors and acceptors (HBDs/HBAs) that are used to form systems of NADES in the last decade is reported. Special attention has been given to report and review the thermophysical properties that are important to the NADES characterization (e.g., density, viscosity, and surface tension). The impact of HBA and HBD on the studied parameters have been discussed herein.

## 3. Thermophysical properties

### 3.1. Phase behavior and melting point

The principal characteristic that defines the DES is the eutectic point, which is the point that the lowest melting point occurs at. For instance, Reline which is the combination of urea as a HBD and choline chloride (ChCl) as HBA, has a eutectic point at a HBD:HBA molar ratio of 2:1 or 66.7 mol/mol urea with 33.3 mol/mol ChCl [35]. Until this time, there is a large absence of details about the eutectic composition and the associated binary phase diagrams for the individual DES. It is important to obtain the phase diagram of the investigated DES as the phase diagram yields information about the range of composition and temperature at which the liquid phase will be expected. This kind of information assists the researchers to design systems of DES that fit their specialized applications. A lot of studies do not justify their choice of composition by providing the binary phase diagram. But in general, the reports of DES work show the analysis of their mixtures at the designed composition for the eutectic mixture. At various compositions of these types of materials, their dynamics and properties vary significantly. Therefore, the studying of compositions other than that of the eutectic fraction can be a helpful

pathway in the DES design field to have well understood solutions design. Because of this ability of the DES to change their dynamics by a slight change on the composition, the composition analysis may give an essential proof to find a practical methods to invest the DES in applications of the industrial scale [46]. Table 2 includes some DES systems melting points.

Typically, the synthesis of any chemical compound includes a chemical reaction or more between two reactants or more to produce a product or more. Nevertheless, the production of DES is simply by the mixing of HBD and HBA. Hence, as far as no presence of chemical reaction engagement, DES are not synthesized but prepared. Occasionally, DES synthesis term has been utilized incorrectly in published works, thus this term should be replaced with DES preparation term [84]. Preparation of DES has been done by multiple approaches such as heating and stirring, freezing-drying, vacuum evaporation, grinding, twin screw extrusion, microwave irradiation, and ultrasound-assisted.

Heating and stirring approach of DES preparation is the most widespread method of DES preparation. A wide range of temperatures have been performed by various works. To our knowledge, the range is between the room temperature and 130 °C. The time of this method is up to few hours based on the boiling and melting points and the reagent stability [85].

The freezing-drying approach includes stoichiometric addition of HBD and HBA amounts and then followed by the addition of distilled water to have an aqueous solution of 5%. Then, the next step is to freeze the aqueous solution at −196 or −20 °C [84]. After that, the solution is freeze-dried by lyophilization to get the viscous clear liquid [86].

To yield a DES by the vacuum evaporation approach, the HBD and HBA are first dissolved in water and then the water is taken off at 50 °C by rotary evaporator [87]. After that, the resulting liquid is dried by silica gel in a desiccator until reaching a constant weight. To be able to use this method, the components must be soluble in the water. Another drawback of this method is that, a complete evaporating of water at 50 °C is time consuming and challenging [84,88].

The grinding approach has been used to avoid the use of heat during the DES preparation. This method is simply grinding and mixing the HBD and HBA in a pestle and mortar till having a homogenous mixture at room temperature. In comparison between the heating and stirring method and the grinding method, it is found the heating and stirring involved in esterification with a percent of 5–30. But in the grinding method there is no esterification results [89,90].

Twin screw extrusion is a mechanochemical method that used for DES preparation on a large scale using a twin-screw extruder. This approach came to avoid the heating and stirring method limitations. DES preparation is done by preheating the sections of the twin screw extruder and then feeding the HBD and HBA through the port of feeding by a specific stoichiometric ratio. Then the produced colorless DES is collected from the other extruder side. This approach has crucial benefits as; DES preparation continuously and efficiently, can be scale up easily to get high productivity, it overrides the problem of thermal degradation because of the short time exposure to the heat, and DES collection easily in a container [91].

Microwave irradiation is ecofriendly technique which reduces the DES preparation energy and time costs [92]. In this method, the DES preparation is performed by enclosing the HBD and HBA in 20 mL vial then for 20 s microwave irradiating it. This technique decreases the time to only 20 s from multiple hours also uses 650 times energy less than that used in the heating and stirring method. In general, this approach is greener, cheaper, faster, and easier way of DES preparation comparing to the conventional techniques [93].

Ultrasound-assisted preparation: in this way of DES preparing, the HBD and HBA are combined in a glass vial and then the vial is sealed and located in the ultrasonic bath at temperature range between the room temperature up to 60 °C based on the involved components, for 1–5 h. Then the produced DES is left in its vial under the ambient condition for 24 h to assure the homogenous mixture formation. In this method the

Table 1

DES types.

| Class     | Generalized formula                                                             | Ref. |
|-----------|---------------------------------------------------------------------------------|------|
| Class I   | $R_1R_2R_3R_4N^+X^-Y^-$<br>$Y = MCl_x, M = Zn, Sn, Fe, Al, Ga$                  | [80] |
| Class II  | $R_1R_2R_3R_4N^+X^-Y^-$<br>$Y = MCl_x \cdot yH_2O, M = Cr, Co, Cu, Ni, Fe$      |      |
| Class III | $R_1R_2R_3R_4N^+X^-Y^-$<br>$Y = R_5Z, Z = -CONH_2, -COOH, -OH$                  |      |
| Class IV  | $2MCl_x + RZ = MCl_{x-1} \cdot RZ + MCl_{x+1}$<br>$M = Al, Zn$ and $Z = CONH_2$ | [81] |
| Class V   | Non-ionic DES, comprised from molecular substances only                         | [82] |

produced DES is stable along the time [94].

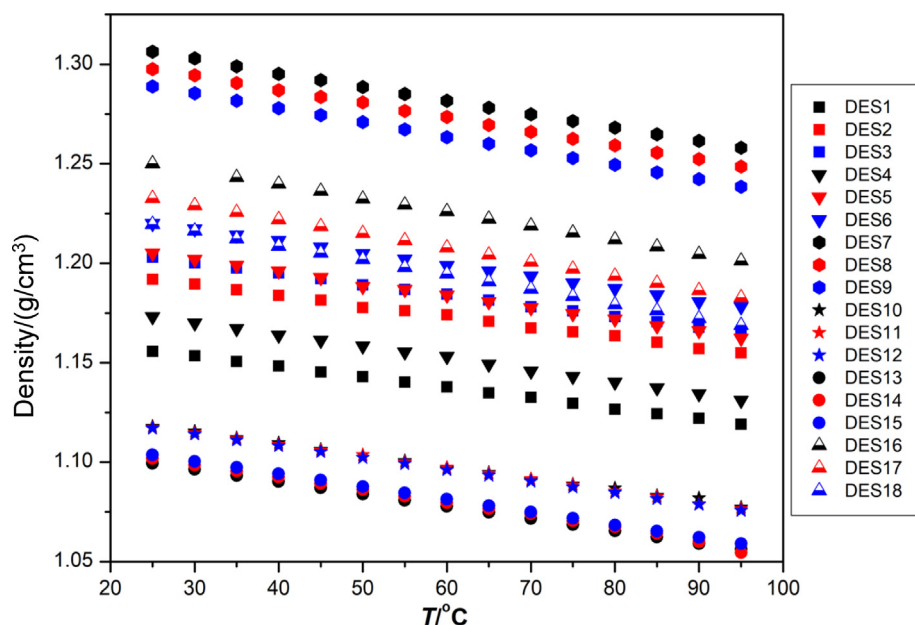
3.2. Density

Density is an essential physical property and is a fundamental to measure density for the materials as it provides information not only the effect of HBA and HBD on the packing order of the DES, but also gives insight about the interactions intermolecularly in the DES. In the typical situation, DES have higher densities in comparison with the one of water. In different cases, the moles ratio between the HBD and HBA and their composition give a way for the eutectic mixture density modification. Also, as expected temperature is an influencer factor on the DES densities, the higher temperature the lower density. DES density measurements that depend on the temperature can be useful in the estimation of

Table 2

Melting point of some DES and NADES.

| HBA                                                                | HBD                                               | [HBA]:[HBD] ratio | Melting point/°C | Ref.    |
|--------------------------------------------------------------------|---------------------------------------------------|-------------------|------------------|---------|
| Choline chloride                                                   | Urea                                              | 1:2               | 12               | [95]    |
|                                                                    | Glycerol                                          | 1:2               | −40              | [81]    |
|                                                                    | Ethylene glycol                                   | 1:2               | −36              | [96]    |
|                                                                    | Imidazole                                         | 3:7               | 56               | [97]    |
|                                                                    | Acrylic acid                                      | 1:1.6             | −4               | [98]    |
|                                                                    | Citric acid                                       | 1:1               | 69               | [81,99] |
|                                                                    | Malonic acid                                      | 1:1               | 10               |         |
|                                                                    | Oxalic acid                                       | 1:1               | 34               |         |
|                                                                    | Phenylacetic acid                                 | 1:2               | 25               |         |
|                                                                    | Phenylpropionic acid                              | 1:2               | 20               |         |
|                                                                    | Succinic acid                                     | 1:1               | 71               |         |
|                                                                    | o-Cresol                                          | 1:3               | −23              | [100]   |
|                                                                    | 2,3-Xylenol                                       | 1:3               | 18               |         |
|                                                                    | Phenol                                            | 1:3               | −20              |         |
| ZnCl <sub>2</sub>                                                  | Ethylene glycol                                   | 1:4               | −30              | [75]    |
|                                                                    | Urea                                              | 1:3.5             | 9                |         |
| Methyltriphenylphosphonium bromide                                 | Ethylene glycol                                   | 1:2               | 4                | [101]   |
|                                                                    | Glycerol                                          | 1:3               | −46              |         |
| 2-Acetyloxy-N,N,N-trimethylethanaminium chloride                   | ZnBr <sub>2</sub>                                 | 1:2               | 48               | [102]   |
|                                                                    | SnCl <sub>2</sub>                                 | 1:2               | 20               |         |
| N-(2-hydroxyethyl)-N,N-dimethylanilinium chloride                  | SnCl <sub>2</sub>                                 | 1:2               | 17               |         |
|                                                                    | FeCl <sub>3</sub>                                 | 1:2               | 21               |         |
| Ethylammonium chloride                                             | Methylurea                                        | 1:1.3             | 29               | [103]   |
| Methyltriphenylphosphonium bromide                                 | 2,2,2-Trifluoroacetamide                          | 1:8               | −69              | [104]   |
| Choline acetate                                                    | Urea                                              | 1:2               | 18               | [105]   |
|                                                                    | Glycerol                                          | 1:1.5             | 13               |         |
|                                                                    | Ethylene glycol                                   | 1:2               | 23               |         |
| Choline nitrate                                                    | Urea                                              | 1:2               | 4                | [35]    |
| Choline fluoride                                                   |                                                   | 1:2               | 1                |         |
| N-ethyl-2-hydroxy-N,N-dimethylethanaminium chloride                |                                                   | 1:2               | −38              |         |
| N-benzyl-2-hydroxy-N,N-dimethylethanaminium chloride               |                                                   | 1:2               | −33              |         |
| N,N,N-trimethyl(phenyl)methanaminium chloride                      |                                                   | 1:2               | 26               |         |
| 2-(Acetyloxy)-N,N,N-trimethylethanaminium chloride                 |                                                   | 1:2               | −14              |         |
| 2-Chloro-N,N,N-trimethylethanaminium chloride                      |                                                   | 1:2               | 15               |         |
| N-benzyl-2-hydroxyN-(2-hydroxyethyl)-N-methylethanaminium chloride |                                                   | 1:2               | −6               |         |
| 2-Fluoro-N,N,N-trimethylethanaminium bromide                       |                                                   | 1:2               | 55               |         |
| Ethylammonium chloride                                             | Urea                                              | 1:1.5             | 29               | [103]   |
|                                                                    | 1-(Trifluoromethyl)urea                           | 1:1.5             | 20               |         |
| Tetrabutylammonium bromide                                         | Imidazole                                         | 3:7               | 21               | [97]    |
| 1-Ethyl-3-butylbenzotriazolium hexafluorophosphate                 |                                                   | 1:4               | 57               |         |
| Tetrabutylammonium chloride                                        | Glycerol                                          | 1:5               | −43              | [106]   |
|                                                                    | Ethylene glycol                                   | 1:3               | −31              |         |
|                                                                    | Triethylene glycol                                | 1:3               | −13              |         |
| N,N-diethylethanolammonium chloride                                | Glycerol                                          | 1:2               | −1               | [101]   |
|                                                                    | Ethylene glycol                                   | 1:2               | −31              |         |
| Benzyltriphenylphosphonium chloride                                | Glycerol                                          | 1:5               | 50               | [104]   |
|                                                                    | Ethylene glycol                                   | 1:3               | 48               |         |
| Tetrapropylammonium bromide                                        | Glycerol                                          | 1:3               | −16              | [107]   |
|                                                                    | Ethylene glycol                                   | 1:4               | −23              |         |
|                                                                    | Triethylene glycol                                | 1:3               | −19              |         |
| 1-Butyl-3-methylimidazolium chloride                               | ZnCl <sub>2</sub>                                 | 1:1               | −50.1            | [108]   |
| Proline                                                            | Glucose (HCl addition)                            | 1:5               | −38.9            | [109]   |
|                                                                    | Glucose (H <sub>2</sub> SO <sub>4</sub> addition) | 1:5               | −29.4            |         |
|                                                                    | Glucose (H <sub>3</sub> PO <sub>4</sub> addition) | 1:5               | −51.1            |         |
|                                                                    | Xylitol (HCl addition)                            | 1:5               | −36.9            |         |
|                                                                    | Xylitol (H <sub>2</sub> SO <sub>4</sub> addition) | 1:6               | −31.5            |         |
|                                                                    | Xylitol (H <sub>3</sub> PO <sub>4</sub> addition) | 1:5               | −44.8            |         |



**Fig. 2.** Density change of three DES classes with temperature [101,114], where DES1: ChCl-Glycerol (1:1), DES2: ChCl-Glycerol (1:2), DES3: ChCl-Glycerol (1:3), DES4: N,N-diethylenethanol ammonium chloride-Glycerol (1:2), DES5: N,N-diethylenethanol ammonium chloride-Glycerol (1:3), DES6: N,N-diethylenethanol ammonium chloride-Glycerol (1:4), DES7: Methyltriphenylphosphonium bromide-Glycerol (1:2), DES8: Methyltriphenylphosphonium bromide-Glycerol (1:3), DES9: Methyltriphenylphosphonium bromide-Glycerol (1:4), DES10: ChCl-Ethylene glycol (1:1.78), DES11: ChCl-Ethylene glycol (1:2), DES12: ChCl-Ethylene glycol (1:2.57), DES13: N,N-diethylenethanol ammonium chloride-Ethylene glycol (1:2), DES14: N,N-diethylenethanol ammonium chloride-Ethylene glycol (1:3), DES15: N,N-diethylenethanol ammonium chloride-Ethylene glycol (1:4), DES16: Methyltriphenylphosphonium bromide-Ethylene glycol (1:3), DES17: Methyltriphenylphosphonium bromide-Ethylene glycol (1:4), DES18: Methyltriphenylphosphonium bromide-Ethylene glycol (1:5.25).

**Table 3**  
Density of some DES at 25 °C.

| HBA                                    | HBD                               | [HBA]:[HBD]<br>ratio | Density/(g/<br>cm <sup>3</sup> ) at<br>25 °C | Ref.  |
|----------------------------------------|-----------------------------------|----------------------|----------------------------------------------|-------|
| Choline chloride                       | Urea                              | 1:2                  | 1.21                                         | [78]  |
|                                        | Glycerol                          | 1:2                  | 1.18                                         | [122] |
|                                        | Ethylene glycol                   | 1:2                  | 1.12                                         | [123] |
|                                        | Fructose                          | 2:1                  | 1.278                                        | [124] |
| Decanoic acid                          | Glucose                           | 2:1                  | 1.242                                        | [125] |
|                                        | Lidocaine                         | 2:1                  | 0.961                                        | [126] |
|                                        | Atropine                          | 2:1                  | 1.027                                        |       |
|                                        | Menthol                           | 1:1                  | 0.899                                        |       |
| Dodecanoic acid                        | Lidocaine                         | 2:1                  | 0.950                                        |       |
|                                        | Atropine                          | 2:1                  | 1.009                                        |       |
|                                        | Lidocaine                         | 2:1                  | 0.939                                        |       |
|                                        | Lidocaine                         | 1:1                  | 0.993                                        |       |
| Menthol                                | Menthol                           | 1:1                  | 0.937                                        |       |
|                                        | Coumarin                          | 1:1                  | 1.092                                        |       |
|                                        | CF <sub>3</sub> CONH <sub>2</sub> | 1:1.5                | 1.273                                        | [41]  |
|                                        | Acetamide                         | 1:1.5                | 1.041                                        |       |
| Thymol                                 | Urea                              | 1:1.5                | 1.14                                         |       |
|                                        | CF <sub>3</sub> CONH <sub>2</sub> | 1:2                  | 1.342                                        |       |
|                                        | Ethylene glycol                   | 1:4                  | 1.36                                         | [75]  |
|                                        | Ethylene glycol                   | 1:4                  | 1.45                                         |       |
| N,N-diethylenethanol ammonium chloride | Hexanediol                        | 1:3                  | 1.38                                         |       |
|                                        | Glycerol                          | 1:2                  | 1.17                                         | [101] |
|                                        | Glycerol                          | 1:3                  | 1.21                                         |       |
|                                        | Glycerol                          | 1:4                  | 1.22                                         |       |
|                                        | Ethylene glycol                   | 1:2                  | 1.1                                          |       |
|                                        | Ethylene glycol                   | 1:3                  | 1.1                                          |       |
|                                        | Ethylene glycol                   | 1:4                  | 1.1                                          |       |
|                                        | Ethylene glycol                   | 1:4                  | 1.1                                          |       |

isobaric thermal expansion coefficients. This coefficient is defined as the negative partial derivative of the density natural logarithm with respect to the temperature at constant pressure. That leads to the ability to calculate the free volume of the DES. Thus, the estimation of these coefficients is very insight to understand the dynamics of the DES specially the viscosity [110,111]. Density of DES can be measured by vibrating U-tube densimeter and pycnometer [112].

NADES density can be modified by the temperature change or by the

change in water content. The increase of temperature will result in greater kinetic energy. As a consequent, the higher amount of energy will lower the density, because of the increase in the solution molar volume and the movement of molecules [113]. By analyzing and fitting the reported density data by Refs. [101,114] in Fig. 2, the linear change of density with temperature has been observed. Also, Shahbaz et al. [114] reported linear experimental and predicted data for the densities of nine different DES.

Water inclusion in the NADES composition leads to weakening the interactions of hydrogen bond, van der Waals, and electrostatic forces in between the components. Thus, the density will be reduced [113]. For example, reline density at the temperature of 30 °C is reported as 1.1945 g/mL by Ref. [115], 1.1952 g/mL by Ref. [116], and 1.1216 g/mL by Ref. [95]. Systematically, water addition causes a decrease in the density of reline. They observed the addition of water by 5 wt% decreases the density by 1% [117]. In most cases, the densities of NADES are higher than the density of water. The general range of NADES densities is from 1.1 up to 1.4 g/mL [118]. Likewise, in regard of the ILs, they have higher densities than water with a typical range from 1 to 1.6 g/mL [119–121]. Table 3 reports the density of a number of DES at 25 °C.

### 3.3. Viscosity

Viscosity is a physical property that can be defined at a certain shear rate as the fluid resistance to the deformation. Practically, the meaning of this concept is that as the viscosity of the liquid increases the flow will be slower and will have the characteristics of the syrup flow. While when the viscosity decreases the flow will be easier and away from the characteristics of the syrup flow. It has been observed that DES viscosities tend to have high magnitudes, which is considered a hurdle on the application of the DES on the commercial scale. The large hydrogen bond network existence in between each component results in a high magnitude of DES viscosity, also reduces the free species mobility inside the DES. In addition to that, in most of DES the very small volume of voids and the large size of ions contribute in resulting of high DES viscosity [41].

