Rotten Eggs Revaluated: Ionic Liquids and Deep Eutectic Solvents for Removal and Utilization of Hydrogen Sulfide

Fangfang Li, Aatto Laaksonen, Xiangping Zhang,* and Xiaoyan Ji*

ABSTRACT: Hydrogen sulfide (H₂S) is highly toxic and one of the problematic impurities in industrial gas streams, calling for H₂S removal down to single-digit ppm levels to protect health and environment, and not to harm to the downstream processes. Here, we discuss the recent developments and challenges of current H₂S removal technologies. Furthermore, we present a comprehensive review of H₂S removal in ionic liquids (ILs), IL-based solvents/adsorbents/membranes, and deep eutectic solvents (DESs) due to their unique advantages. We analyze theoretical studies to better understand the microscopic details behind H₂S removal. We discuss new research on IL/DES-based H₂S removal processes from an industrial perspective. Finally, we summarize the utilization of H₂S in IL/DES-based systems for the recovery of sulfur and hydrogen, and synthesis of value-added chemicals. This review will provide both general and in-depth knowledge of the achievements, difficulties, and research priorities in developing novel ILs/DESs for efficient and sustainable H₂S removal and utilization.

1. INTRODUCTION

Hydrogen sulfide (H₂S) is regularly present in biogas, natural gas, refined gas, liquefied petroleum gas, and other industrial gas streams, which is one of the major problems for many industries due to its high toxicity, corrosivity, etc. The toxicity verge of H₂S is about 10 ppm, and the damage to health increases rapidly with the increase of H₂S concentration.1 Besides, the weak acidity of H₂S causes serious corrosion to piping and production facilities.2 A trace amount of H₂S is poisonous for many metal catalysts.3 H₂S, on the other hand, is an important feedstock of the productions of sulfur,4 hydrogen,5 and some value-added metal sulfides and thio-organic chemicals, such as bis(2-phenylethyl) sulfide.6 Therefore, both removal and further utilization of H₂S from gas streams are of great importance for human health, environmental protection, downstream operation, and resource reutilization.

The concentration of H₂S can be quite different depending on the sources, and thus different technologies have been developed for H₂S removal both in academic research laboratories and industries, to fulfill the international environmental regulations and to achieve a desirable removal of H₂S. In general, these technologies can be classified as absorption, adsorption, membrane separation, and biological removal.7 Membrane separation is an energy-efficient technology, but the high cost of the membrane modules, their poor resistance to corrosion, and short lifetime all limit their industrial applications. Biological methods have the advantages of both mild operating conditions and low cost, but they are currently not able to treat H₂S at moderate to high concentrations, and the technology is still underdeveloped.8 Chemical absorption and adsorption are the most widely used methods due to their simple operation, high maturity, strong adaptability, and high efficiency. For the chemical absorption, alkaline solutions, such as amine and sodium hydroxide (NaOH), are usually used as absorbents via acid–base reactions.9,10 In the industrial adsorption, metal oxides are important chemical adsorbents, and they react with H₂S to form stable sulfides.11 The current status associated with different H₂S removal technologies is summarized in Figure 1.

Received: October 18, 2021
Revised: December 29, 2021
Accepted: February 1, 2022
Published: February 11, 2022
Related to the utilization of H$_2$S, nonthermal plasma (NTP), electrochemistry, and the Claus process are general methods for sulfur and hydrogen recovery. NTP includes dielectric barrier, electrospinning, and microwave plasmas. In the studies conducted on the first three plasmas, the energy costs are high. Gliding arc and microwave plasmas are more effective with high energy efficiency. However, all plasma technologies are currently not suitable for industrial application as H$_2$S needs to be diluted in advance. Electrochemical conversion of H$_2$S is usually carried out at room temperature, which is an energy-efficient technology. However, direct conversion of H$_2$S suffers from the drawback of anode passivation due to the aggregation of sulfur. Indirect electrochemical conversion of H$_2$S by introducing redox couples (such as Fe$^{3+}$/Fe$^{2+}$) is a feasible way to avoid the passivation of sulfur on the anode, but it is difficult to separate sulfur from the electrolytes. The Claus process is the most common method for the recovery of sulfur from H$_2$S, in which H$_2$S is catalyzed to elemental sulfur and water. The Claus process is always operated above the dew point of sulfur (180 °C) to avoid the deactivation of catalysts due to the precipitation of sulfur on their surface. Such a high temperature is not beneficial to the conversion of H$_2$S as the reaction is highly exothermic. The development of a liquid-phase Claus reaction realizes the oxidation of H$_2$S under relatively mild conditions. In the wet-oxidation process, aqueous iron(III) chelate is an attractive catalytic solution for the low sulfur recovery processes below 6 ton-S/day, but it still suffers from challenges, such as low concentrations of ferric complexes in solution, degradation of iron(III) chelate, and side reactions during H$_2$S oxidation. Therefore, there is a pressing demand to find a novel reaction medium with a favorable conversion efficiency, low volatility and toxicity, and high stability and regeneration performance for efficient utilization of H$_2$S.