The general range of the DES viscosity at the temperature of 25 °C is between 50 and 5000 mPa · s [127]. NADES have a higher magnitude of viscosity than the DES [128]. For instance, in the comparison between the viscosity of water and that of ethaline at 20 °C, the viscosity of

**Table 4**  
Dynamic viscosity of some DES.

| HBA                                  | HBD              | [HBA]:[HBD] ratio | Viscosity/(mPa · s) at 25 °C | Ref.         |
|--------------------------------------|------------------|-------------------|------------------------------|--------------|
| Choline chloride                     | Urea             | 1:2               | 750                          | [78,137,138] |
|                                      | Glycerol         | 1:2               | 259                          |              |
|                                      | Ethylene glycol  | 1:2               | 41                           | [124]        |
|                                      | Fructose         | 2:1               | 11733                        |              |
|                                      | Glucose          | 2:1               | 8045                         | [125]        |
|                                      | Acrylic acid     | 1.6:1             | 115 (at 22 °C)               | [98]         |
|                                      | Acetic acid      | 1:1               | 162                          | [139]        |
|                                      | Levulinic acid   | 1:2               | 227                          | [140]        |
|                                      | Glutaric acid    | 1:1               | 2015                         | [46]         |
|                                      | Citric acid      | 1:1               | 9126                         |              |
|                                      | Malonic acid     | 1:1               | 1638                         | [141]        |
|                                      | Oxalic acid      | 1:1               | 597                          |              |
|                                      | Succinic acid    | 1:1               | 1489                         | [100]        |
|                                      | Malic acid       | 1:1               | 1100                         |              |
|                                      | Phenol           | 1:3               | 44                           | [97]         |
|                                      | o-Cresol         | 1:3               | 77                           |              |
|                                      | Imidazole        | 3:7               | 15 (at 70 °C)                | [46,142]     |
|                                      | Monoethanolamine | 1:6               | 52 (at 20 °C)                |              |
|                                      | Diethanolamine   | 1:6               | 567 (at 20 °C)               | [46]         |
|                                      | Triethanolamine  | 1:1               | 125 (at 30 °C)               |              |
| ZnCl <sub>2</sub>                    | Choline chloride | 1:2               | 85000                        | [102]        |
|                                      | Urea             | 1:3.5             | 11340                        | [46]         |
| Benzyltriphenylphosphonium chloride  | Ethylene glycol  | 1:1               | 57 (at 20 °C)                | [96]         |
| Methyltriphenylphosphonium bromide   | Ethylene glycol  | 1:2               | 177 (at 20 °C)               |              |
| N,N-diethylethanol ammonium chloride | Ethylene glycol  | 1:2               | 50                           | [133]        |
|                                      | Glycerol         | 1:3               | 513                          | [133]        |
| Methyltriphenyl phosphonium bromide  | Glycerol         | 1:3               | 2220                         | [46]         |
| Tetra-n-butylammonium bromide        | Glycerol         | 1:4               | 877                          |              |
| Tetrabutylammonium chloride          | Imidazole        | 3:7               | 810 (at 20 °C)               | [97]         |
|                                      | Decanoic acid    | 1:2               | 429                          | [143]        |
| Decanoic acid                        | Methanol         | 1:1               | 20                           | [126]        |
|                                      | Atropine         | 2:1               | 5985                         |              |
| Dodecanoic acid                      | Lidocaine        | 2:1               | 371                          |              |
|                                      | Atropine         | 2:1               | 5600                         |              |
| Methanol                             | Lidocaine        | 2:1               | 68                           |              |
| Thymol                               | Lidocaine        | 1:1               | 177                          |              |
| MnCl <sub>2</sub> ·4H <sub>2</sub> O | Coumarin         | 1:1               | 29                           | [144]        |
|                                      | Acetamide        | 1:7               | 112.8 (at 21 °C)             |              |
|                                      | Glycerol         | 1:1               | 1221.25 (at 21 °C)           |              |
|                                      | D(+)-Glucose     | 1:1               | 434.3 (at 21 °C)             |              |
|                                      | D(-)-Fructose    | 1:1               | 570.4 (at 21 °C)             |              |
|                                      | D(-)-Fructose    | 1:2               | 6689.25 (at 21 °C)           |              |

ethaline is 52 times than that for the water (at 20 °C, water viscosity is 1 mPa · s and ethaline viscosity is 52 mPa · s). Going from the importance of this property, the experiments wanted to draw the characteristics of DES flow and recognize which model is the best to illustrate these traits. Among the various existing models, the Arrhenius equation is the most frequently applied model in addition to the Vogel Fulcher Tammann (VFT) equation model. Arrhenius equation is only applied for liquids when the measurements of viscosities are carried on a small range of temperature or at high temperatures [90,129–131]. VFT equation is applied commonly when the measurements of liquid viscosity carried on a wide temperature range. The use of this model is usually the description of glass-forming liquids temperature dependent viscosity. The glass-forming liquids indicate the intermolecular interaction contribution such as hydrogen bonding and van der Waals type interactions [132]. NADES viscosity correlates essentially with the temperature and the water content. As the temperature increases, the cohesive forces in the NADES can be more regulated. NADES viscosity has a high sensitivity to the kinetic energy, the intermolecular forces strength will be overcome by the high kinetic energy and then lower the viscosity. In parallel with the temperature impact, as the water amount increases the NADES viscosity significantly decreases [36]. For instance, absorption of water by only 5 wt% decreases the viscosity of urea-choline chloride by 83% [118].

Siongco and Gajardo-Parra et al. [133,134] measured the viscosity in their experimental work using an automated version of the falling ball micro-viscometer. They determined the sample viscosity by recording

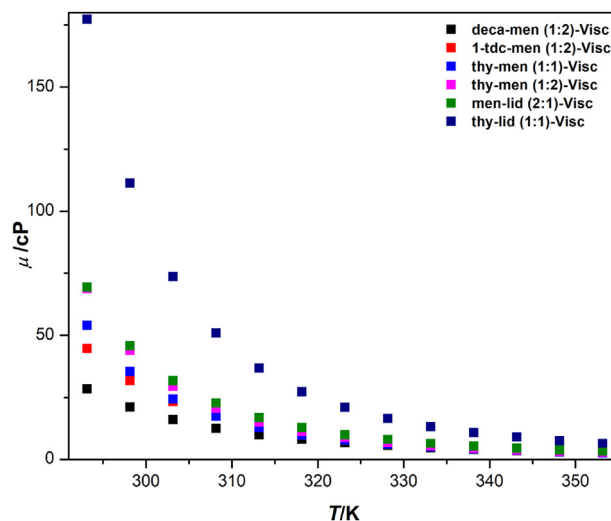


Fig. 3. Viscosities of selected DES over a range of temperatures [145].

the solid steel ball rolling time in the inclined filled capillary tube with the liquid sample under the gravity force. The recorded time is the needed time for the ball to travel a fixed distance within the sample and it is logged by two inductive sensors. The inclination angle was specified in

**Table 5**

Surface tension of some DES.

| HBA                                    | HBD                  | [HBA]:[HBD] ratio | Surface tension/(mN/m) at 25 °C | Ref.     |
|----------------------------------------|----------------------|-------------------|---------------------------------|----------|
| Choline chloride                       | Urea                 | 1:2               | 64.14                           | [156]    |
|                                        | Glycerol             | 1:2               | 58                              | [46]     |
|                                        | Ethylene glycol      | 1:2               | 52                              | [157]    |
| Methyltriphenylphosphonium bromide     | Ethylene glycol      | 1:3               | 67                              | [96]     |
| Benzyltriphenylphosphonium chloride    |                      | 1:11              | 65                              |          |
| Tetra- <i>n</i> -butylammonium bromide | Ethylene glycol      | 1:2               | 51                              |          |
|                                        | Glycerol             | 1:4               | 37                              | [122]    |
| Choline chloride                       | Methyldiethanolamine | 1:6               | 32                              | [46,142] |
|                                        | Monoethanolamine     | 1:6               | 48                              |          |
|                                        | Diethanolamine       | 1:6               | 45                              | [142]    |

such a manner that prevents the ball from travelling the distance within less than 10 s, in order to avoid turbulence presence. Pishro et al. [135] measured the DES viscosities by Ubbelohde viscometer. They immersed the sample in a temperature controlled thermostatic bath. The immersion was for 15 min. Then they measured the time of efflux by a stopwatch. Cui et al. [136] used a rotary viscometer to measure the viscosity in their study. Hayyan et al. [124] measured the viscosity of the DES by a rotational viscometer. Table 4 reports the dynamic viscosity magnitude of a number of DES at the condition of room temperature.

Fig. 3, which is adopted from the data of [145], shows the trends of the viscosities of six DES over the same range of temperatures. The DES were decanoic acid-menthol (1:2) [deca-men (1:2)], thymol-menthol (1:1) [thy-men (1:1)], thymol-menthol (1:2) [thy-men (1:2)], thymol-lidocaine (1:1) [thy-lid (1:1)], menthol-lidocaine (2:1) [men-lid (2:1)], and 1-tetradecanol-menthol (1:2) [1-tdc-men (1:2)]. The general trend is noticeable as the temperature increases, the viscosities go down.

### 3.4. Surface tension and contact angle

Surface tension is defined as a measure of the required energy to increase the material surface area and is the material bias to come up with the smallest possible surface area [146]. The effects of the surface tension are predominantly in the liquids and that is because of the interactions in between the liquid molecules [46]. The determination of this physical factor gives the ability to understand how much the intermolecular forces are intense [96]. It is measured by different methods, such as Du Noüy ring [147], pendant drop [148], and Wilhelmy plate [149]. Surface tension data measurements have a main role in bubbling, wetting, lubrication, and permeability. Also, it is important for a better chemical process design in the absorption, extraction, and distillation processes. A low surface tension value increases the spread of the liquid phase over the area of contact [150]. In DES, the surface tension is measured beside the other measurable properties including ionic conductivity, viscosity, and density in order to identify the molecular environment shifts of the DES according to the temperature and composition changes [46]. There are works that have predicted the DES surface tension successfully, that would be beneficial to compare the surface tension values coming from the empirical models to that one from the experimental determination [101,151,152]. Surface tension is affected by the water content and temperature. By a linear trend, the surface tension decreases when the temperature increases [10]. Hydrogen bonds increase by the addition of water to the DES which increases the surface

**Table 6**

Contact angles of some DES on some metal surfaces.

| HBA              | HBD             | [HBA]:[HBD] ratio | Contact angle/° |        |      |            |                 | Ref.  |
|------------------|-----------------|-------------------|-----------------|--------|------|------------|-----------------|-------|
|                  |                 |                   | Al              | Bronze | Cu   | Mild steel | Stainless steel |       |
| Choline chloride | Urea            | 1:2               | 74.4            | 93.2   | 94.9 | 90.5       | 90.7            | [158] |
|                  | Glycerol        | 1:2               | 79.5            | 77.5   | 84.7 | 92.2       | 86.3            |       |
|                  | Ethylene glycol | 1:2               | 66.1            | 72.7   | 88.3 | 70.9       | 82.4            |       |
|                  | Oxalic acid     | 1:1               | 76.5            | 30.4   | 28.7 | 40.8       | 51.7            |       |

**Table 7**

Vapor pressure of some DES.

| DES                                   | Sample weight/mg | T/°C | Vapor pressure/Pa | Ref.  |
|---------------------------------------|------------------|------|-------------------|-------|
| ChCl-Urea (1:2) (Reline)              | 29.3             | 80   | 2.12              | [162] |
|                                       | 28               | 100  | 7.52              |       |
|                                       | 32.2             | 120  | 29.46             |       |
|                                       | 25.5             | 140  | 104.03            |       |
| ChCl-Ethylene glycol (1:2) (Ethaline) | 40               | 37.8 | 8.18              |       |
|                                       | 50               | 34.1 | 19.1              |       |
|                                       | 60               | 31   | 38.21             |       |
|                                       | 70               | 35.5 | 59.75             |       |
| ChCl-Glycerol (1:2) Glyceline         | 80               | 37.3 | 94.79             |       |
|                                       | 100              | 28.1 | 6.97              |       |
|                                       | 120              | 29.2 | 27.49             |       |
|                                       | 140              | 29.5 | 79.3              |       |
| Im-Bu <sub>4</sub> NBr (7:3)          | 160              | 31.8 | 161.95            |       |
|                                       | 60               | 28.6 | 2.75              |       |
|                                       | 80               | 30.6 | 9.4               |       |
|                                       | 100              | 30.7 | 29.46             |       |
|                                       | 120              | 29.8 | 73.76             |       |

tension [153]. Table 5 shows the surface tension values of ten DES at 25 °C.

Contact angle is that between the substrate and the tangent of the liquid drop at the three-phase contact point. This property is affected by both liquid and the substrate. It is used to characterize the liquid wetting on a surface. A high contact angle means weak wetting characteristic of the liquid [154]. The phenomenon of wetting is central for the processes of industry, such as coatings, adhesion, lubrication, fluid handling, microelectronics fabrication, repellency, and printing [155].

Water has contact angles of 70, 63.8, and 62.1° with copper, aluminum, and stainless steel, respectively [159]. According to Giridhar et al. [160], the contact angle that is consider as a good wetting angle is that one less than 90°. If it is equal to 90° or greater, it is classified as limited wetting properties due to hydrophobic behavior of the liquid. In general, contact angles in Table 6 are in the range of good wetting except the angles between reline and bronze, copper, and steel, these four angles are in the region of incomplete wetting. Also, the contact angle between glyceline and mild steel is in the range of incomplete wetting too.

### 3.5. Vapor pressure

Vapor pressure is defined as the pressure that is exerted by the vapor

**Table 8**

Total vapor pressure and viscosity of some DES [164].

| DES                           | $P_{\text{Total, Vap/Pa}}$ | Viscosity/(Pa · s) |
|-------------------------------|----------------------------|--------------------|
| Decanoic acid-Menthol (1:1)   | 540.9                      | 0.028              |
| Decanoic acid-Thymol (1:1)    | 466.3                      | 0.020              |
| Thymol-Lidocaine (2:1)        | 329.4                      | 0.124              |
| Decanoic acid-Lidocaine (4:1) | 87.5                       | 0.182              |
| Decanoic acid-Lidocaine (3:1) | 81.2                       | 0.285              |
| Decanoic acid-Lidocaine (2:1) | 55.5                       | 0.340              |

**Table 9**

Acidity of some DES.

| HBA              | HBD                  | [HBA]:[HBD]<br>ratio | pH at 25 °C      | Ref.  |
|------------------|----------------------|----------------------|------------------|-------|
| Choline chloride | Urea                 | 1:2                  | 10.07 (at 30 °C) | [95]  |
|                  | Glycerol             | 1:2                  | 4.47             | [46]  |
|                  | Ethylene glycol      | 1:2                  | 4.38             |       |
|                  | Malonic acid         | 1:1                  | 1.28             |       |
|                  | Malic acid           | 1:1                  | 1.61             |       |
|                  | Oxalic acid          | 1:1                  | 1.22             |       |
|                  | Citric acid          | 1:1                  | 1.73             |       |
|                  | Monoethanolamine     | 1:6                  | 12.8             |       |
|                  | Methyldiethanolamine | 1:6                  | 11.04            |       |
|                  | Lactic acid          | 1:2                  | 2.45             |       |
| Betaine          | Alanine              | 9:1                  | 2.15             |       |
|                  | Glycine              | 1:2                  | 2.74             | [165] |

phase when it is thermodynamically in equilibrium with its liquid phase. Like in the case of ILs, it has been reported in numerous studies that the vapor pressure values of DES are negligible. This assumption is due to the non-volatility of one of the DES constituent components [161]. Another reason of this assumption is the strong interactions of hydrogen bonding between the HBA and the HBD [162]. Only some studies that have performed indirect or direct vapor pressure measurements for the DES. Based on the measurements of the isobaric liquid-vapor equilibrium, Boisset et al. [127] reported their vapor pressure determination of the lithium bis(trifluoromethylsulfonyl)imide and N-methylacetamide DES with a molar ratio of 1:4 at 313 K to be as 20 Pa. This value of the vapor pressure is much higher than the typical aprotic ILs vapor pressure and less than the water vapor pressure which is around 7.4 kPa. The vapor pressure of the DES and NADES is very low, which is similar to the traditional ILs [163]. Table 7 reports the vapor pressure of four DES at different temperatures.

Dietz et al. [164] determined the vapor pressure of six DES experimentally by a head-space gas chromatography mass spectrometry (HS-GC-MS). They stated that, for the DES the higher total vapor pressure the lower viscosity. And they justified that by the reason of low attraction interactions between the HBA and the HBD makes the viscosity lower and the vapor pressure higher. Table 8 shows their results.

In addition to the viscosity of DES that were mentioned previously in Fig. 3; [deca-men (1:2)], [thy-men (1:1)], [thy-men (1:2)], [thy-lid (1:1)], [men-lid (2:1)], and [1-tdc-men (1:2)], vapor pressure over a range of temperature was studied [145]. The trend was clear, as the temperature increases the vapor pressure goes high. As a result of this trend, it can be inferred that the higher viscosity the lower vapor pressure which agrees with the conclusion of the previous reference [164].

### 3.6. Acidity (pH)

pH is a measure for the solution acidity and is another essential physical property for the DES development to determine whether the defined systems are formed by the mixing of Brønsted or Lewis acids and bases. The pH value changes with acidity of the cationic and anionic

**Table 10**

Effect of temperature on the acidity of three selected DES [80,166].

| Benzyl tri-methylammonium chloride:p-Toluenesulfonic acid (3:7) |        | Benzyl tri-methylammonium chloride:Oxalic acid (1:1) |        | Benzyl tri-methylammonium chloride:Citric acid (1:1) |        |
|-----------------------------------------------------------------|--------|------------------------------------------------------|--------|------------------------------------------------------|--------|
| T/K                                                             | pH     | T/K                                                  | pH     | T/K                                                  | pH     |
| 292.8                                                           | −1.43  | 292.9                                                | −0.943 | 292.9                                                | −0.023 |
| 298.1                                                           | −1.38  | 297.9                                                | −0.942 | 297.9                                                | 0.015  |
| 303.2                                                           | −1.58  | 302.9                                                | −0.942 | 302.9                                                | 0.053  |
| 308.3                                                           | −1.613 | 308.1                                                | −0.941 | 308.0                                                | 0.072  |
| 313.2                                                           | −1.612 | 312.9                                                | −0.940 | 313.2                                                | 0.055  |
| 318.0                                                           | −1.611 | 317.9                                                | −0.939 | 317.9                                                | 0.101  |
| 323.0                                                           | −1.601 | 322.9                                                | −0.929 | 322.9                                                | 0.093  |
| 328.2                                                           | −1.57  | 327.9                                                | −0.928 | 327.7                                                | 0.094  |
| 333.0                                                           | −1.56  | 332.8                                                | −0.899 | 332.9                                                | 0.104  |

groups that are combined (Table 9). Mixture acidity is not critical only for the system characteristics defining. Also, it is essential for industrial applications in the future. The knowledge about the pH is necessary for the piping materials selection in the industrial processes because of the troubles of the corrosion and chemical reactions [46]. In many cases, acidic DES is employed as a catalyst and solvent mainly in the processes of *trans*-esterification and esterification. For these purposes, the acidity determination is crucial. From the data in Table 10, it is obvious that the effect of temperature on the acidity magnitude is weak [80].

### 3.7. Ionic conductivity

By the common sense, ionic conductivity is the ability of a material to conduct the ions flow or the material permittivity for the current flow by the ionic conduction mechanism. DES conductivity is a main interest for the efforts of research that is involved in the applications of power systems. An example of these application is the probable use in the redox flow batteries (RFBs) as advanced electrolytes [54]. DES ionic conductivity have the tendency to be less conductive in comparison with the high-temperature molten salts [46]. Some DES ionic conductivity is reported in Table 11.

### 3.8. Refractive index

It is a dimensionless property of the material which is quantified for a medium by the ratio of the light speed in the vacuum to the light speed when it passes that medium. At present, there are not much studies that report the DES refractive index values [168]. Nevertheless, a few research groups executed their studies by procedure that deliver important information for the field. For instance, a case exploited the refractive index to explain the association of the organic molecules with each other in alcoholic binary mixture. Another use for the refractive index is to examine the DES electrical properties. However, the DES refractive index is mostly disregarded or is not utilized enough, but it can be a tool that add measurements of a physical property to be an evidence on the formation of the hydrogen bond [46]. Some refractive index data are included in Table 12.

### 3.9. Desorption enthalpy

Desorption from NADES/DES at low temperature offers benefits in the regard of the actual utilization as solvents on the industrial scale. Meaning, low heat consumption and further economical operations. Typical aqueous monoethanolamine (MEA) has a heat of absorption magnitude of ~80 kJ/mol CO<sub>2</sub> [170]. Chemisorption which forms carbamate leads to a greater absorption heat as MEA case and the other capture process based on chemisorption. Consequently, when the capture process is not within the

**Table 11**  
Ionic conductivity of some DES.

| HBA                                    | HBD               | [HBA]:[HBD] ratio | Ionic conductivity/(mS/cm) at 25 °C | Ref.  |
|----------------------------------------|-------------------|-------------------|-------------------------------------|-------|
| Choline chloride                       | Urea              | 1:2               | 2.31                                | [95]  |
|                                        | Glycerol          | 1:2               | 0.985                               | [46]  |
|                                        | Ethylene glycol   | 1:2               | 7.63                                | [157] |
|                                        | Oxalic acid       | 1:1               | 0.38                                | [99]  |
|                                        | Triethanolamine   | 1:1               | 0.474 (at 40 °C)                    | [167] |
|                                        | Phenol            | 1:3               | 3.14                                | [100] |
|                                        | o-Cresol          | 1:3               | 1.21                                |       |
|                                        | Imidazole         | 3:7               | 12 (at 50 °C)                       | [97]  |
|                                        | ZnCl <sub>2</sub> | 1:2               | 0.06 (at 42 °C)                     | [75]  |
|                                        | Urea              | 1:3.5             | 0.18 (at 42 °C)                     |       |
| ZnCl <sub>2</sub>                      | Ethylene glycol   | 1:2               | 5.27                                | [96]  |
| N,N-diethylethanolammonium chloride    |                   | 1:2               | 0.635                               |       |
| Tetra- <i>n</i> -butylammonium bromide |                   |                   |                                     |       |
| MnCl <sub>2</sub> ·4H <sub>2</sub> O   | Acetamide         | 1:7               | 0.127 (at 29.4 °C)                  | [144] |
|                                        | Glycerol          | 1:1               | 0.031 (at 29.5 °C)                  |       |
|                                        | D(+)-Glucose      | 1:1               | 0.099 (at 27.7 °C)                  |       |
|                                        | D(-)-Fructose     | 1:1               | 0.077 (at 28.9 °C)                  |       |
|                                        | D(-)-Fructose     | 1:2               | 0.007 (at 28.1 °C)                  |       |

**Table 12**  
Refractive index of some DES.

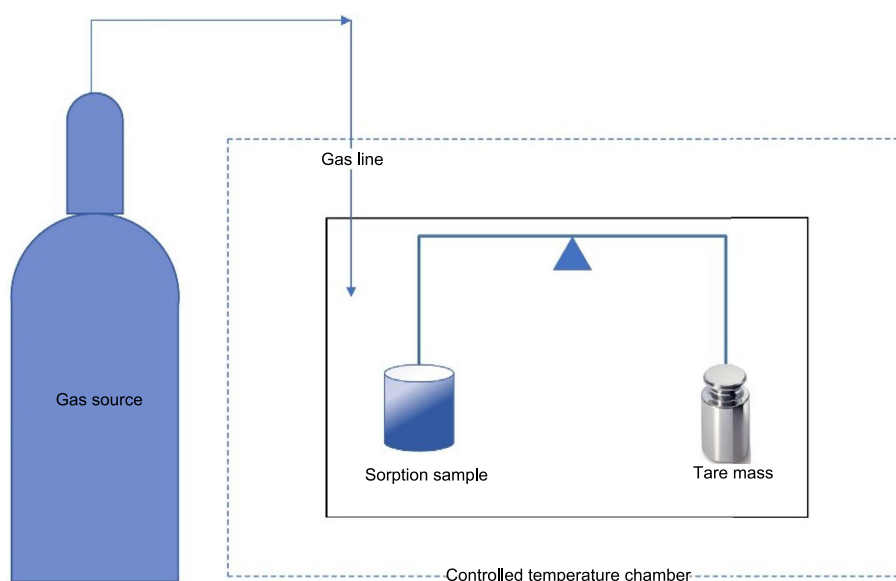
| HBA                                  | HBD              | [HBA]:[HBD] ratio | Refractive index at 25 °C | Ref.  |
|--------------------------------------|------------------|-------------------|---------------------------|-------|
| Choline chloride                     | Urea             | 1:2               | 1.504 (at 30 °C)          | [95]  |
|                                      | Glycerol         | 1:2               | 1.487                     | [169] |
|                                      | Ethylene glycol  | 1:2               | 1.468                     |       |
|                                      | Phenylactic acid | 1:2               | 1.526                     | [46]  |
|                                      | Citric acid      | 1:1               | 1.502                     |       |
| N,N-diethylethanol ammonium chloride | Ethylene glycol  | 1:2               | 1.468                     | [133] |
|                                      | Glycerol         | 1:2               | 1.486                     |       |

chemisorption range of enthalpy, the DES regeneration process shall be less intensive in energy and shall be carried out with the pressure release. NADES that are composed of carvone, cineole, menthol, and thymol with 1:1 ratio showed heat of adsorption values less than 70 kJ/mol CO<sub>2</sub> within

the pressure range of 5–10 bar. At higher pressure up to 40 bar, all the values are less than 20 kJ/mol CO<sub>2</sub> which is lower than that of MEA [171]. Alkhatib et al. [172] observed the enthalpy of desorption for [TBA][Cl]-LA (1:2) and [TEA][Cl]-LA (1:2) DES and it was approximately 12 kJ/mol CO<sub>2</sub> for both of them. This value is lower than the one of 30 wt% of aqueous MDEA which is 52.5 kJ/mol CO<sub>2</sub>.

#### 4. Experimental measure methods for solubility

There are several experimental measure methods that are used to quantify the gas solubility in ILs. These methods are mostly physical mechanism based methods [173]. DES are being called the current century green solvents. They are designable and considered as the replacements to ILs [13]. Hence, the suitable methods for the gas capture by the ILs are suitable to the DES for the gas capture too. Amongst the solubility techniques, the isochoric method, gravimetric microbalance method, and synthetic method (bubble point) are the most frequently used by the scientists.



**Fig. 4.** Gravimetric microbalance equipment for the gas sorption measurements. Adapted with permission from Ref. [175]. Copyright 2005 American Chemical Society.

#### 4.1. Gravimetric microbalance quantifying method

Originally, this technique was employed to gauge the gas solubility in the polymers [174]. After that it was expanded to be used for the diffusivity and the solubility of gases in the ILs [173]. Fig. 4 shows the gravimetric microbalance. In this method, the observer is allowed to observe the pressure, temperature, and the change in the mass over time in order to calculate the gas sorption precisely. The liquid sample is placed in the balance in contact with desired gas. When there is no more change in the mass, this means that the sample reached the equilibrium state [175].

#### 4.2. Quartz crystal microbalance quantifying method

A film of the liquid sample in this method covers a quartz resonator. The principle of this method is that when the gas dissolves in the liquid sample, the quartz crystal microbalance detects the frequency change.

Then it measures the mass change based on the frequency change [176]. Fig. 5 shows the setup of this method.

#### 4.3. Weight method

Here, samples of the liquid and the gas are taken from equilibrium cell. The liquid sampler stream is brought to determine the composition by mass change measuring of the liquid before and after the gas sorption. The stream of the gas is connected to a gas chromatography device to analyze if there is any amount of the liquid sample in the gas. A schematic Fig. 6 shows the principle of this method [177,178].

#### 4.4. Isochoric method

Isochoric process means a process occurring under the condition of a constant volume [179]. The principle of the solubility measurements by

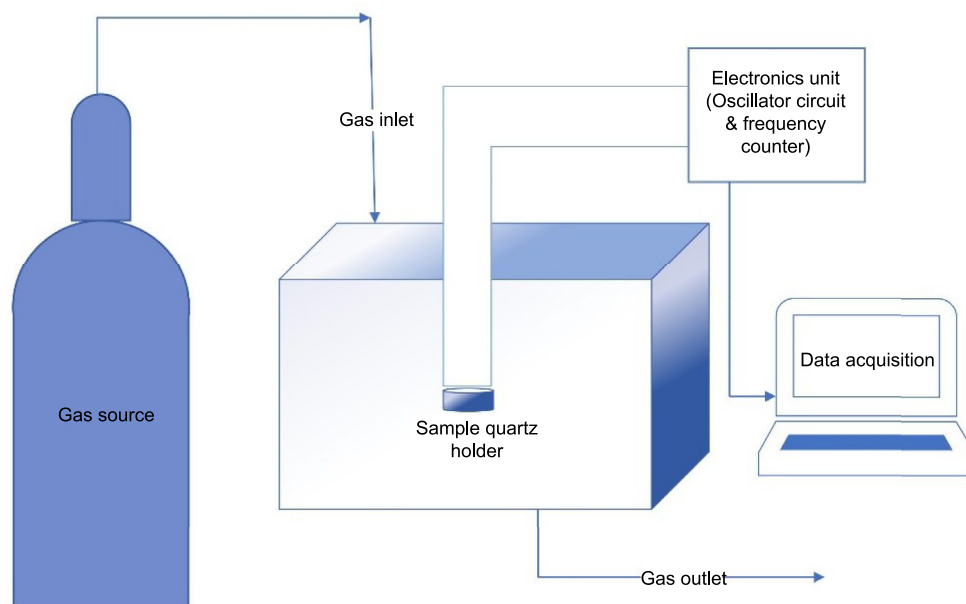


Fig. 5. Quartz crystal microbalance quantifying method of the gas dissolution. Adapted with permission from Ref. [176]. Copyright 2004 American Chemical Society.

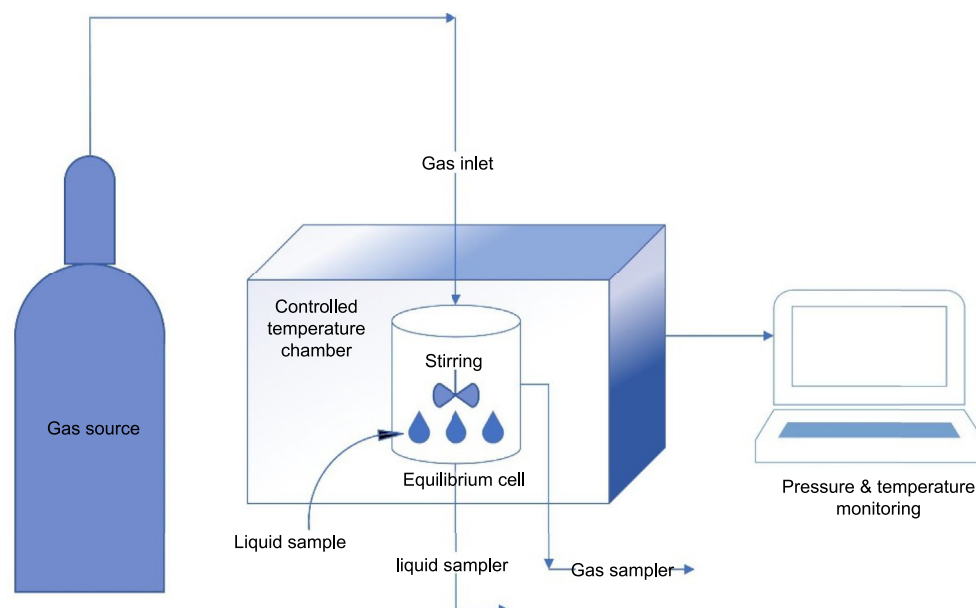


Fig. 6. Weight method for the measuring of gas absorption by liquids. Adapted with permission from Ref. [177]. Copyright 2010 American Chemical Society.

this technique is using a known gas amount in isolated equilibrium cell to be in contact with the liquid sample at a constant temperature [180]. Fig. 7 shows a standard chart for this method. In this method the mass of the liquid sample is known. During the time of the measurement the pressure decreases until reaching the equilibrium state and then the solubility is calculated in terms of mole fraction of the gas in the liquid sample. This method can be used in a wide range of pressure (0.1–700 bar) [173].

#### 4.5. Synthetic (bubble point) method

Generally, synthetic method is implemented in the apparatus of Cailletet in a pressure limit up to 150 bar [181]. Also, this method can be applied on a higher limit of pressure up to a thousand bar using an autoclave apparatus. This technique is useable with single gas solubility measuring in liquids, such as the solubility in ILs of the gases CO, CO<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>. At a fixed temperature and defined composition of a liquid, the pressure inside the system is increased, until the observation of phase change visually by the transparent window, using a pressure generator. The method has two advantages which are the short time of measurements and it is suitable for the very high pressure work [173]. During the observation of bubbles appearance from a single homogenous phase by the slow pressure reducing, the measured value of pressure at the appearance of the first bubble is the bubble point pressure [182]. Also, the bubble point can be defined in an opposite way as the final bubble vanishes by a slow pressure increasing from a gas-liquid phase [183]. Based on this definition, the synthetic method is called as bubble point method [173]. Fig. 8 demonstrates the synthetic method.

#### 4.6. Transient thin-film method

The liquid sample is constructed as a thin layer inside a closed cell. In the course of time, the pressure change is recorded right away when the gas gets into the cell. From the obtained experimental data, the constant of Henry's law and diffusivity are calculated based on the nonlinear least-square method. The method is demonstrated by Fig. 9. In comparison with the semi-infinite method, which will be shown in the following section, transient thin-film method gives results with a higher accuracy than the obtained results by semi-infinite method. That because the pressure change is cautiously monitored within longer time segment of CO<sub>2</sub> diffusivity and solubility measurements [184].

#### 4.7. Semi-infinite volume method

In this model the diffusion is measured over the first 20 min without mixing in the equilibrium cell. After that period of time the solubility is measured under a vigorous mixing in the cell in purpose of equilibrium time reduction. These are the differences between this method and the transient thin-film method. In addition to that, in this method the needed volume of liquid is larger than that in the transient thin-film method. The reason behind the larger volume in this method is that, during the mass transfer equation, solving the volume is assumed to be infinite [173]. The device comprises mainly of two units; the first one serves as a place to let the gas reaches the desirable temperature and the second one is the equilibrium chamber in which the solubility will take place in that as shown in Fig. 10 [185,186].

#### 4.8. Comparative analysis of experimental solubility methods

The gravimetric microbalance method provides precision as it allows for the direct observation of mass changes over time, enabling the exact calculation of gas sorption. However, it necessitates careful monitoring and the maintenance of stable conditions to reach an equilibrium state. The quartz crystal microbalance technique offers sensitivity to minor frequency changes, a result of gas dissolution, thereby enabling detection of slight variations. A potential drawback could be its heavy reliance on

the physical stability of the liquid film on the resonator. On the other hand, the weight method provides a direct measurement of mass changes before and after gas sorption, but the procedure is quite complex as it involves equilibrium cell sampling and chromatography analyses. The isochoric method can operate over a wide range of pressure conditions, rendering it highly versatile. However, maintaining a constant temperature, a requirement for this method, can be challenging and necessitates precise controls. The synthetic or bubble point method has its advantages in allowing quick measurements and being suitable for high-pressure conditions, but it relies on the visual observation of phase changes, which may introduce subjective bias. The transient thin-film method offers high accuracy due to the careful monitoring of pressure changes over a longer time segment, but ensuring a stable thin liquid layer could be a technical challenge. Lastly, the semi-infinite volume method is suitable for larger liquid volumes, as the method assumes an infinite volume for solving mass transfer equations. However, the need for vigorous mixing to reduce the equilibrium time could introduce additional variability.

### 5. Theoretical/simulation methods

#### 5.1. Molecular dynamics (MD) simulations

MD simulations are one of the most extensively used computational methods for understanding macromolecular structure to function relationships in a system. In the last few years, developing faster processors and integration with lab-scale experiments played an important role in MD simulations. It become much more powerful and accessible, and increased the ability to visualize structural models of molecules and periodic systems [187]. These tools were used to interpret experimental results, guide experimental work and macroscopic observations, discriminate among various competing models, and provide the basis for prediction to test the validity of the scientific hypothesis [188]. Modern molecular modeling has high accuracy with a variety of computer platforms ranging from personal computers to massively parallel supercomputers. This improvement has generated a surprisingly large number of MD applications such as protein structure, drug discovery, and gas capture [189].

The basic idea of MD is treating the molecule as an isolated entity (gas phase molecule) or solvated (by using an advance modeling approach) ion or molecule. MD simulations evaluate the interaction energies for a given structure or configuration based on the equations of classical mechanics and, therefore, describe how every atom in a molecular system will move over a time scale of pico- and nanoseconds, derived from a general model of the physics governing interatomic interactions and tracking particle trajectory to analytical expressions that have been parameterized with quantum calculations. MD simulations use Laplace's vision and Newtonian physics to provide insight into molecular motion on an atomic scale [190]. Each type of atom in the system corresponds to a different set of parameters, characterized by force constants, atomic data (radii, charge, mass, etc.), and structural equilibrium values. These parameters can be obtained either from experimental data or through mechano-quantum calculations and take into consideration intra-molecular effects related to bonded interactions such as stretching, bending, and torsional, along with electrostatic charge distribution such as vdW and electrostatic.

The variation of molecular simulations in representing complex systems and their molecular interactions stems from using a representation of atom-atom interactions in the form of a molecular force field. The force field refers to the parameters and equations that are used to specify the atoms, the bonds, and the mathematical treatment that relates them. There are multiple types of force fields, one of the most used is the MMFF94 (Merck Molecular Force Field) [191]. The general form of a MMFF is described as Eq. (1):

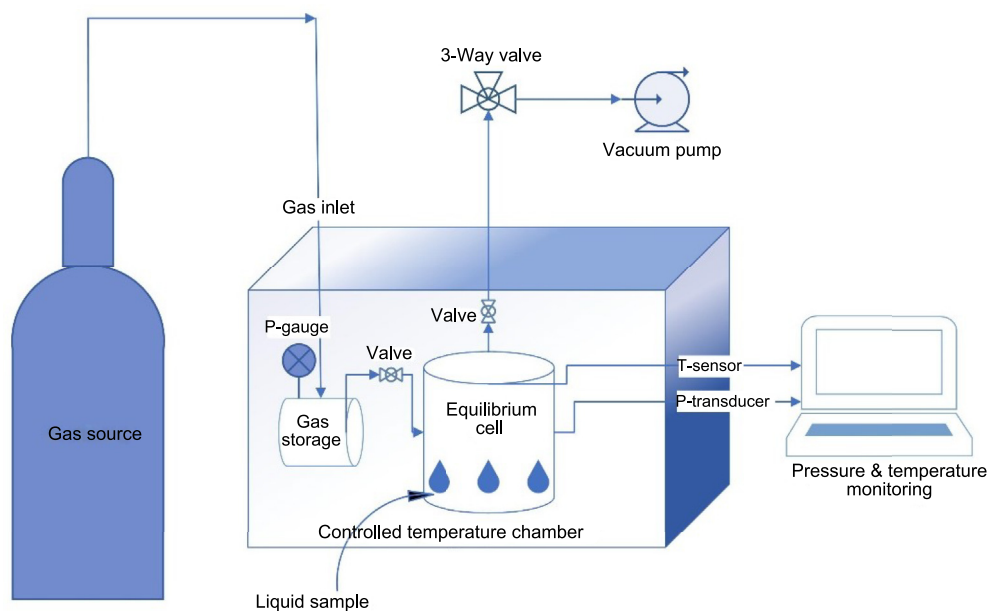


Fig. 7. Isochoric method of gas capture by liquids at low- and high-pressure ranges. Adapted with permission from Ref. [173]. Copyright 2014 American Chemical Society.