Ionic liquids (ILs) are molten salts below 100 °C, which consist of organic cations, including imidazolium, pyridinium, phosphonium, and ammonium, as well as organic/inorganic anions. Nowadays, ILs have been considered as “green solvent” for a variety of applications attributable to their many unique advantages, such as negligible vapor pressure, high thermal stability, and high liquid range. Moreover, their physicochemical properties can be easily tuned to fulfill a specific application demand by selecting appropriate cations and anions, or by introducing functional groups into ILs. Deep eutectic solvents (DESs), composed of hydrogen-bond acceptors (HBAs) and hydrogen-bond donors (HBDs), have received more attention because of their additional advantages compared to ILs, such as low cost, low environmental impact, easy preparation, no purification, etc. In the field of gas purification, ILs and DESs have been hot research topics in recent years and some ILs/DESs showed attractive application potential for the capture of CO$_2$, H$_2$S, SO$_2$, and other gases.

In H$_2$S capture, the inherent polarity of ILs increases their affinity to polar H$_2$S molecules giving a convincing reason to develop ILs for H$_2$S removal. Jou et al. were the first to investigate H$_2$S absorption in 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF$_6$]). However, in a physiosorption, the conventional ILs can only be applied for gas streams with high partial pressure of H$_2$S. Later, functionalized ILs were reported to show an increased H$_2$S absorption capacity even at low partial pressures. For instance, the H$_2$S solubility in triethylbutylammonium N$_2$N-dimethyl-glycinate ([N$_2224$]-[DMG]) increased up to 106.1 mg-H$_2$S/g-IL at 60 °C and 1 bar. Even though some ILs show good performance, their high viscosities limit their large-scale applications. To overcome this drawback, several strategies have been proposed: typically, mixing high viscosity ILs with less viscous organic solvents and/or water, also, using ILs as key components in adsorbents and membranes, such as IL/metal organic framework (IL/MOF) composites, and supported IL membranes. In recent years, deep eutectic solvents (DESs), analogous to ILs, have received more attention, because they have many additional advantages, such as low cost, low environmental impact, easy preparation, and no purification required, etc. More and more DESs have been developed for H$_2$S removal. Owing to the unique advantages of both ILs and DESs, intensive work is also ongoing to develop ILs and DESs for the utilization of H$_2$S.

Several review articles about H$_2$S removal using different technologies have already been published, witnessing the importance to suppress the emissions of H$_2$S. Shah et al. presented recent progress on H$_2$S capture by using polar liquids, oxides, zeolites, MOFs, and membranes. Chiappe et al. discussed the specific influence of anions, cations, and functional groups of ILs on H$_2$S capture and oxidation. Wang et al. reviewed the selective absorption of H$_2$S/CO$_2$ and CO$_2$/CH$_4$ in pure ILs. Haider et al. reviewed the simultaneous capture of acid gases using ILs. Kumar et al. discussed the potential application of IL–amine blends and binding organic liquids for natural gas sweetening. Liu et al. summarized the recovery of sulfur from H$_2$S in metal-based ILs. However, to the best of our knowledge, no review is specifically dedicated to cover IL-based solvents, IL-reinforced adsorbents and membranes, to discuss both the theoretical studies and industrial perspectives of the IL/DES-based sorbents for H$_2$S removal, as well as to analyze the potential of developing ILs/DESs for H$_2$S conversion to produce sulfur, hydrogen, and value-added chemicals.

In this review, the research work on H$_2$S removal with chemical absorption and adsorption methods from 2018 is surveyed and discussed, considering their promising prospects. H$_2$S removal by using pure ILs, IL-based sorbents, IL-reinforced adsorbents/membranes, and DESs is summarized. The theoretical studies, including quantum chemical calculations, Molecular Dynamics simulations, thermodynamic models, and Machine learning approaches for predicting H$_2$S solubility are reviewed to investigate molecular interactions and mechanisms between IL/DES-systems and H$_2$S. On the large scale applications, process design and industrial perspectives of using ILs and DESs for H$_2$S removal are discussed. Finally, developing ILs and DESs for recycling and utilization of H$_2$S is summarized.
2. RECENT STATUS OF CHEMICAL ABSORPTION AND ADSORPTION

2.1. Chemical Absorption. Chemical absorption using alkanolamines is currently one of the most mature technologies for industrial H₂S removal from gases. Conventional processes with amines are mainly applied in the packed/tray columns under conditions of 30−50 °C and 5−205 bar. The current scale for H₂S removal in amines with subsequent sulfur recovery in Claus plants is up to 50 tons-S/day. Monoethanolamine (MEA) and diethanolamine (DEA) are the most frequently used absorbents. N-Methyldiethanolamine (MDEA) has gradually appeared in industrial processes due to its low energy cost, low corrosive impact on equipment, and high absorption capacity. MDEA has also been used together with other alkanolamines to provide a synergetic effect and improved performance. For example, Tian et al. studied H₂S absorption in a tray column with MEA-activated MDEA aqueous solutions as solvents. Their results showed that the addition of MEA could increase both H₂S absorption capacity and removal efficiency.

It is common that CO₂ is involved as a cocomponent in the gas streams together with H₂S. A considerable amount of research work has been conducted for such streams. For example, Zhan et al. prepared a mixed solution of MDEA and piperazine (PZ) for simultaneous absorption of H₂S and CO₂ in a rotating packed bed. In some industrial applications, there is a need to separate H₂S from CO₂, and thus a novel alkanolamine absorbent with high H₂S selectivity needs to be developed. For this purpose, hindered amines, such as 2-(cyclic-butylamino)-ethanol (TBE) and 2-amino-2-methyl-1-propanol (AMP), were found as potential absorbents for selective H₂S removal.

However, for the chemical absorption with alkanolamines, the main issues, associated with the commercial MEA and DEA, are their high energy requirement during regeneration, high solvent loss, and degradation. MDEA is a promising solvent with a high H₂S absorption capacity, low energy usage, low corrosion rate, and good degradation resistance, but it shows a relatively low kinetics. MDEA has also been used together with other alkanolamines to improve absorption performance. However, application of the mixed solvents complicates the H₂S absorption mechanisms, and makes it difficult to regenerate and recycle. Overall, the technology based on chemical absorption needs to be further optimized to become more efficient, and more efforts should be directed to developing novel solvents with a high degradation resistance, high absorption capacity and kinetics, and desirable regeneration capacity.

2.2. Adsorption. The strong affinity between the used adsorbent and H₂S molecules is the main mechanism to achieve a high H₂S selectivity and adsorption capacity. Besides, the morphology of the adsorbents, such as their size and shape, can also influence the H₂S selectivity over other components in gas streams. The most common adsorbents include metal oxides, carbon materials, zeolites, and metal−organic frameworks (MOFs). Of them, metal oxides have been widely studied and applied in the industry due to their low cost, high adsorption capacity, and abundance.

Iron oxide (Fe₂O₃) is a potential adsorbent for low-temperature H₂S removal with the removal rate less than 200 kg/S/day. The adsorption of H₂S using iron oxides is usually carried out at temperatures below 500 °C. This is because high temperatures are undesirable for the exothermic sulfurization reaction, even if kinetically beneficial. The commercialization of Fe₂O₃ for H₂S removal is limited due to their low specific surface area and small pore-volume, as well as the pores getting blocked during the adsorption. As a result, Fe₂O₃ is commonly combined with other materials, such as mesostructured silica supports (M41S), semicoke, oxygenated porous carbon (OPC), red clay, and so on, to increase the stability of Fe₂O₃ and the desulfurization performance. Zinc oxide (ZnO), as a commonly used desulfurizer, has good thermal stability and strong desulfurization ability. In recent years, H₂S removal at not so high, or even room temperature, has received wide attention in order to reduce energy usage. However, the adsorption capacity of ZnO is quite low at room temperature due to slow kinetics. Supporting ZnO on porous materials (e.g., mesoporous silica, activated carbon, ceramic, molecular sieves, semicoke, etc.), mixing with other metal oxides, and doping with impurity atoms are simple and effective methods to increase the specific area of the adsorbents, and thus improve H₂S adsorption capacity. Copper oxide (CuO) has been increasingly developed as an adsorbent for H₂S removal due to its higher reaction equilibrium constant with H₂S compared with Fe₂O₃ and ZnO. Nevertheless, aggregation and low regeneration are the main drawbacks of CuO, which is similar
to most metal oxides. To solve these problems and enhance desulfurization performance, different porous materials, including activated carbon nanofibers and mesoporous silica, were introduced into CuO nanoparticles.