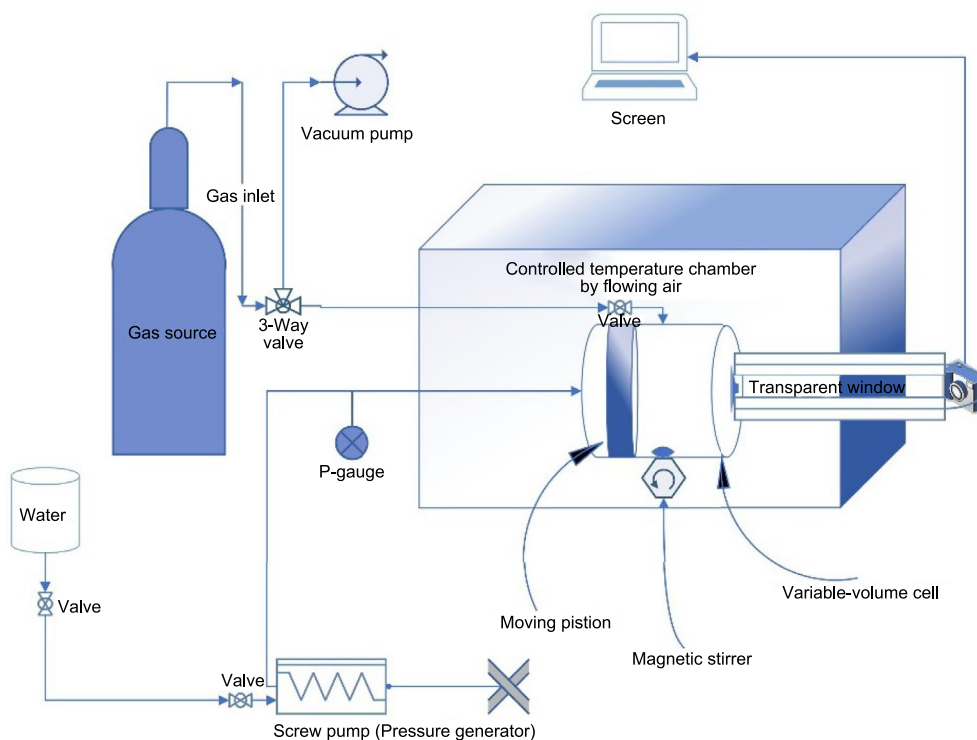


Fig. 8. Gas solubility in liquids measuring equipment by synthetic/bubble point method. Adapted with permission from Ref. [173]. Copyright 2014 American Chemical Society.

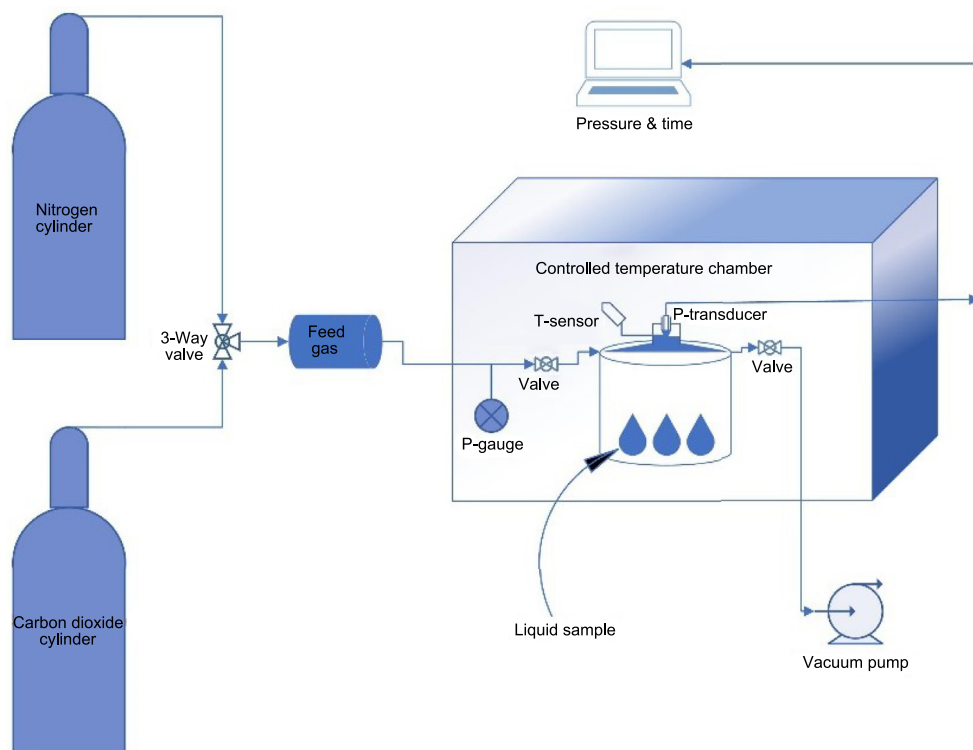
$$E = \sum_{\text{bonds}} k_r (r - r_{eq})^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_{eq})^2 + E_{\text{tor}} + \sum_i \sum_j \left\{ 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j e^2}{4\pi\epsilon_0 r_{ij}} \right\} \quad (1)$$

Dihedrals ( $E_{\text{tor}}$ ) and improper dihedrals were described according to:

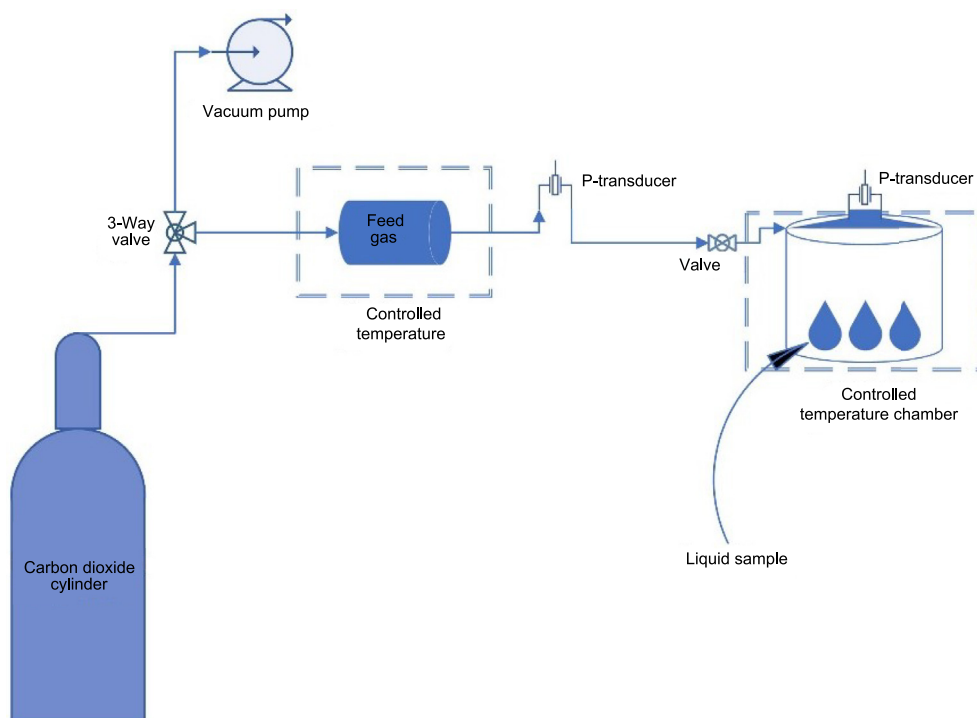
$$E_{\text{tor}} = \sum_{\text{torsions}} k_\phi \left[ 1 + \cos(m\phi - \delta) \right] \quad (2)$$

$$E_{\text{improper}} = k_\phi (\phi - \phi_0)^2 \quad (3)$$

Where  $E$  is the energy,  $k_r$ ,  $k_\theta$ , and  $k_\phi$  are force constants of bonds, angles, dihedrals and improper dihedrals terms (respectively),  $r$  and  $r_{eq}$  are bond length and equilibrium bond length,  $\theta$  and  $\theta_{eq}$  are bond angle



**Fig. 9.** Solubility of gases in liquids measurement by the transient thin-film method. Adapted with permission from Ref. [184]. Copyright 2007 American Chemical Society.



**Fig. 10.** Demonstration of the gas capture procedure by the semi-infinite volume method. Adapted with permission from Ref. [186]. Copyright 2006 American Chemical Society.

and equilibrium bond angle,  $E_{\text{tor}}$  is torsion energy,  $\epsilon_{ij}$  is Lennard-Jones (LJ, vdW) well-depth between atoms  $i$ - $j$ ,  $\sigma_{ij}$  is Lennard-Jones radius between atoms  $i$ - $j$ ,  $r_{ij}$  is the distance between atoms  $i$ - $j$ ,  $q_i$  and  $q_j$  are the charges of atoms  $i$  and  $j$ ,  $e$  is the proton charge,  $\epsilon_0$  is the dielectric constant,  $m$  is an integer,  $\phi$  is the torsion (and improper) angle,  $\phi_0$  is the

equilibrium improper angle, and  $\delta$  is the electrostatic damping constant.

In addition to MD, another widely used method for molecular modelling is Monte Carlo, that uses the same concept. Monte Carlo simulation uses random sampling and statistical modeling to estimate mathematical functions and simulate the operations of complex systems

to obtain the statistical properties [192]. Monte Carlo simulations have been very valuable in understanding the structure and properties of systems with many coupled degrees of freedom, such as fluids, disordered materials. For example, Monte Carlo simulations with accurate energy potentials can estimate liquid densities and heats of vaporization with few percent accuracy. Monte Carlo simulations can provide information about the structure of hydration shells around solutes and allow to estimate how different solvents alter the energy profiles in chemical reactions [193]. For systems that has solvents in their systems like DES, Monte Carlo methods uses optimization, and generating draws from a probability distribution [194]. When the probability distribution of the variable is obtained, a Markov Chain Monte Carlo (MCMC) sampler used to evaluate the sample from the desired distribution [195]. In general, Monte Carlo method requires many samples to get a good approximation which make this computational method cost high. And may incur an arbitrarily large total runtime if the processing time of a single sample is high. This large cost can be reduced using parallel computing strategies in local processors, clusters, and cloud computing [196].

Both MD and MC models investigate the effect of temperature, pressure, and composition on a molecular system in statistical mechanics ensembles. Monte Carlo methods are extensively used for systems where the temporal evolution is not relevant for properties calculation such as density, while molecular dynamics are mainly used for calculation of transport properties [189]. For example, Monte Carlo simulations cannot be used to estimate free energies of macromolecules in solution, partially because transitions from one conformer to another occur infrequently. While Molecular Dynamics simulations frequently offer more efficient sampling of conformational space [196]. The limited use of MC simulations for DES availability in literature is likely because of the strong intermolecular interactions, including hydrogen bonding, that result in a high viscosity of most common DES, and may cause slow equilibration, difficult molecule insertions, and inefficient sampling of the phase-space [197].

## 5.2. Density functional theory (DFT) calculations

DFT is one of the most popular quantum mechanical tools, to probe various properties of matter in a system through its wavefunction which is found out by solving the Schrodinger equation for that system. DFT modeling a small but sufficient fragment simulation employed to show positively affected and guided for the promising DES design for the next generation capture solvents such as CO<sub>2</sub>, SO<sub>2</sub>, and CH<sub>4</sub>. DFT commonly used to calculate the type and intensity of the interactions and equilibrium geometries of single molecules or complexes of molecules bound by networks of various interactions in the gas phase or by applying continuum solvation models to simulate the effects of a solution [198]. DFT studies the DES properties by analysis its obtained parameters like Bader's quantum theory of atoms in a molecule (QTAIM), electrostatic potentials (ESP), and reduced density gradients (RDG). RDG analysis can characterize non-covalent interactions such as H-bonds, van der Waals interactions, and steric effects [199]. Classification of H-bonds, the corresponding bond strengths, and covalency can be completed by analyzing bond critical points (BCP) in the QTAIM representation based on electron density and its derivatives [200].

Using DFT, Atilhan et al. [198] studied 9 different DES compounds and their affinity towards SO<sub>2</sub>. They presented a detailed QTAIM showing a mechanism of interaction sites and the strongest interaction paths between the DES and SO<sub>2</sub> and RDG analysis to visual the interaction type between the studied structures and parameterize, such as van der Waals type interaction between DES and SO<sub>2</sub>. Their findings presented the density of states (DOS) that showed the nature of the charge transfer that occurs between the various active sites of the DES and SO<sub>2</sub> molecules, and they combined these results with Homo-Lumo analysis. The DOS data characterize which anion or cation from the corresponding HBA plays the major role on the charge transfer process. ESP analysis was also included to visualize isosurfaces of the total charge distribution and

relative polarity of the DES + SO<sub>2</sub> structures. García et al. [201] also used DFT to study choline chloride based DES including glycerol and malonic acid as HBDs in CO<sub>2</sub> capture. The obtained parameters showed the suitability of DES as CO<sub>2</sub> capture agents. DFT approach was used by McGaughy et al. [202] to prepare and evaluate their system of DES (choline chloride and urea at a 1:2 M ratio and methyl-triphenylphosphonium bromide (METPB) and ethylene glycol at a 1:3 M ratio) for CO<sub>2</sub> and SO<sub>2</sub> capture. DFT analysis showed both solvents were able to fully dissolve and capture all SO<sub>2</sub> present in the flue gas. The Henry law constants and densities calculations for both solvents are too high, requiring high-pressure absorption systems to achieve even 30% CO<sub>2</sub> removal. Wu et al. [203] used both DFT and MD to explain their experimental results for 1-ethyl-3-methylimidazolium chloride ([Emim] Cl) + imidazole DES for H<sub>2</sub>S and CO<sub>2</sub> absorption. According to this study, the H<sub>2</sub>S solubilities in the [Emim]Cl + imidazole DES are much higher than those of CO<sub>2</sub>. It is demonstrated that the strong interaction was found between the H of H<sub>2</sub>S and Cl<sup>−</sup> of [Emim]Cl, which contributes to the excellent performance of [Emim]Cl + imidazole DES in separation of H<sub>2</sub>S from CO<sub>2</sub>. [Emim]Cl + imidazole and this DES have extremely high efficiency for H<sub>2</sub>S absorption and large selectivity towards CO<sub>2</sub>.

## 5.3. COSMO-RS calculations

COSMO-RS (Conduct or-like screening model for real solvents) is a method to describe the thermodynamic properties of pure compounds and mixtures of compounds based on the unimolecular quantum chemical calculations of constituents. These thermodynamic properties including solubility, partition coefficient, henry constant, sigma profiles ( $\sigma$ -profiles), and the liquid–liquid equilibria [204]. These macro-scale models mostly rely on input data from empirical observations or on the results of other calculation methods. COSMO-RS combines quantum chemical calculations with statistical thermodynamic approaches to overcome the limitations of dielectric continuum solvation models, in which the solvent is modeled as a polarizable continuum to decrease the computational intensity [205]. The model uses the output of DFT such as the charge-density surface of the molecule ( $\sigma$ -surface). The model transforms this into discrete surface segments with an area and screening density charge. Here the contribution of hydrogen-bonding, electrostatic misfit (the deviation of the electrostatic interaction energy from the idealized contact of same charges with different polarities), and van der Waals interactions are considered. Next, the model calculates the sigma profiles: the screening density charge distribution of the molecule surface. The sigma profile of the complete system is the sum of the individual sigma profiles weighted with the molar ratio of the compounds. The chemical potential is calculated by an iterative function of the sigma profile of the system [206].

COSMO-RS was primarily applied in screening of DES for applications in which aiming to model DES properties in the bulk rather than *via* the direct intermolecular interactions among the constituent's solvation energies and thermodynamic equilibrium properties of liquids [206]. Liu et al. [205] investigated the data of 502 experimental for CO<sub>2</sub> solubilities and 132 for Henry's constants of CO<sub>2</sub> in DES that are available in literatures and used COSMO-RS to verify these results. Large systematic deviations of 62.2%, 59.6%, 63.0%, and 59.1% for the logarithmic CO<sub>2</sub> solubilities in the DES (1:2, 1:3, 1:4, and 1:5) were observed for the prediction with the original COSMO-RS, while the predicted Henry's constants of CO<sub>2</sub> in the DES (1:1.5, 1:2, 1:3, 1:4, 1:5) at temperatures ranging of 293.15–333.15 K are more accurate than the predicted CO<sub>2</sub> solubility with the original COSMO-RS. They used their findings to describe relation between the  $\sigma$ -profiles and the strength of molecular interactions between an HBA (or HBD) and CO<sub>2</sub>, determining the CO<sub>2</sub> solubility, and the dominant interactions for CO<sub>2</sub> capture in DES are the H-bond and van der Waals forces.

Gas absorption capabilities can be investigated using COSMO-RS by the determination of liquid-vapor equilibria. For this purpose, Wang et al. [207] used COSMO-RS for solubility calculations. They determined the

phase behavior of the eutectic systems with CO<sub>2</sub> and the pure-component parameters. Their results showed the effect in solubility of the involved variables in COSMO-RS model ranked as pressure > HBA type > HBD type > [HBA]:[HBD] molar ratio > temperature. Their findings also showed agreement between the COSMO-RS calculations and the experimental values.

## 6. Gas solubility

### 6.1. Experimental data from literature

#### 6.1.1. CO<sub>2</sub>

CO<sub>2</sub> capture by chemical absorption is a favored choice particularly the processes that are amine-based. But it has a number of drawbacks which include the massive energy use, high costs and corrosion, and the degradation of the solvent [208]. For the majority of the applications, the CO<sub>2</sub> separation cost by the amine-based techniques is very high which varies from 50 to 100 US dollars per carbon ton [209]. NADES show the ability to be a feasible substitute for the other solvent. That is because NADES have exceptional low magnitude of vapor pressure [41]. In addition to that the production cost of NADES is cheap. Also, NADES are biocompatible and biodegradable that makes the disposal process economical and simple [44]. First published work which addressed the solubility of CO<sub>2</sub> in a DES was conducted by Li and his group [210] in 2008. The used DES in that work were choline chloride (ChCl) and urea with different molar ratios. These components (ChCl and urea) are naturally-occurring materials [212]. Based on the previously mentioned definition of NADES, it can be said the first work that addressed the solubility of CO<sub>2</sub> in a DES technically addressed the CO<sub>2</sub> solubility in a NADES. Li and his group [210] worked on a temperature range of 313.15–333.15 K and pressure range 10–130 bar. They concluded that, the solubility of CO<sub>2</sub> in the DES affected by the temperature, pressure, and molar ratio of the ChCl to the urea. Table 13 represents different DES system combinations and their CO<sub>2</sub> capture capacity at pressure and temperature ranges of work.

The solubility of CO<sub>2</sub> in DES and NADES is a complex phenomenon influenced by a myriad of factors, both intrinsic to the solvent and extrinsic process conditions. At the molecular level, the solubility of CO<sub>2</sub> is significantly affected by the shape, charge density, and size of the ions present in the DES. These factors influence the structuring of the solvents, especially when a salt is added, and the type of solvation of the ions [213]. For instance, NADES containing allyltriphenyl phosphonium bromide and diethylene glycol or triethylene glycol have shown variations in CO<sub>2</sub> solubility, emphasizing the role of the solvent's chemical structure [214].

The chemical nature of the NADES also plays a crucial role. For example, hydrophobic deep eutectic solvents based on decanoic acid have shown promising results for CO<sub>2</sub> capture, with solubilities comparable to renowned fluorinated ILs. Furthermore, the solution thermodynamics of the CO<sub>2</sub>-solvent system suggests that solvents with low-to-mid-range enthalpies of solution are optimal for CO<sub>2</sub> capture [215]. Machine learning models have also been employed to mine the relationships between CO<sub>2</sub> solubility and various experimental conditions, providing insights into the intrinsic trends of CO<sub>2</sub> solubility in blended solutions [216]. Such models can offer a deeper understanding of the complex interplay between solvent characteristics and process conditions.

The solubility of CO<sub>2</sub> in NADES is influenced by a combination of intrinsic solvent properties and external process conditions. Among the external factors, temperature and pressure play pivotal roles in determining the solubility of CO<sub>2</sub> in NADES. Experimental studies have shown that increasing the pressure enhances the solubility of CO<sub>2</sub> in various solvents, including NADES. Conversely, as the temperature rises, the solubility of CO<sub>2</sub> tends to decrease [216]. This inverse relationship between temperature and solubility is consistent with the behavior of gases in liquids, as described by Henry's law. Furthermore, a study on amine-based deep eutectic solvents, which can be considered as a subset

of NADES, revealed that both temperature and pressure have a profound effect on CO<sub>2</sub> solubility. The solubility was found to increase with increasing CO<sub>2</sub> partial pressure, especially at lower temperatures [217]. This behavior can be attributed to the increased interactions between CO<sub>2</sub> molecules and the solvent components under high-pressure conditions, leading to enhanced dissolution.

The cyclability and the reuse of DES have a vital task in industrial applications. Gu et al. [233] tested the reuse of [TETA]Cl-Thymol (1:3) and [TEPA]Cl-Thymol (1:3) DES for the CO<sub>2</sub> capture at 1.013 bar and 50 °C. They found that, these DES could be reused for 5 consecutive cycles without a recognizable loss in the capacity. A group of researchers [210,218,225] collected absorption data of CO<sub>2</sub> by ChCl-Urea (1:2) over the range of pressure between 15 and 40 bar at 303, 313, and 323 K. They used the DES for three cycles, and they did not observe any degradation in the absorption performance within the cyclic tests. Additionally, they explored the CO<sub>2</sub> absorption by 4 NADES systems that are comprised of carvone, cineole, menthol, and thymol with 1:1 M ratio at two isotherms 298 and 308 K under a pressure up to 40 bar. They computed the heat of absorption and found it falls in the physisorption range. They approved that by the observation of no change in the Fourier Transform Infrared Spectroscopy (FTIR) before and after the CO<sub>2</sub> capture process. This means that the regeneration of the NADES should be done with pressure release only and no heat is needed. Therefore, the degradation will be marginal do to the avoidance of the heat in the regeneration/desorption process [171]. Bi's group [235] explored the regeneration and the cyclability of the [MEACl][MEA]-EG and [MEACl][MEA]-G by repeating the absorption-desorption process consecutively 5 times. The desorption was done at the temperature of 110 °C. The DES were recycled successfully without a drop in the uptake capacity of CO<sub>2</sub>. Consequently, the tested DES showed a robust recycling performance in the process of CO<sub>2</sub> capture.

#### 6.1.2. CH<sub>4</sub>

As it was mentioned previously in the introduction, CH<sub>4</sub> gas is one of the gases that contribute to global warming and the environmental worries. That is because of the high potential of CH<sub>4</sub> in global warming. Its potential was estimated over a 20 years and it was 86 times of the global warming potential of the CO<sub>2</sub> [19]. EPA considers the industrial emissions of methane as a greenhouse gas [20]. Also, the dominant role of the warming pace is belong to the methane emissions [21]. On the other hand, the clean burning properties of the natural gas, which is consisted of methane with 90% [18], raised the use of it in the US as fuel for the transportation and electricity production [23]. In addition to that, it is the essential supply of hydrogen production [24]. In the global market of energy, the consumption of the natural gas is expected in the near future to be higher than petroleum and coal consuming [236]. Despite of all that importance of the CH<sub>4</sub>, the research is limited in the area of CH<sub>4</sub> capture by the DES and NADES. Table 14 shows experimental data of CH<sub>4</sub> capture.

The solubility of CH<sub>4</sub> in DES and NADES is a multifaceted phenomenon, influenced by both the process conditions and the molecular intricacies of the solvent, necessitating a holistic approach to harness their potential for gas solvation applications. CH<sub>4</sub> solubility in DES is governed by a combination of process conditions and the intrinsic chemical structure of the solvent. It was revealed that the solubility of CH<sub>4</sub> in ChCl based NADES increases with decreasing temperature and increasing pressure [237]. This observation underscores the importance of process conditions in determining the solubility of gases in DES and NADES. Furthermore, the molecular structure of the DES plays a pivotal role in its solvation capabilities. For instance, the nanostructure of the solvent can undergo changes upon hydration, which can influence their interaction with additive components [238]. Another study by García et al. [239] proposed a methodology that demonstrates the feasibility of tailoring macroscopic properties of DES through the molecular structure of the involved compounds. This approach emphasizes the significance of understanding the molecular-level interactions to optimize the solubility of

**Table 13**The solubility of CO<sub>2</sub> in different DES/NADES at different ranges of temperatures and pressures.

| HBA                                    | HBD                   | [HBA]:[HBD] ratio | <i>P</i> range/bar | <i>T</i> range/K | <i>x</i> <sub>CO2</sub> | Ref.      |
|----------------------------------------|-----------------------|-------------------|--------------------|------------------|-------------------------|-----------|
| ChCl                                   | Urea                  | 1:1.5             | 8.5–125.2          | 313.15–333.15    | 0.033–0.201             | [210]     |
|                                        | Urea                  | 1:2               | 10–127.3           |                  | 0.051–0.309             |           |
|                                        | Urea                  | 1:2.5             | 10.6–125.5         |                  | 0.032–0.203             |           |
|                                        | Urea                  | 1:2               | 2.99–59.11         | 303.15–343.15    | 0.013–0.24              | [218]     |
|                                        | Ethylene glycol       | 1:2               | 2.36–63.23         |                  | 0.006–0.275             | [219]     |
|                                        | Glycerol              | 1:2               | 1.87–63.47         |                  | 0.006–0.398             | [220]     |
|                                        | Tri-ethylene glycerol | 1:4               | 10                 | 298.15           | 0.0419                  | [211,221] |
|                                        | Ethylene glycol       | 1:4               |                    |                  | 0.023                   |           |
|                                        | Ethylene glycol       | 1:8               |                    |                  | 0.0262                  |           |
|                                        | Urea                  | 1:4               |                    |                  | 0.024                   |           |
|                                        | Urea                  | 1:2.5             |                    |                  | 0.0211                  |           |
|                                        | Glycerol              | 1:3               |                    |                  | 0.0454                  |           |
|                                        | Glycerol              | 1:8               |                    |                  | 0.0306                  |           |
|                                        | Ethanolamine          | 1:6               |                    |                  | 0.1096                  |           |
|                                        | Diethanolamine        | 1:6               |                    |                  | 0.0925                  |           |
|                                        | Glycerol              | 1:12              |                    |                  | 0.0511                  |           |
|                                        | Ethylene glycerol     | 1:12              |                    |                  | 0.0503                  |           |
| Benzyl-triphenyl-phosphonium chloride  | Ethanol amine         | 1:6               |                    |                  | 0.0716                  |           |
| n-Butyl-triphenyl-phosphonium bromide  | Ethanol amine         | 1:7               |                    |                  | 0.0643                  |           |
| Methyl-triphenyl-phosphonium bromide   | Ethanol amine         | 1:8               |                    |                  | 0.0632                  |           |
|                                        | Ethanol amine         | 1:6               |                    |                  | 0.0591                  |           |
|                                        | Di-ethanol amine      | 1:6               |                    |                  | 0.0373                  |           |
|                                        | Tri-ethanol amine     | 1:3               |                    |                  | 0.0207                  |           |
|                                        | 1,4-Butanediol        | 1:3               | 1.11–5.26          | 293.15–323.15    | 0.002–0.016             | [222]     |
| ChCl                                   | 1,4-Butanediol        | 1:4               | 1.06–5.19          |                  | 0.002–0.015             |           |
|                                        | 2,3-Butanediol        | 1:3               | 1.07–5.29          |                  | 0.003–0.015             |           |
|                                        | 2,3-Butanediol        | 1:4               | 1.07–5.12          |                  | 0.003–0.019             |           |
|                                        | 1,2-Propanediol       | 1:3               | 1.08–5.24          |                  | 0.002–0.016             |           |
|                                        | 1,2-Propanediol       | 1:4               | 1.04–5.26          |                  | 0.002–0.016             |           |
| ChCl                                   | Phenol                | 1:2               | 0.99–5.2           |                  | 0.002–0.021             | [223]     |
|                                        | Phenol                | 1:3               | 1.01–5.14          |                  | 0.003–0.021             |           |
|                                        | Phenol                | 1:4               | 1.08–5.29          |                  | 0.003–0.021             |           |
|                                        | Diethylene glycol     | 1:3               | 1.13–5.18          |                  | 0.003–0.019             |           |
|                                        | Diethylene glycol     | 1:4               | 1.10–5.27          |                  | 0.002–0.021             |           |
| ChCl                                   | Triethylene glycol    | 1:3               | 1.09–5.16          |                  | 0.003–0.027             |           |
|                                        | Triethylene glycol    | 1:4               | 1.09–5.2           |                  | 0.003–0.028             |           |
|                                        | Levulinic             | 1:3               | 0.79–5.83          | 303.15–333.15    | 0.002–0.03              | [224]     |
|                                        | Levulinic             | 1:4               | 0.72–5.87          |                  | 0.002–0.032             |           |
|                                        | Levulinic             | 1:5               | 0.72–5.81          |                  | 0.003–0.033             |           |
| ChCl                                   | Furfuryl alcohol      | 1:3               | 0.81–5.86          |                  | 0.002–0.02              |           |
|                                        | Furfuryl alcohol      | 1:4               | 0.82–5.85          |                  | 0.002–0.023             |           |
|                                        | Furfuryl alcohol      | 1:5               | 0.77–5.77          |                  | 0.002–0.023             |           |
|                                        | Urea                  | 1:2               | 0.4–1.53           | 309–329          | 0.0009–0.004            | [225]     |
|                                        | Ethylene glycol       | 1:2               | 0.47–1.54          |                  | 0.0007–0.003            |           |
| ChCl                                   | Phenol                | 1:2               | 17.1–133           | 313.15–333.15    | 0.07–0.275              | [226]     |
|                                        | Phenol                | 1:3               | 19.1–118.2         | 313.15           | 0.086–0.274             |           |
|                                        | Phenol                | 1:4               | 21–121.7           |                  | 0.087–0.293             |           |
|                                        | Phenol                | 1:3               | 23.6–121.7         |                  | 0.094–0.262             |           |
|                                        | Phenol                | 1:3               | 21.2–111.7         |                  | 0.075–0.233             |           |
| N,N,N-trimethyl-methanaminium chloride | Levulinic acid        | 1:3               | 0.66–5.72          | 303.15–333.15    | 0.003–0.031             | [227]     |
| N,N,N-triethyl-ethanaminium chloride   | Levulinic acid        | 1:3               | 0.66–5.83          |                  | 0.004–0.028             |           |
| Acetylcholine chloride                 | Levulinic acid        | 1:3               | 0.69–5.88          |                  | 0.033–0.028             |           |
| Tetraethylammonium chloride            | Levulinic acid        | 1:3               | 0.63–5.9           |                  | 0.005–0.04              |           |
| Tetraethylammonium bromide             | Levulinic acid        | 1:3               | 0.7–5.86           |                  | 0.006–0.037             |           |
| Tetrabutylammonium chloride            | Guaiacol              | 1:3               | 0.51–5.36          | 293.15–323.15    | 0.001–0.021             | [228]     |
| Tetrabutylammonium bromide             | Guaiacol              | 1:4               | 0.52–5.43          |                  | 0.001–0.022             |           |
| ChCl                                   | Guaiacol              | 1:5               | 0.53–5.39          |                  | 0.001–0.023             |           |
|                                        | Guaiacol              | 1:3               | 0.45–5.29          |                  | 0.002–0.025             |           |
|                                        | Guaiacol              | 1:4               | 0.49–5.51          |                  | 0.002–0.026             |           |
| Diethylamine hydrochloride             | Guaiacol              | 1:5               | 0.54–5.35          |                  | 0.002–0.027             |           |
|                                        | Guaiacol              | 1:3               | 0.54–5.35          |                  | 0.002–0.026             |           |
|                                        | Guaiacol              | 1:4               | 0.55–5.59          |                  | 0.002–0.025             |           |
| Acetylcholine chloride                 | Guaiacol              | 1:5               | 0.49–5.36          |                  | 0.002–0.026             |           |
|                                        | Ethylene glycol       | 1:2               | 6.44–12.46         | 303.15           | 0.026–0.052             | [229]     |
|                                        | Diethylene glycol     | 1:3               | 5.64–11.12         |                  | 0.018–0.035             |           |
| ChCl                                   | Diethylene glycol     | 1:4               | 5.24–11.2          |                  | 0.017–0.036             |           |
|                                        | Methyldiethanol amine | 1:6               | 4.46–10.96         |                  | 0.106–0.156             |           |
|                                        | Methyldiethanol amine | 1:7               | 5.94–10.34         |                  | 0.119–0.199             |           |
| Tetrabutyl ammonium bromide            | Diethanol amine       | 1:6               | 6.64–9.71          |                  | 0.032–0.09              |           |
|                                        | Ethylene glycol       | 1:2               | 4.12–12.79         |                  | 0.015–0.054             |           |
|                                        | Ethylene glycol       | 1:3               | 5.02–12.49         |                  | 0.017–0.052             |           |
|                                        | Ethylene glycol       | 1:4               | 5.43–13.75         |                  | 0.019–0.050             |           |
|                                        | Diethylene glycol     | 1:2               | 7.21–13.92         |                  | 0.034–0.099             |           |
|                                        | Diethylene glycol     | 1:3               | 6.88–12.05         |                  | 0.038–0.088             |           |

(continued on next page)

Table 13 (continued)

| HBA                               | HBD                   | [HBA]:[HBD] ratio | <i>P</i> range/bar | <i>T</i> range/K | <i>x</i> <sub>CO2</sub> | Ref.  |
|-----------------------------------|-----------------------|-------------------|--------------------|------------------|-------------------------|-------|
| Tetrabutylphosphonium bromide     | Diethylene glycol     | 1:4               | 5.9–10.48          | 313.15–333.15    | 0.047–0.09              | [230] |
|                                   | Methyldiethanol amine | 1:3               | 4.23–10            |                  | 0.086–0.204             |       |
|                                   | Methyldiethanol amine | 1:4               | 5.02–10.21         |                  | 0.11–0.225              |       |
|                                   | Diethylene amine      | 1:6               | 6.1–10.11          |                  | 0.046–0.102             |       |
|                                   | Phenol                | 1:4               | 1.64–15.78         |                  | 0.018–0.205             |       |
| Allyltriphenylphosphonium bromide | Diethylene glycol     | 1:4               | 0.94–13.98         | 313.15           | 0.017–0.212             | [231] |
|                                   | Phenol                | 1:4               | 1.83–13.45         |                  | 0.020–0.213             |       |
|                                   | Phenol                | 1:6               | 1.83–13.87         |                  | 0.021–0.195             |       |
| DL-menthol                        | Dodecanoic acid       | 2:1               | 40                 | 313.15           | 0.345                   | [232] |
| Methyltriocetylammmonium chloride | Decanoic acid         | 1:2               | 0.9–19             | 298.15–308.15    | 0.0112–0.252            | [233] |
| Tetraoctylammmonium chloride      | Decanoic acid         | 1:2               | 0.9–19             | 298.15–323.15    | 0.0117–0.284            |       |
| Methyltriocetylammmonium bromide  | Decanoic acid         | 1:2               | 0.9–19             | 313.15           | 0.0114–0.284            | [234] |
| Tetraoctylammmonium bromide       | Decanoic acid         | 1:2               | 0.9–19             |                  | 0.01107–0.257           |       |
| Triethylenetetramine-Cl           | Thymol                | 1:3               | 1                  |                  | 1.298 (mol/mol)         |       |
| Tetraethylpentamine-Cl            | Thymol                | 1:3               | 1                  | 353.13           | 1.355 (mol/mol)         | [234] |
| L-arginine                        | Glycerol              | 1:5               | 1                  |                  | 0.403 (mol/mol)         |       |
|                                   | Glycerol              | 1:6               | 1                  |                  | 0.457 (mol/mol)         |       |
|                                   | Glycerol              | 1:7               | 1                  | 298–308          | 0.451 (mol/mol)         | [171] |
| Carvone                           | Menthol               | 1:1               | 4.5–40.0           |                  | 0.04–0.50               |       |
|                                   | Thymol                |                   | 5.0–35.0           |                  | 0.025–0.48              |       |
| Cineole                           | Menthol               |                   | 5.0–35.0           |                  | 0.025–0.51              |       |
|                                   | Thymol                |                   | 5.0–35.0           |                  | 0.025–0.50              |       |

Table 14

The solubility of CH<sub>4</sub> in different DES/NADES at different ranges of temperatures and pressures.

| HBA                                       | HBD                        | [HBA]:[HBD] ratio | <i>P</i> range/bar | <i>T</i> range/K | <i>x</i> <sub>CH4</sub> | Ref.  |
|-------------------------------------------|----------------------------|-------------------|--------------------|------------------|-------------------------|-------|
| Alanine                                   | Lactic acid                | 1:1               | 1–50               | 298.15           | 0.01–0.372              | [241] |
| Betaine                                   | Lactic acid                | 1:1               |                    |                  | 0.009–0.348             |       |
| ChCl                                      | Lactic acid                | 1:1               |                    |                  | 0.011–0.403             | [236] |
|                                           | Malonic acid               | 1:1               |                    |                  | 0.01–0.309              |       |
|                                           | Phenylacetic acid          | 1:2               |                    |                  | 0.012–0.476             |       |
|                                           | Urea                       | 1:1.5             | 0.10–2.03          | 313.15–353.15    | 0.00006–0.0008          |       |
|                                           | Urea                       | 1:2               | 0.13–2.03          |                  | 0.00007–0.0008          |       |
| ChCl                                      | Urea                       | 1:2.5             | 0.11–2.03          |                  | 0.00004–0.0009          | [242] |
|                                           | Urea                       | 1:2               | 5.48–36.18         | 308.2–328.2      | 0.012–0.089             |       |
|                                           | 2-Methylaminoethanol (MAE) | 1:4               | 2.1–6.6            | 303–323          | 0.0021–0.01 (mol/mol)   | [12]  |
| Benzyltriethyl ammonium chloride (BTEACl) | 2-Methylaminoethanol (MAE) | 1:4               | 1.9–6.6            |                  | 0.0018–0.0084 (mol/mol) |       |
| Tetrabutyl ammonium bromide (TBAB)        | 2-Ethylaminoethanol (EAE)  | 1:4               | 1.8–10.4           |                  | 0.0025–0.048 (mol/mol)  |       |
| Benzyltriethyl ammonium chloride (BTEACl) | 2-Ethylaminoethanol (EAE)  | 1:4               | 1.8–7.4            |                  | 0.002–0.02 (mol/mol)    |       |

gases like CH<sub>4</sub>. Additionally, Alizadeh et al. [240] highlighted that the presence of stretched side chains in such solvents can maximize potential interaction sites for both polar and nonpolar parts, making such compounds valuable for exploiting the microheterogeneity in the solvents.

### 6.1.3. Nitrogen oxides (NO<sub>x</sub>)

NO<sub>x</sub> such as NO and NO<sub>2</sub> are primarily produced by the combustion of coal. These oxides cause many problems as the ozone (O<sub>3</sub>) layer damage, acidic rain, mist, and it damage the health of the humans [16]. Metal surface treatment industry produces a lot of NO<sub>2</sub> emissions. In the production of stainless steel or monocrystalline silicon, the emissions of NO<sub>2</sub> are produced by the process of acid pickling. It comes out as a reaction byproduct of the metals, such as ferric oxide and copper, and the nitric acid [243–245]. The typical gas streams of the flues have 95% NO of the NO<sub>x</sub> emissions. The solubility of NO is extremely low, because of that the followed method of removing the NO is converting the NO into NO<sub>2</sub> to be removed by a proper adsorbent [246]. However, the typical used adsorbent, for example, the alkaline solutions, to capture the NO<sub>2</sub> are satisfying the needed efficiency. As a result of that, an extra amount of O<sub>3</sub> is required to change the NO<sub>2</sub> to NO<sub>3</sub> [247]. Consequently, a proper and cost-effective adsorbent of NO<sub>2</sub> could treat the NO<sub>x</sub> emissions efficiently [248]. A number of investigations were done on the liquid adsorbents to explore their ability of treating the flue gas containing NO<sub>x</sub> [249,250]. They found that, during the process of NO<sub>2</sub> absorption in different aqueous solutions, the diffusional resistances act as a hinder of using the adsorbents on the commercial scale. In addition to that, the toxicity and the price of these adsorbents prevent the commercial application [243].

As the focus of this work on the NADES/DES, the gas capture by them is growing but with respect to the NO<sub>2</sub> capture by the NADES/DES is yet limited. Table 15 shows experimental absorption data by DES.

The solubility of N<sub>2</sub> in DES is profoundly influenced by the molecular architecture of the solvent. At the heart of this influence lies the nature and strength of hydrogen bonding within the NADES. The choice of HBA and HBD in the NADES can significantly modulate N<sub>2</sub> solubility. For instance, DESs formulated with potent hydrogen bond donors typically exhibit augmented N<sub>2</sub> solubility [251]. Additionally, specific functional groups present in the DES can play a pivotal role in determining N<sub>2</sub> solubility. The incorporation of ether groups, for example, can enhance the solubility of N<sub>2</sub> due to the heightened polarity which these groups introduce. The type of anion in the NADES also holds considerable sway over solubility dynamics. Certain anions, such as acetate, have been identified to favor higher N<sub>2</sub> solubility compared to their counterparts. The microheterogeneity inherent to DESs, stemming from their intricate liquid structures, further impacts gas solubility. This microheterogeneity, often a result of specific molecular interactions and structures within the solvent, can significantly modulate the solubility of gases like N<sub>2</sub> [252]. Beyond the chemical structure, external process conditions, especially temperature, play a role in N<sub>2</sub> solubility. A rise in temperature typically correlates with diminished N<sub>2</sub> solubility in DES [221]. It's also worth noting that the potential formation of metastable polymorphs in DES can lead to skewed estimates of properties, emphasizing the need for careful characterization [253].

#### 6.1.4. Sulfur oxides ( $\text{SO}_x$ )

Fossil fuel burning and the eruptions of the volcanoes produce acidic  $\text{SO}_2$ . Also, the waste gas of industry contains  $\text{SO}_2$ . The existence of the  $\text{SO}_2$  in the atmosphere in large amounts is a reason of acidic rain, human tumors, and air pollution [16]. Because of the high hazardous impact of the  $\text{SO}_2$ , the capture of this toxic gas is needed with low cost, high performance, and high sustainability. The capture of such gases will enhance the quality of the air and will keep the ozone layer protected.  $\text{SO}_2$  is a beneficial decolorizer, preservative, and bactericides [29]. Until this time, various methods were developed in order of  $\text{SO}_2$  emissions control. A common technology that is used to capture the  $\text{SO}_2$  is the limestone/lime technology [260]. In this method, the absorbents are needed in a large amount. In addition to that, the absorption process is irreversible. Also, this process produces wastewater and different side products. Organic solvents are used mainly in other methods of absorption [261–263]. In these techniques, the volatility of the solvents cannot be ignored [264]. Thus, the need to produce green, reversible, and efficient absorbents for desulfurization is the motivation of the studies that explored different types of DES. Table 16 reports the experimental  $\text{SO}_2$  solubility data in DES.

$\text{SO}_2$  solubility in NADES is influenced by a myriad of factors, both from the perspective of process conditions and the inherent chemical structure of the solvent. A study by Ghobadi et al. [265] highlighted that the high solubility of  $\text{SO}_2$  in certain DES and NADES that are formed with ILs based HBA is attributed to the combined interactions of  $\text{SO}_2$  with methanesulfonate anion and ether oxygen atom(s) on the imidazolium ring, as evidenced by FTIR spectroscopic and quantum mechanical calculations. Furthermore, Zhou et al. [266] investigated renewable phenol-based DES with varying molar ratios of phenols to  $\text{ChCl}$  for  $\text{SO}_2$  absorption. Their findings revealed that certain ratios, particularly GC-CC (3:1), exhibited maximum absorption capacities of 0.528 g  $\text{SO}_2$  per g NADES, demonstrating their potential as promising absorbents for  $\text{SO}_2$ . The interaction between  $\text{ChCl}$ -glycerol and  $\text{SO}_2$ , as studied by Li et al. [267], is consistent with the notion that efficient solvents for  $\text{SO}_2$  absorption should not only possess solvation capabilities but also be regenerable. Garcia et al. [268] emphasized the importance of understanding molecular-level factors to achieve high  $\text{SO}_2$  solubility in similar solvents, which is pivotal for the future application of these materials. In essence, the solubility of  $\text{SO}_2$  in DESs is a complex interplay of molecular interactions, solvent structure, and process conditions, necessitating comprehensive studies to optimize and harness their potential for industrial applications.

#### 6.1.5. $\text{H}_2\text{S}$

$\text{H}_2\text{S}$  is a very corrosive and toxic gas [286]. It typically presents in the biogas, oil, coal gasification gas, and natural gas [287–291]. The  $\text{H}_2\text{S}$  corrosivity and toxicity can cause severe problems for the health and can damage the industrial pipelines [292]. Also, that can poison the noble metal catalysts [293]. One of the most common  $\text{H}_2\text{S}$  gas absorption methods in the industry is the absorption by alcohol amine solution [287]. The classical method of absorption by amine has many drawbacks as the high flammability and volatility, high consumption of energy, and high cost of regeneration. Also, within the long-time operation, the water evaporation will make the pipelines and equipment corroded faster. In addition to that, at high temperatures the process cannot be operated [294]. Other methods of desulfurization utilize widely the molecular sieves, the membrane reactors, and the activated carbon [295]. The methods that use these materials have problems of the cost and the low efficiency of desulfurization [293]. Therefore, the importance of finding alternative materials for the  $\text{H}_2\text{S}$  capture attracted the researchers to find promising options. To our knowledge, the studies that explored the applications of the DES are still very limited and the available data are summarized in Table 17.

#### 6.1.6. $\text{NH}_3$

$\text{NH}_3$  is a corrosive, toxic, and pollutant gas which has a major

contribution of particulate solid formation in the air. Also, it causes pharyngitis/rhinitis. The main sources of the  $\text{NH}_3$  are the urea prilling towers exhausted gas and the  $\text{NH}_3$  production process purge gas. Additionally, other manufacturing actions as the refrigeration emit  $\text{NH}_3$  amounts to the air that are considerable and cannot be neglected [14]. The  $\text{NH}_3$  release can severely disturb the living environment and the human being health. On the contrary, many chemicals production is based on  $\text{NH}_3$  as a raw material. Moreover,  $\text{NH}_3$  can be utilized as a biofuel to be a providing energy source [300]. Hence, the capture of  $\text{NH}_3$  from the streams of industry is crucial in order to recycle a source of nitrogen and control air pollution [301]. One of the common methods of gas capture is the absorption by liquid solvents [302]. For  $\text{NH}_3$  capture, inorganic acids (for instance  $\text{H}_3\text{PO}_4$  and  $\text{H}_2\text{SO}_4$ ) and water are widely used for this purpose [303]. Nevertheless, in the regard of the green and sustainability of the solvents, these solvents are not favorable [301]. In 2017, the importance of the hydrogen bond networks in the efficient absorption of  $\text{NH}_3$  was demonstrated [304]. At that time, the capture of  $\text{NH}_3$  by DES started and different DES were designed reversible and efficient  $\text{NH}_3$  absorption [305]. Table 18 shows the data of  $\text{NH}_3$  capture by DES.

#### 6.1.7. Other gases

The research investigations in the field of gas capture by the NADES/DES are focused mainly on the  $\text{CO}_2$  and  $\text{SO}_2$  solubility. There are very few published data on  $\text{N}_2$ ,  $\text{CO}$ , and  $\text{H}_2$ . To our knowledge, all available data for these gases are reported in Tables 19–21.

#### 6.1.8. Molar ratio, HBA, and HBD effect on gas solubility

The molar ratio of HBA to HBD in the DES is a crucial factor affecting the solubility of gases. The first work that compares the effect of the molar ratio on the solubility of  $\text{CO}_2$  was carried out on the molar ratios of  $\text{ChCl}$  to urea. The ratios were 1:1.5, 1:2, and 1:2.5 [210]. In that work, the molar ratio of 1:2 has the best performance in terms of dissolving  $\text{CO}_2$ . This could be justified by that the real formation of the DES happened at the ratio of 1:2. Meanwhile, the lowest melting point could be achieved and the interaction between the molecules favors the gas dissolution at that ratio [210,316]. In 2019, the group of Liu [236] investigated the solubility of  $\text{CO}_2$  in  $\text{ChCl}$ -Urea with the same ratios of the first study. Their analysis found that the lowest magnitude of Henry's constant is at 1:2, demonstrating that the ultimate solubility was at that ratio which is in agreement with the previous study. The dissolution of  $\text{CO}_2$  was studied in a group of DES composed of  $\text{ChCl}$ ,  $\text{DH}$ , and  $\text{ACC}$  with guaiacol at the ratios of 1:2, 1:3, and 1:4 [228]. They revealed that the solubility of  $\text{CO}_2$  in the same DES increased by increasing guaiacol molar ratio, which can be reasoned by its hydroxyl group [317]. The interaction nature, either physical or chemical, between  $\text{CO}_2$  and the DES is determined by HBD [318]. Haider and his group [229] studied the effect of HBD to HBA ratio effect on the  $\text{CO}_2$  solubility in a set of DES. They revealed that in all the studied cases. The increase of solubility happened when the molar ratio of HBD/HBA increased. In the glycols HBD case, the increase happened because of the hydrogen bond decrease in the DES. The case of amine increases as HBD, the solubility increased following the amine affinity toward  $\text{CO}_2$ . HBA has a crucial role in gas solubility, because it has the ability to influence the dissolution more than the HBD [319]. A group of researchers observed the quaternary ammonium salts influence on the absorption of  $\text{CO}_2$ . It is found that the absorption is cation structure related rather than the anion. The solubility will be increasing with the bigger cation [226]. For  $\text{SO}_2$ , the absorption capacity is defined by the performance of the anions. Also, for  $\text{SO}_2$ , ester group performance has more effect compared to the hydroxyl group [229,320].

Mixing ratios and solvents compositions contribute to the NADES/DES capacity of absorption regardless of the preparation process. Consequently, DES/NADES and their properties are tunable corresponding to the demands and the implementations by choosing the proper molar ratios and constituents. Further research is yet required to explore the effects of different aspects such as the water effect on the

**Table 15**The available experimental data of NO<sub>x</sub> absorption by DES.

| HBA                  | HBD             | [HBA]:[HBD]<br>ratio | P range/bar                                                                                                                             | T range/K     | NO <sub>x</sub> solubility           | Ref.  |
|----------------------|-----------------|----------------------|-----------------------------------------------------------------------------------------------------------------------------------------|---------------|--------------------------------------|-------|
| ChCl                 | Glycerol        | 1:2                  | 0.111–1.013                                                                                                                             | 298.15        | NO <sub>2</sub><br>0.027–0.356 (g/g) | [243] |
| ChCl                 | Glycerol        | 1:4                  |                                                                                                                                         |               | NO <sub>2</sub><br>0.077–0.371 (g/g) |       |
| ChCl                 | Ethylene glycol | 1:2                  |                                                                                                                                         |               | NO <sub>2</sub><br>0.04–0.396 (g/g)  |       |
| ChCl                 | Ethylene glycol | 1:4                  |                                                                                                                                         |               | NO <sub>2</sub><br>0.099–0.551 (g/g) |       |
| P <sub>4444</sub> Cl | Tetz            | 1:1                  | 1.013                                                                                                                                   | 303.15–343.15 | NO<br>1–2.1 (mol/mol)                | [254] |
| N <sub>4444</sub> Cl | Tetz            | 1:1                  |                                                                                                                                         |               | NO<br>0.48–1.46 (mol/mol)            |       |
| P <sub>4444</sub> Br | Tetz            | 1:1                  |                                                                                                                                         |               | NO<br>0.221–0.48 (mol/mol)           |       |
| N <sub>4444</sub> Br | Tetz            | 1:1                  |                                                                                                                                         |               | NO<br>0.221–0.32 (mol/mol)           |       |
| P <sub>4444</sub> Cl | Triz            | 1:1                  |                                                                                                                                         | 343.15        | NO<br>0.16–0.54 (mol/mol)            |       |
| P <sub>4444</sub> Cl | Imid            | 1:1                  |                                                                                                                                         |               | NO<br>0.13–0.34 (mol/mol)            |       |
| ChCl                 | Tetz            | 1:1                  |                                                                                                                                         |               | NO<br>0.86 (mol/mol)                 |       |
| ChCl                 | Triz            | 1:1                  |                                                                                                                                         |               | NO<br>0.67 (mol/mol)                 |       |
| ChCl                 | Imid            | 1:1                  |                                                                                                                                         |               | NO<br>0.47 (mol/mol)                 |       |
| P <sub>4444</sub> Cl | 1,3-DMTU        | 1:3                  | 1.013                                                                                                                                   | 303.15        | NO<br>4.25 (mol/mol)                 | [255] |
| P <sub>4444</sub> Cl | 1,3-DMTU        | 1:2                  |                                                                                                                                         |               | NO<br>3.18 (mol/mol)                 |       |
| P <sub>4444</sub> Cl | 1,3-DMTU        | 1:1                  |                                                                                                                                         |               | NO<br>2.13 (mol/mol)                 |       |
| P <sub>4444</sub> Br | 1,3-DMTU        | 1:1                  |                                                                                                                                         |               | NO<br>1.13 (mol/mol)                 |       |
| N <sub>4444</sub> Cl | 1,3-DMTU        | 1:1                  |                                                                                                                                         |               | NO<br>2.05 (mol/mol)                 |       |
| N <sub>4444</sub> Br | 1,3-DMTU        | 1:1                  |                                                                                                                                         |               | NO<br>1.0 (mol/mol)                  |       |
| TETA-Cl              | Ethylene glycol | 1:1                  | 1.0                                                                                                                                     | 303.15        | NO<br>2.49 (mol/mol)                 | [256] |
| TEPA-Cl              | Ethylene glycol | 1:1                  | 1.0                                                                                                                                     | 303.15        | NO<br>3.1 (mol/mol)                  |       |
| TEPA-Cl              | PEG             | 1:1                  | 1.0                                                                                                                                     | 303.15        | NO<br>3.45 (mol/mol)                 |       |
| TEPA-Cl              | Glycerol        | 1:1                  | 1.0                                                                                                                                     | 303.15        | NO<br>3.35 (mol/mol)                 |       |
| TEPA-Cl              | 1,3-PG          | 1:1                  | 1.0                                                                                                                                     | 303.15        | NO<br>3.25 (mol/mol)                 |       |
| TEPA-Cl              | Ethylene glycol | 1:3                  | 1.0                                                                                                                                     | 303.15        | NO<br>4.52 (mol/mol)                 |       |
| DBU                  | Oxaz            | 2:1                  | 1.0                                                                                                                                     | 303.2         | NO<br>4.64 (mol/kg)                  | [257] |
|                      | Pyrr            |                      |                                                                                                                                         |               | NO<br>5.16 (mol/kg)                  |       |
|                      | Oxaz            |                      |                                                                                                                                         | 313.2         | NO<br>3.62 (mol/kg)                  |       |
|                      | Pyrr            |                      |                                                                                                                                         |               | NO<br>4.0 (mol/kg)                   |       |
|                      | Py              | 2:1                  |                                                                                                                                         | 313.2         | NO<br>3.7 (mol/kg)                   | [258] |
|                      | EU              |                      |                                                                                                                                         |               | NO<br>3.7 (mol/kg)                   |       |
|                      | Py              |                      |                                                                                                                                         | 303.2         | NO<br>4.4 (mol/kg)                   |       |
| TEAB                 | EG              | 1:5                  | 0.1% SO <sub>2</sub> and 0.15% NO <sub>2</sub> vol. fraction (In units of grams of NO <sub>2</sub> and SO <sub>2</sub> per gram of DES) | 323.2         | NO <sub>2</sub><br>0.186 (g/g)       | [259] |
| TPAB                 |                 |                      |                                                                                                                                         |               | NO <sub>2</sub><br>0.206 (g/g)       |       |
| TBAB                 |                 |                      |                                                                                                                                         |               | NO <sub>2</sub><br>0.296 (g/g)       |       |

**Table 16**Experimental SO<sub>2</sub> solubility data in different DES at different ranges of temperatures and pressures.

| HBA                  | HBD                             | [HBA]:[HBD] ratio | P range/bar | T range/K     | SO <sub>2</sub> solubility | Ref.  |
|----------------------|---------------------------------|-------------------|-------------|---------------|----------------------------|-------|
| PPZBr                | Glycerol                        | 1:4               | 0.01–1.0    | 293.15        | 0.980–3.97 (mol/mol)       | [136] |
|                      | Glycerol                        | 1:5               |             |               | 0.96–4.1 (mol/mol)         |       |
|                      | Glycerol                        | 1:6               |             |               | 0.99–4.28 (mol/mol)        |       |
| ChCl                 | Levulinic acid                  | 1:3               | 1.0         | 293.15–343.15 | 0.123–0.557 (g/g)          | [269] |
| ACC                  | Levulinic acid                  |                   |             |               | 0.145–0.567 (g/g)          |       |
| TEAC                 | Levulinic acid                  |                   |             |               | 0.172–0.625 (g/g)          |       |
| TEAB                 | Levulinic acid                  |                   |             |               | 0.158–0.622 (g/g)          |       |
| TBAC                 | Levulinic acid                  |                   |             |               | 0.116–0.541 (g/g)          |       |
| TBAB                 | Levulinic acid                  |                   |             |               | 0.169–0.547 (g/g)          |       |
| ChCl                 | Ethylene glycol                 | 1:2               | 1.0         | 293.15–333.15 | 0.98–2.88 (mol/mol)        | [71]  |
|                      | Malonic acid                    | 1:1               |             |               | 0.64–1.88 (mol/mol)        |       |
|                      | Urea                            | 1:2               |             |               | 0.69–1.41 (mol/mol)        |       |
|                      | Thiourea                        | 1:1               |             |               | 1.32–2.96 (mol/mol)        |       |
| ChCl                 | Glycerol                        | 1:1               | 1.0         | 293.15–353.15 | 0.158–0.678 (g/g)          | [270] |
|                      | Glycerol                        | 1:2               |             |               | 0.091–0.482 (g/g)          |       |
|                      | Glycerol                        | 1:3               |             |               | 0.066–0.380 (g/g)          |       |
|                      | Glycerol                        | 1:4               |             |               | 0.055–0.320 (g/g)          |       |
| ChCl                 | Guaiacol                        | 1:4               | 1.0         | 293.15        | 4.968 (mol/mol)            | [271] |
|                      | Guaiacol                        | 1:5               |             |               | 5.688 (mol/mol)            |       |
|                      | Cardanol                        | 1:3               |             |               | 3.221 (mol/mol)            |       |
|                      | Cardanol                        | 1:4               |             |               | 3.599 (mol/mol)            |       |
|                      | Cardanol                        | 1:5               |             |               | 3.862 (mol/mol)            |       |
| ACC                  | Imidazole                       | 1:1.5             | 0.1         | 303.15        | 0.356 (g/g)                | [272] |
|                      | Imidazole                       | 1:2               | 0.1         |               | 0.381 (g/g)                |       |
|                      | Imidazole                       | 1:3               | 0.1         |               | 0.383 (g/g)                |       |
|                      | 1,2,4-Triazole                  | 1:1               | 0.1         |               | 0.277 (g/g)                |       |
| EmimCl               | Dimethylurea                    | 2:1               | 0.1–1.0     | 293.15        | 2.5–7.26 (mol/mol)         | [273] |
|                      | N-methylurea                    | 2:1               |             |               | 2.06–6.25 (mol/mol)        |       |
|                      | Thioacetamide                   | 2:1               |             |               | 2.13–6.79 (mol/mol)        |       |
|                      | Caprolactam                     | 2:1               |             |               | 2.86–8.0 (mol/mol)         |       |
| BmimCl               | 4-Methylimidazole               | 1:1               | 1.0         | 293.15        | 1.42 (mol/mol)             | [274] |
|                      | 4-Methylimidazole               | 2:1               |             |               | 1.37 (mol/mol)             |       |
|                      | 4-Methylimidazole + Ethylenurea | 1:1:1             |             |               | 1.58 (mol/mol)             |       |
|                      | 4-Methylimidazole + Ethylenurea | 2:1:1             |             |               | 1.54 (mol/mol)             |       |
|                      | 4-Methylimidazole + Ethylenurea | 1:2:1             |             |               | 2.29 (mol/mol)             |       |
|                      | 4-Methylimidazole + Ethylenurea | 1:1:2             |             |               | 2.07 (mol/mol)             |       |
| EmimCl               | Dicyandiamide                   | 1:3               | 0.006–1.02  | 298.2–353.2   | 0.63–16.58 (mol/kg)        | [275] |
| EmimCl               | N-Formylmorpholine              | 1:1               | 0.01–0.1    | 293.15–313.15 | 0.135–0.429 (g/g)          | [276] |
| TBAB                 | Caprolactam                     | 1:1               | 1.0         | 293.15        | 2.54 (mol/mol)             | [277] |
|                      | Caprolactam                     | 1:2               |             |               | 2.18 (mol/mol)             |       |
|                      | Caprolactam                     | 1:3               |             |               | 1.86 (mol/mol)             |       |
|                      | Caprolactam                     | 1:4               |             |               | 1.68 (mol/mol)             |       |
| [EimH]Cl             | EG                              | 3:1               | 0.014–1.192 | 293.2–323.2   | 0.235–12.69 (mol/kg)       | [278] |
|                      |                                 | 2:1               | 0.012–1.267 |               | 0.259–12.12 (mol/kg)       |       |
|                      |                                 | 1:1               | 0.009–1.273 |               | 0.186–11.27 (mol/kg)       |       |
|                      |                                 | 1:2               | 0.006–1.238 |               | 0.1–9.221 (mol/kg)         |       |
| [MimH]Cl             | 2-Mim                           | 1:1               | 0.1–1       | 293.2         | 0.56–1.46 (g/g)            | [279] |
|                      | 4-Mim                           |                   |             |               | 0.54–1.39 (g/g)            |       |
|                      | Im                              |                   |             |               | 0.45–1.14 (g/g)            |       |
|                      | Triz                            |                   |             |               | 0.32–1.04 (g/g)            |       |
| DMU                  | TMU                             | 1:2               | 0.02–1.12   | 298.2         | 0.06–0.81 (g/g)            | [280] |
| Eim                  | Im                              | 1:1               | 0.002–1.04  |               | 0.08–1.04 (g/g)            |       |
| NMP                  | 2-Pyr                           | 1:1               | 0.001–1.04  |               | 0.05–0.92 (g/g)            |       |
| AA                   | MAA                             | 1:3               | 0.015–1.0   |               | 0.02–0.65 (g/g)            |       |
| 2-Im1                | DMI                             | 1:3               | 0.001–1.06  |               | 0.002–0.8 (g/g)            |       |
| Betaine              | Glycerol                        | 1:2               | 0.02–0.6    | 313.2         | 0.1–1.95 (mol/kg)          | [281] |
| TEACl                | Im                              | 1:3               | 0.1–1       | 293.2–333.2   | 0.5–1.25 (g/g)             | [282] |
|                      | Pyz                             | 1:2               |             |               | 0.28–0.82 (g/g)            |       |
|                      | Pyz                             | 1:3               |             |               | 0.25–0.9 (g/g)             |       |
|                      | Tetz                            | 1:2               |             |               | 0.21–1.0 (g/g)             |       |
| EmimCl               | TEG                             | 6:1               | 0.1–1.0 atm | 293.2–333.2   | 0.54–1.27 (g/g)            | [283] |
|                      |                                 | 4:1               |             |               | 0.5–1.18 (g/g)             |       |
|                      |                                 | 2:1               |             |               | 0.38–1.05 (g/g)            |       |
|                      |                                 | 1:1               |             |               | 0.31–0.91 (g/g)            |       |
| EmimCl               | EU                              | 1:1               | 1 atm       | 293.15        | 1.14 (g/g)                 | [284] |
| BmimCl               |                                 |                   |             |               | 1.07 (g/g)                 |       |
| BmimBr               |                                 |                   |             |               | 0.91 (g/g)                 |       |
| N <sub>4444</sub> Cl |                                 |                   |             |               | 0.81 (g/g)                 |       |
| P <sub>4444</sub> Cl |                                 |                   |             |               | 0.81 (g/g)                 |       |
| EmimCl               | DMU                             | 1:1               | 1 atm       | 293.15        | 1.14 (g/g)                 |       |
| BmimCl               |                                 |                   |             |               | 1.04 (g/g)                 |       |
| BmimBr               |                                 |                   |             |               | 0.92 (g/g)                 |       |
| N <sub>4444</sub> Cl |                                 |                   |             |               | 0.83 (g/g)                 |       |
| P <sub>4444</sub> Cl |                                 |                   |             |               | 0.83 (g/g)                 |       |

(continued on next page)

Table 16 (continued)

| HBA    | HBD | [HBA]:[HBD] ratio | P range/bar | T range/K     | SO <sub>2</sub> solubility | Ref.  |
|--------|-----|-------------------|-------------|---------------|----------------------------|-------|
| BmimCl |     | 1:2               |             |               | 0.95 (g/g)                 |       |
| BmimCl | EU  | 2:1               |             | 293.15–333.15 | 0.59–1.18 (g/g)            |       |
| BmimCl | DMU | 2:1               |             |               | 0.59–1.14 (g/g)            |       |
| Bet    | EG  | 1:3               | 0.02–1 atm  | 313.15        | 0.07–0.366 (g/g)           | [285] |

capturing capacity and affinity, the mechanism of the absorption (physical/chemical/both), absorbed gases regeneration, solvents reusability and cyclability, and the materials actual costs.

## 6.2. Molecular simulation studies from literature

The most recent applications of DFT, MD, MC, and COSMO-RS methods for modelling DES in gas capture of CO<sub>2</sub>, SO<sub>2</sub>, and CH<sub>4</sub> are discussed in this section.

### 6.2.1. CO<sub>2</sub>

CO<sub>2</sub> capture is an important issue in environmental protection and sustainable development that has been intensively researched and developed in the last decades. There are different physicochemical processes for CO<sub>2</sub> capture, such as adsorption, absorption, or the use of membranes. For the last decade, membrane technology has been the most studied and widely used in the industry. Membranes separate gases based on the contrasts in physical and chemical interactions between the different gases that make up the flue gas and the membrane, allowing only CO<sub>2</sub> to pass preferentially through them based on kinetics and thermodynamics aspects, while excluding other components of the flue gas such as N<sub>2</sub>, O<sub>2</sub>, etc. [321,322]. The most important part of this process is obviously the membrane, which is made of a material (usually a composite polymer) of which a thin selective layer is bonded to a thicker, non-selective, and low-cost layer that provides mechanical support to the membrane [323].

Some strategies that identify promising membranes for CO<sub>2</sub> capture

for further experimental synthesis and characterization are computational methods. In recent years, a graphdiyne-like membrane (GDY-H, with two layers of GDY-H adjacent to each other and 1,3,5-triaminobenzene inserted between them) which is used to separate a mixture of H<sub>2</sub> and CO<sub>2</sub> gases via DFT and MD simulations exhibits good selectivity and excellent permeances for H<sub>2</sub> and CO<sub>2</sub> passing through the membrane [324]. Another study by Ref. [321] used both DFT and MD simulations to investigate the gas separation performance of a H-passive (H-pore-10, H-pore-13, and H-pore-16) nanopores graphene membrane. They considered a mixture of CO<sub>2</sub>/N<sub>2</sub> gas molecules and three different pore sizes for the H-passive membrane. They found that H-pore-13 (among H-pore-10 and H-pore-16) had higher interaction energy with CO<sub>2</sub> in comparison with N<sub>2</sub>. Also, the barrier energy of CO<sub>2</sub> (0.19 eV) is much more than that of N<sub>2</sub> (0.05 eV), so N<sub>2</sub> could permeate through H-pore-13, whereas CO<sub>2</sub> could not. It is also important to mention that available membrane literature data shows that the performance of a membrane system is strongly affected by the flue gas conditions such as low CO<sub>2</sub> concentration and pressure [322,325–327]. Many other researchers used adsorbents for gas adsorption such as activated carbon, carbon nanotubes, Pt-doped and Au-doped single-walled carbon nanotubes, zeolites, titan dioxide, graphene, magnesium oxide, or graphite [328–330]. A current study investigated the interaction of SO<sub>2</sub> and CO<sub>2</sub> molecules on a graphite surface, where SO<sub>2</sub> molecule was strongly adsorbed on the vacancy-defected graphite compared to CO<sub>2</sub> [331].

After 2012, there has been an important increase in the number of articles related to the use of novel DES as highly promising solvents for CO<sub>2</sub> capture (Fig. 11) due to their unique properties and relative

Table 17

Experimental H<sub>2</sub>S solubility data in different DES at different ranges of temperatures and pressures.

| HBA                         | HBD            | [HBA]:[HBD] ratio | P range/bar | T range/K     | x <sub>H2S</sub>    | Ref.  |
|-----------------------------|----------------|-------------------|-------------|---------------|---------------------|-------|
| ChCl                        | Urea           | 1:1.15            | 0.1–2.02    | 313.15–353.15 | 0.0014–0.0554       | [236] |
| ChCl                        | Urea           | 1:2               | 0.1–2.02    |               | 0.0016–0.0464       |       |
| ChCl                        | Urea           | 1:2.5             | 0.12–2.01   |               | 0.0014–0.0351       |       |
| [Emim]Cl                    | Imidazole      | 2:1               | 0.06–2.4    | 298.2–353.2   | 0.1–2.8 (mol/kg)    | [296] |
| [Emim]Cl                    | Imidazole      | 1:1               | 0.06–2.06   |               | 0.1–2.6 (mol/kg)    |       |
| [Emim]Cl                    | Imidazole      | 1:2               | 0.06–2.0    |               | 0.1–2.2 (mol/kg)    |       |
| ChCl                        | Formic acid    | 1:2               | 1.1–5.1     | 298           | 0.38–1.8 (mol/kg)   | [73]  |
| ChCl                        | Formic acid    | 1:3               | 1.75–5.1    |               | 0.37–1.7 (mol/kg)   |       |
| ChCl                        | Formic acid    | 1:4               | 2.0–5.4     |               | 0.35–1.63 (mol/kg)  |       |
| ChCl                        | Acetic acid    | 1:2               | 1.5–5.24    |               | 0.54–2.46 (mol/kg)  |       |
| ChCl                        | Acetic acid    | 1:3               | 1.63–5.05   |               | 0.47–2.21 (mol/kg)  |       |
| ChCl                        | Acetic acid    | 1:4               | 2.07–5.34   |               | 0.44–2.19 (mol/kg)  |       |
| ChCl                        | Propionic acid | 1:2               | 1.85–5.4    |               | 0.71–3.63 (mol/kg)  |       |
| ChCl                        | Propionic acid | 1:3               | 1.53–5.01   |               | 0.47–3.0 (mol/kg)   |       |
| ChCl                        | Propionic acid | 1:4               | 1.93–5.05   |               | 0.51–2.84 (mol/kg)  |       |
| TBAB                        | Propionic acid | 1:1               | 1.78–5.5    | 298–318       | 0.38–3.66 (mol/kg)  |       |
| TBAB                        | Propionic acid | 1:4               | 1.84–5.36   | 298           | 0.14–0.51           |       |
| TBAB                        | Formic acid    | 1:4               | 1.83–5.15   |               | 0.27–0.65           |       |
| TBAB                        | Acetic acid    | 1:4               | 1.76–5.37   |               | 0.22–0.6            |       |
| [C <sub>4</sub> -TMEDA][Cl] | 1,2,3-Triaz    | 1:2               | 0.01–1.0    | 303.2         | 0.01–0.24 (mol/mol) | [297] |
| [C <sub>4</sub> -TMEDA][Cl] | 1,2,4-Triaz    | 1:2               | 0.01–1.05   |               | 0.01–0.28 (mol/mol) |       |
| [C <sub>4</sub> -TMEDA][Cl] | Im             | 1:2               | 0.01–1.03   |               | 0.02–0.37 (mol/mol) |       |
| [C <sub>4</sub> -TMPDA][Cl] | Im             | 1:2               | 0.01–1.0    |               | 0.03–0.48 (mol/mol) |       |
| [C <sub>4</sub> -TMHDA][Cl] | Im             | 1:2               | 0.004–1.0   |               | 0.04–1.0 (mol/mol)  |       |
| [C1-TMHDA]Ac                | MDEA           | 1:2               | 0.02–1.0    | 313.2         | 0.22–1.45 (mol/mol) | [298] |
|                             | Pyrol          |                   | 0.02–1.0    |               | 0.20–1.17 (mol/mol) |       |
|                             | AA             |                   | 0.04–1.01   |               | 0.27–1.08 (mol/mol) |       |
|                             | Im             |                   | 0.002–1.03  |               | 0.03–1.02 (mol/mol) |       |
| β-PEA                       | EG             | HBA wt% = 20%     | 0.01–1.0    | 303.15–333.15 | 0.11–1.03 (mol/mol) | [299] |
| CHA                         |                |                   | 0.006–0.94  |               | 0.26–1.11 (mol/mol) |       |
| MCHA                        |                |                   | 0.0004–0.95 |               | 0.19–1.13 (mol/mol) |       |
| DMCHA                       |                |                   | 0.02–0.81   |               | 0.1–1.1 (mol/mol)   |       |

**Table 18**Experimental NH<sub>3</sub> solubility data in different DES at different ranges of temperatures and pressures.

| HBA                      | HBD                      | [HBA]:[HBD] ratio | <i>P</i> range/bar | <i>T</i> range/K | NH <sub>3</sub> solubility/(mol/kg) | Ref.  |
|--------------------------|--------------------------|-------------------|--------------------|------------------|-------------------------------------|-------|
| ChCl                     | Glycerol                 | 1:2               | 0.099–5.68         | 303.15–333.15    | 0.29–15.35                          | [306] |
| ChCl                     | Ethylene glycol          | 1:2               | 0.129–5.515        |                  | 0.343–16.27                         |       |
| ChCl                     | N-Methyl urea            | 1:2               | 0.513–5.687        | 313.15–333.15    | 0.319–6.215                         | [307] |
| ChCl                     | Trifluoroacetamide       | 1:2               | 0.241–5.732        | 303.15–333.15    | 0.45–11.67                          |       |
| ChCl                     | Xylose                   | 1.5:1             | 0.049–2.28         | 323.2–343.2      | 0.8–5.95                            |       |
| ChCl                     | Xylose                   | 1:1               | 0.026–2.32         | 333.2            | 0.72–5.98                           |       |
| ChCl                     | Xylose                   | 2:1               | 0.097–2.42         |                  | 0.98–4.81                           |       |
| ChCl                     | Ribose                   | 1.5:1             | 0.034–2.3          |                  | 0.95–5.38                           | [308] |
| ChCl                     | Fructose                 | 1.5:1             | 0.052–2.26         |                  | 0.83–5.95                           |       |
| Ethylamine hydrochloride | Glycerol                 | 1:2               | 0.074–2.41         | 298.2–353.2      | 0.33–16.49                          |       |
| Ethylamine hydrochloride | Glycerol                 | 1:3               | 0.04–2.45          |                  | 0.43–16.56                          |       |
| Ethylamine hydrochloride | Glycerol                 | 1:4               | 0.039–2.46         |                  | 0.36–16.77                          |       |
| Ethylamine hydrochloride | Glycerol                 | 1:5               | 0.077–2.42         |                  | 0.35–16.27                          | [301] |
| Ethylamine hydrochloride | Phenol                   | 1:2               | 0.04–2.4           | 313.2            | 2.04–9.5                            |       |
| Ethylamine hydrochloride | Phenol                   | 1:3               | 0.006–2.4          |                  | 0.63–10.16                          |       |
| Ethylamine hydrochloride | Phenol                   | 1:5               | 0.024–2.44         |                  | 0.89–11.09                          |       |
| Ethylamine hydrochloride | Phenol                   | 1:7               | 0.018–2.4          |                  | 0.074–11.53                         |       |
| 1,2,4-Triazole           | Glycerol                 | 1:3               | 1                  | 313.15           | 6.706                               | [309] |
| ChCl                     | 1,4-Butanediol           | 1:3               | 0.312–4.166        | 303.15–333.15    | 0.42–8.852                          |       |
| ChCl                     | 1,4-Butanediol           | 1:4               | 0.232–4.074        |                  | 0.413–8.94                          | [310] |
| ChCl                     | 2,3-Butanediol           | 1:3               | 0.255–4.022        |                  | 0.359–7.514                         |       |
| ChCl                     | 2,3-Butanediol           | 1:4               | 0.37–4.027         |                  | 0.359–7.917                         | [311] |
| ChCl                     | 1,3-Propanediol          | 1:3               | 0.314–4.014        |                  | 0.338–8.648                         |       |
| ChCl                     | 1,3-Propanediol          | 1:4               | 0.294–0.964        |                  | 0.341–9.873                         |       |
| ChCl                     | Phenol + Ethylene glycol | 1:5:4             | 1.0                | 313.2            | 6.988                               |       |
| ChCl                     | Phenol + Ethylene glycol | 1:7:4             | 1.0                | 313.2            | 7.652                               |       |
| ChCl                     | Urea                     | 1:1.5             | 0.108–3.073        | 313.2–353.2      | 0.097–3.875                         | [15]  |
| ChCl                     | Urea                     | 1:2               | 0.113–3.021        | 298.2–353.2      | 0.119–6.879                         |       |
| ChCl                     | Urea                     | 1:2.5             | 0.198–2.996        | 313.2–353.2      | 0.136–4.028                         |       |
| Pyrazole                 | Glycerol                 | 1:1               | 0.125–3.25         | 293.2–313.2      | 0.9–18.4                            | [312] |
|                          |                          | 1:2               | 0.125–3.9          |                  | 1.2–15.9                            |       |

cheapness [325,332].

Perkins [333] was the first to apply MD simulations for investigating the molecular structure and main intermolecular interactions governing the formation of several ChCl based DES. The objective of using MD simulations and DFT calculations to design DES solvents for CO<sub>2</sub> capture is to predict thermodynamic properties and insight on the structural, energetic characteristics, and dominating intermolecular interactions. On the one hand, DFT calculations allow to infer the strength of the H-bonds formed between HBAs and HBDs, to calculate the binding energy of the ionic pairs, as well as to detect the most energetically favorable positions of solvated molecules with respect to DES molecules. On the other hand, MD simulations allow to obtain some important parameters such as intermolecular interaction energies, radial distribution functions (RDFs), spatial distribution functions (SDFs), number and extension of H-bonds, residence times, etc., as well as to predict some physicochemical properties of the fluids such as densities, viscosities, etc. Most currently studies combine both methods, estimating the behaviour of CO<sub>2</sub> and DES molecules in a full atomic detail and at very fine temporal resolution. Some examples of novel DES for CO<sub>2</sub> capture that have been studied in recent years from DFT and MD approaches include those based on ammonium, arginine, betaine, and cineole [334–338]. A recent study investigated DES solvent for CO<sub>2</sub> capture is ChCl:ethylene glycol (2 EG) due to their low density and high ionic conductivity. This HBD (2 EG), which contains two hydroxyl groups, has a higher density than other alcohols of the same family such as glycerol, which contains three hydroxyl groups (Fig. 12a) [339]. ChCl:glycerol was also reviewed by

another researcher to show excess of glycerol had sufficient stabilization of chloride anions due to the high amount of hydroxyl group in them [340]. Likewise, it should be noted that predicted densities by MD simulations and experimental densities for ChCl:2 EG (1:2) DES in Fig. 12b [333] show a slight difference (density deviations less than 3%), so density is correctly predicted by MD simulations. The same is true for ChCl:3 EG (1:3) DES in Fig. 12c [341,342], with density deviations less than 4% [342].

This increase in the density of the ChCl:2 EG (1:2) compared to ChCl:3 EG (1:3) also occurs in the viscosity (Fig. 13). The high viscosity of ChCl:2 EG is attributed to the presence of a strong HB network between each component in this solvent, which results in a lower mobility of free species within the DES. In addition, ChCl:urea (1:2) or ChCl:glucose (1:1) viscosity measurements indicate that these DES are examples of highly viscous liquids, while others containing 2 EG, phenol or levulinic acid as HBDs are types of low-viscosity DES for practical purposes including CO<sub>2</sub> capture [334,343–346].

In addition, according to the available literature data on the ionic conductivities of ChCl:2 EG (1:2) and ChCl:3 EG (1:3) DES at different temperatures and 1 bar pressure, there is a significant increase with increasing temperature due to a decrease of the DES viscosities.

Another example of DES for CO<sub>2</sub> capture that has been investigated for some time both theoretically and experimentally with almost identical results is 1-ethyl-3-methylimidazolium acetate ([EMIM][Ac]). CO<sub>2</sub> showed a remarkably high solubility in [EMIM][Ac]. On the one hand, CO<sub>2</sub> solubility decreases steeply by isothermally decreasing the pressure

**Table 19**N<sub>2</sub> solubility data in different DES at different ranges of temperatures and pressures.

| HBA     | HBD         | [HBA]:[HBD] ratio | <i>P</i> range/bar | <i>T</i> range/K | <i>x</i> <sub>N<sub>2</sub></sub> | Ref.  |
|---------|-------------|-------------------|--------------------|------------------|-----------------------------------|-------|
| ChCl    | Urea        | 1:2               | 6.89–45.36         | 308.2–328.2      | 0.012–0.086                       | [242] |
| Betaine | Lactic acid | 1:1               | 0.0626–49.94       | 298.15–328.15    | 0.065–6.7 (mmol/g)                |       |
| Betaine | Malic acid  | 1:1               | 0.058–49.93        | 318.15–328.15    | 0.045–2.66 (mmol/g)               | [72]  |
| Alanine | Lactic acid | 1:1               | 0.057–49.94        | 298.15–328.15    | 0.043–6.63 (mmol/g)               |       |
| Alanine | Malic acid  | 1:1               | 0.057–49.94        | 298.15–328.15    | 0.07–5.50 (mmol/g)                |       |

**Table 20**

CO solubility data in different DES at different ranges of temperatures and pressures.

| HBA                  | HBD                           | [HBA]:[HBD] ratio | P range/bar | T range/K   | x <sub>CO</sub>      | Ref.  |
|----------------------|-------------------------------|-------------------|-------------|-------------|----------------------|-------|
| ChCl                 | Urea                          | 1:2               | 7.04–45.05  | 308.2–328.2 | 0.009–0.076          | [242] |
| [BimH]Cl             | CuCl + ZnCl <sub>2</sub>      | 1:1:0.8           | 0.4–5.0     | 353.2       | 0.01–0.27 (mol/mol)  | [313] |
| [BimH]Cl             | CuCl + ZnCl <sub>2</sub>      | 1:1:1             | 0.4–4.75    | 353.2       | 0.012–0.33 (mol/mol) |       |
| [BimH]Cl             | CuCl + ZnCl <sub>2</sub>      | 1:1:1.2           | 0.4–4.8     | 353.2       | 0.01–0.25 (mol/mol)  |       |
| [Emim]Cl             | CuCl                          | 1:1               | 1           | 298.2       | 0.038 (mol/mol)      | [314] |
|                      | CuCl + ZnCl <sub>2</sub>      | 1:1:1             |             |             | 0.295 (mol/mol)      |       |
|                      | CuCl + ZnCl <sub>2</sub> + EG | 1:1:1:1           |             |             | 0.934 (mol/mol)      |       |
|                      |                               |                   |             | 303.2       | 0.741 (mol/mol)      |       |
|                      | CuCl + EG                     | 1:1:1             |             | 298.2       | 0.073 (mol/mol)      |       |
|                      | ZnCl <sub>2</sub> + EG        | 1:1:1             |             |             | 0.001 (mol/mol)      |       |
| [HDEEA][Cl] + [CuCl] | EG                            | 1:1:4             | 0.1–5.0     | 293.2       | 0.026–0.55 (mol/mol) | [315] |
|                      |                               | 1:1:2             |             |             | 0.021–0.5 (mol/mol)  |       |
|                      |                               | 1:1:1             |             |             | 0.011–0.38 (mol/mol) |       |

**Table 21**H<sub>2</sub> solubility data in DES.

| HBA  | HBD  | [HBA]:[HBD] ratio | P range/bar | T range/K   | x <sub>H2</sub> | Ref.  |
|------|------|-------------------|-------------|-------------|-----------------|-------|
| ChCl | Urea | 1:2               | 6.73–45.53  | 308.2–328.2 | 0.010–0.073     | [242] |

(Fig. 14). On the other hand, since the high temperature condition prevents the interaction between CO<sub>2</sub> and DES, the solubility of CO<sub>2</sub> in DES-rich phase decreases with increasing temperature [203,347].

A study by Alioui et al. [206] used MD simulations to study the relationship between the solubility of CO<sub>2</sub> molecules and the energy of their molecular interaction with some DES. The solubility of CO<sub>2</sub> in the selected DES becomes greater when the energy of attraction is higher and vice versa.

In general, CO<sub>2</sub> capture process must be able to operate at high temperatures and be environmentally benign and balance between adsorption (binding) and desorption. It is also important to analysis the reactivity of the solvent and CO<sub>2</sub> while the designing of effective carbon capture solvents, an optimal DES solvent should have a high reaction rate with CO<sub>2</sub>, low volatility, high capture capacity, and low solvent regeneration energy [348–350].

#### 6.2.2. CH<sub>4</sub>

Another gas that has been most studied by computational methods in recent years is CH<sub>4</sub>. It should be noted that all the available literature data that consider CH<sub>4</sub> separation showed low solubility compared to other fuel gases. A MD simulation work by Amhamed et al. [237] studied ILs based solvents to investigate the transport properties of CO<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> molecules across choline-benzoate and choline-lactate ILs showed the largest resistance to CH<sub>4</sub> molecules. The permeability coefficients of the chosen molecules were calculated using the free energy and diffusion rate profiles. Another study conducted by Ilyas et al. [351] in a selective supported IL membrane based on 3-aminopropyl-trimethoxysilane and acetic acid protic IL showed a CO<sub>2</sub>/CH<sub>4</sub> selectivity of 41 (high) for CO<sub>2</sub> removal from a mixed CO<sub>2</sub>/CH<sub>4</sub> gas, also with a high thermal stability up to 600 °C. Altamash et al. [241] studied CH<sub>4</sub> solubility in NADES in both DFT and classical MD simulations approaches. They used alanine (Al), betaine (Be), and ChCl as HBAs and lactic acid (La), malic acid (Ma), and phenylacetic acid (Paa) as HBDs. Their MD simulations analysis showed that the observed NADES can be used for selective CO<sub>2</sub>/CH<sub>4</sub> separation in gas processing. They also observed that the main role on CH<sub>4</sub> clustering in the studied NADES samples is led by HBA (ChCl > Al > Be), whereas a minor role is inferred for the HBD (La > Ma > Paa). Shen et al. [352] also investigated CH<sub>4</sub>/CO<sub>2</sub> gas separation 5:95 M ratio using MD simulations to study the performance of slit graphite and titania (rutile) pores partially and completely filled with DES or ILs. The porous materials have a pore size of 5.2 nm, and they considered ethaline (an 1:2 M mixture of ChCl and ethylene glycol) and levuline (ChCl and levulinic acid with a molar ratio of 1:2) as DES; the IL considered was [Bmim<sup>+</sup>][NTf<sub>2</sub><sup>-</sup>] at a

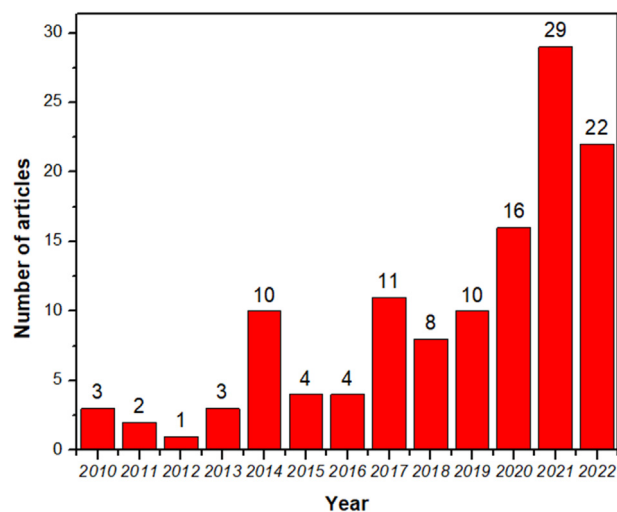


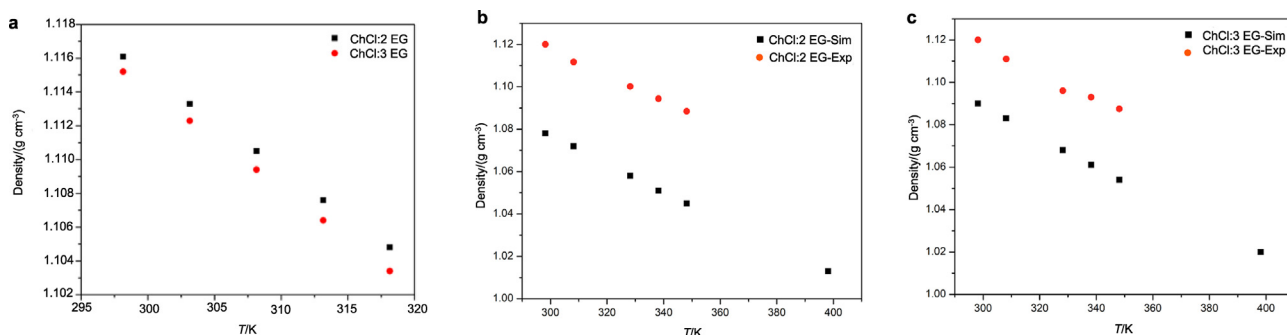
Fig. 11. Number of articles investigating CO<sub>2</sub> capture using DES from 2010 to 2022, obtained from Scopus database.

temperature of 318 K and pressures 100 bar was compared against results obtained for carbon and rutile pores without preabsorbed solvent, as well as against the performance of bulk liquid solvents. In terms of solubility selectivity, empty rutile pores have the largest value among all systems evaluated, followed by bulk ethaline, rutile pores filled by the IL, graphite and rutile pores filled with ethaline, and bulk levuline (Fig. 15).

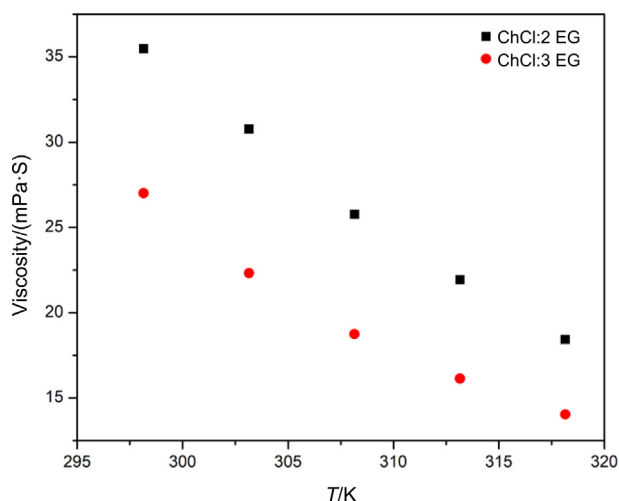
Malik et al. [353] used ab initio molecular dynamics (AIMD) simulations to elucidate the solvation structure around a CH<sub>4</sub> molecule dissolved in reline and ethaline DES. Ethaline, chloride ions play an active role in solvating CH<sub>4</sub>. Focusing on the key interactions that stabilize CH<sub>4</sub> in DES, they found in reline, chloride ions do not interact much with the CH<sub>4</sub> molecule in the first solvation shell. In reline, choline cations approach the CH<sub>4</sub> molecule from their hydroxyl group side, whereas urea molecules approach CH<sub>4</sub> from their carbonyl oxygen as well as amide group sides. In ethaline, ethylene glycol and Cl<sup>-</sup> dominate the nearest neighbor solvation structure around the CH<sub>4</sub> molecule. In both the DES, no significant CH<sub>4</sub>-DES charge transfer interactions were observed.

#### 6.2.3. SO<sub>2</sub>

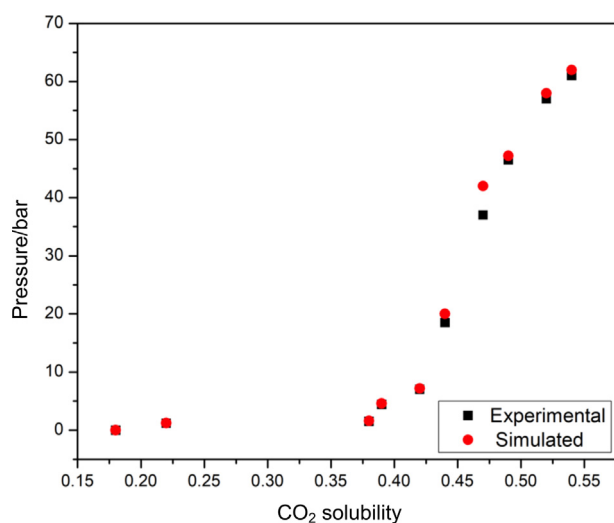
In this regard, a large number of theoretical studies have been



**Fig. 12.** (a) Experimental density values of ChCl:2 EG (1:2) and ChCl:3 EG (1:3) between 298 and 318 K and 1 bar [339]; (b) Comparison between experimental and predicted density values of ChCl:2 EG (1:2) at different temperatures and 1 bar [333]; (c) Comparison between experimental and predicted density values of ChCl:3 EG (1:3) at different temperatures and 1 bar [341,342].

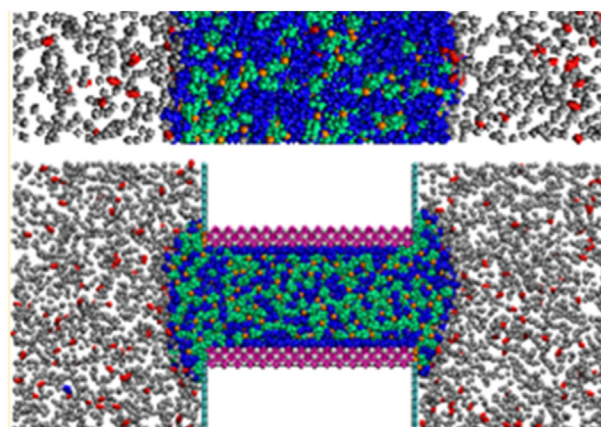


**Fig. 13.** Experimental viscosity values of ChCl:2 EG (1:2) and ChCl:3 EG (1:3) between 298 and 318 K and 1 bar [334,344].



**Fig. 14.** Experimental and predicted values by using COSMO-RS software of CO<sub>2</sub> solubilities in [EMIM][Ac] DES at 298.15 K and different pressures [347].

reported in recent years [206,346]. An investigation by Khnifira et al. [331] described a DFT and MD study to evaluate the adsorption behavior of SO<sub>2</sub> and CO<sub>2</sub> molecules on a graphite surface. DFT data showed good adsorption ability between both gas molecules and graphite, with very negative values of interaction energies between SO<sub>2</sub>/CO<sub>2</sub> and graphite

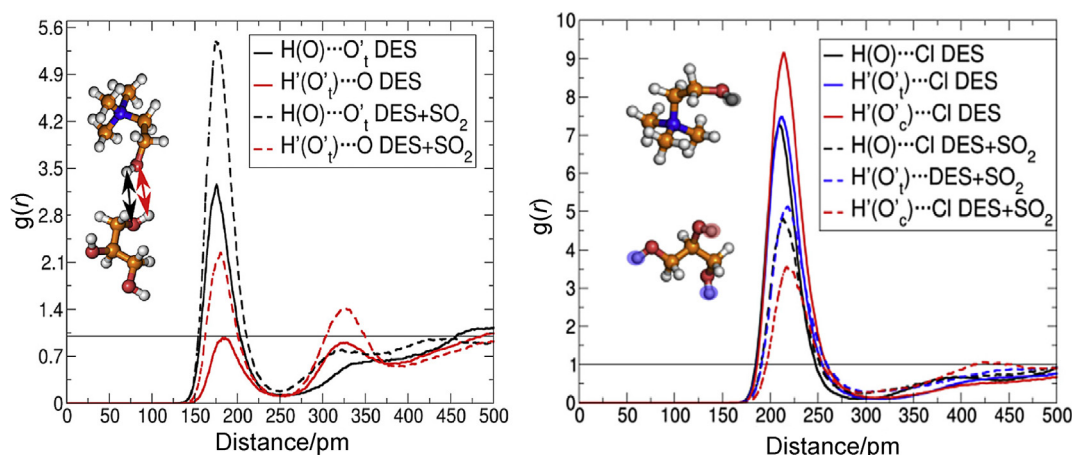


**Fig. 15.** Representative simulation snapshots show pore systems partially or completely filled with solvents at equilibrium at T = 318 K. Molecules/atoms are colored as follows: DES/IL: green = cation (choline), orange = anion (chloride), blue = HBD (ethylene glycol/levulinic acid), red = CO<sub>2</sub>, silver = CH<sub>4</sub>. Reprinted with permission from Ref. [352]. Copyright 2019 American Chemical Society.

due to the strong electron acceptor ability of both gas molecules. In addition, MD simulations estimated the most stable configuration of SO<sub>2</sub> and CO<sub>2</sub> molecules on the graphite surface. The higher adsorption energy and shorter binding distances indicate that graphite exhibits higher sensitivity to interact with SO<sub>2</sub> and CO<sub>2</sub> molecules.

Another recent study by Kapoor et al. [354] performed MD simulations to compare four examples of ILs. The ILs selected were 1-*n*-butyl-3-methylimidazolium ([C4mim]<sup>+</sup>) as cation and four different anions, chloride (Cl<sup>-</sup>), methylsulfate ([MeSO<sub>4</sub>]<sup>-</sup>), dicyanamide ([DCA]<sup>-</sup>), and bis(trifluoromethanesulfonyl)imide ([NTf<sub>2</sub>]<sup>-</sup>). The gases considered were CH<sub>4</sub>, CO<sub>2</sub>, NH<sub>3</sub>, and SO<sub>2</sub>. Calculations were performed at three temperatures of 333, 353, and 373 K. Results showed that SO<sub>2</sub> is the most soluble gas of those studied in this work due to the strongest interaction with ILs (since Henry's constants increase with increasing temperature, which implies that gas solubility decreases), followed by NH<sub>3</sub>, CO<sub>2</sub>, and CH<sub>4</sub> [208,328], and all the force fields could reproduce the experimentally observed gas solubility trend [355,356].

Korotkevich et al. [346] used AIMD to investigate the pure DES ChCl/glycerol and SO<sub>2</sub> dissolved in the ChCl/glycerol liquid. The radial distribution functions, and integration of their first peaks to obtain coordination numbers, strong hydrogen bonding of the OH groups of the glycerol with the chloride anion. There is also hydrogen bonding of the OH groups between all combinations of the choline cation and glycerol. These bonds seem to be less strong than the ones with the anion. Interplay between the C-H groups and the anion is also apparent in some cases, especially between the cation and the anion. Considering the



**Fig. 16.** On the right, RDFs of anion-hydrogen atom interactions. On the left, RDFs of hydrogen atom and oxygen atom interactions of the cation and glycerol. Solid lines: pure DES; Dashed lines: DES + SO<sub>2</sub>. Reprinted with permission from Ref. [346]. Copyright 2017 Elsevier.

interactions between the C–H groups only, the major contributions to this dispersion-like interaction comes from the glycerol-glycerol and glycerol-cation combination (Fig. 16). Comparing these results to the SO<sub>2</sub>-diluted system, we observe a strong interaction between the anion and the SO<sub>2</sub>. SO<sub>2</sub> and the OH groups do not show strong spatial correlations, but SO<sub>2</sub> molecules among themselves and with the nonpolar CH groups show sizable first RDF peaks and coordination numbers. All this accompanies a disruption of the anion-OH network to a third of its original constitution. The nonpolar-nonpolar network is also disturbed in now and participates in it. The OH network increases only a bit, and almost maintains its original structure. All the above listed findings lead to the following emerging picture: the chloride anions bind to the SO<sub>2</sub> molecules inside the liquids. One might speculate that once enough SO<sub>2</sub> is absorbed, it behaves like liquid SO<sub>2</sub>. It was shown by Ribeiro [357] that liquid SO<sub>2</sub> is very Lennard-Jones-like. It also interacts with the hydrophobic part of the liquid which might be another reason for the good absorption.

## 7. Conclusion

DES offer excellent alternatives with high gas capture capacity to battle global warming and reduce its environmental impacts with minimum retrofitting requirements in existing industrial process infrastructures. Furthermore, DES are highly tunable and referred to as designer solvents as their structure can be altered by changing the HBDs and HBAs and their molar mixing ratios to obtain task-specific solvents for desired applications. Besides their technical capabilities in gas solubility performance, they also offer advantages such as low production cost (easier preparation with no further purification steps) and lower ecological footprint with lower toxicity and higher biodegradability.

In this review, hundreds of DES were studied and analyzed for their thermophysical properties and their gas solubility performances. Most relevant thermophysical properties were curated that play a critical role in process equipment design for gas sorption applications. The different absorption methods and techniques were considered, and their experimental pros and cons were highlighted in this review. The effect of DES structure on gas solubilities, such as HBD, HBA, and molar mixing ratios, were studied and analyzed. In addition, the gas solubility mechanism in DES through the molecular simulation approach was considered in the context of the review. The nanoscopic viewpoint obtained from DFT and MD simulations in the literature on how gases interact with DES in the bulk mixture and at the interphases infers how DES work in capturing greenhouse gases, and these studies pave the future research path on the design of new DES for more specific applications.

Although the number of gas solubility in DES studies has been

continuously increasing in recent years, there is still a lot to be done, especially in utilizing DES in near real-life process conditions, such as at gas solubility at high pressures (~50 bar). Such studies will make it possible to implement the DES on a pilot scale in the near future and will also make it possible to prepare thermodynamic models and parameterization of the existing models for quick and reliable solubility predictions for DES, which would allow process simulation packages to handle these solvents seamlessly within their existing framework.

## Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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