Metal oxides are promising adsorbents for H$_2$S removal from different gas streams due to their high reactivity. However, issues such as low porosity, low surface area, aggregation during regeneration, and metal evaporation remain as major drawbacks, leading to a reduced H$_2$S adsorption capacity. The preparation of metal oxide-based adsorbents by combining them with porous materials, supporting them on other metal oxides, and doping them with impurity atoms to improve the specific adsorption area and further enhance the structural stability has been proposed to tackle the issues. The adsorption performance of several metal oxide-based adsorbents has been reported, while their regeneration is still difficult. Therefore, future research should focus on developing metal oxide-based adsorbents to not only increase H$_2$S adsorption capacity but also enhance the regeneration capacity.

3. ILS AND DESS FOR H$_2$S REMOVAL

As already pointed out, chemical absorption technology using alkalanolamines has disadvantages due to high solvent loss, a high energy requirement, and low thermal stability; while adsorption using metal oxides shows a low adsorption capacity and poor regeneration capacity. ILS have become potential candidates for H$_2$S removal to overcome the above-listed drawbacks of current conventional sorbents. This is highly due to their extremely low vapor pressure, low heat capacity, high thermal stability, chemically tunable nature, and a strong affinity to the polar H$_2$S molecule in particular, as illustrated in Figure 2. As summarized in Table 1, ILS are used in different forms, including pure IL absorbents, IL-based solvents, IL-reinforced adsorbents, and membranes. Further, the research work on developing DESSs for H$_2$S removal is also included in this section. The structure of ILS and DESSs are summarized as shown in Figure 3.

3.1. ILS as Pure Absorbents.

3.1.1. “Physical” ILS. According to the structure of ILSs and the interaction with H$_2$S, ILSs can be divided into “physical” and “functionalized” ILSs. The reported physical ILSs for H$_2$S removal mainly include imidazolium-based and pyridinium-based ILSs. Jou et al. were the first to study the absorption of H$_2$S in [Bmim][PF$_6$] at the temperatures of 25–130 °C and pressures up to 96 bar. The pressure-dependent H$_2$S solubility indicated that [Bmim][PF$_6$] is a physical solvent. H$_2$S absorption in physical ILSs is affected by both the cations and anions. For the imidazolium-based ILSs with different cations and anions, the solubilities of H$_2$S in mole fraction basis follow the order of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][TF$_2$N]) > 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]) > [Bmim][PF$_6$].

3.1.2. Functionalized ILS. Functionalized ILSs have been developed to improve the H$_2$S absorption capacity at low pressures. As reported, [Emim]-based ILSs with different carboxylate anions, including acetate ([Ac$^-$]), propionate ([Prop$^-$]), and lactate ([Lac$^-$]), showed much higher H$_2$S solubility compared with the commonly used ILSs at low pressures. More specifically, the solubility of H$_2$S in [Emim]−[Ac] at 60 °C and 1 bar is 18 times higher than that in [Emim][TF$_2$N] under the same conditions. Moreover, the H$_2$S solubility increased dramatically in these ILSs at low pressures (0.5 bar) and almost linearly at high pressures (>0.5 bar), which means both chemical and physical absorptions can occur during the absorption of H$_2$S. Later, H$_2$S solubility and the H$_2$S/CO$_2$ selectivity in three functionalized ILSs, triethylammonium N,N-dimethylglycinate ([N$_{2221}$][DMG]), triethylammonium 1-imidazololate ([N$_{2224}$][IMA]), and triethylammonium nicotinate ([N$_{2224}$][NIA]) were studied, and high H$_2$S solubilities of 48.1–106.1 mg H$_2$S/g-IL with H$_2$S/CO$_2$ selectivities of 13–26 were obtained at 60 °C and 1 bar. The selectivity can be even higher than 100 at low pressures and high temperatures due to the strong interaction of carboxyl–H$_2$S–amine and the large difference in binding energy between anion-H$_2$S and anion-CO$_2$. This can also explain the reason that the solubilities of H$_2$S in 1-butyl-3-methylimidazolium acetate ([Bmim][Ac]) are much higher than those for CO$_2$ reported by Haghitalab et al. Proton ILSs are considered as better absorbents for the separation of H$_2$S from CO$_2$. H$_2$S/CO$_2$ selectivities could be up to 8.9 and 15.1 at 30 °C in two proton ILSs, that is, methylidythanolammonium acetate ([MDEAH][Ac]) and dimethylethanolammonium acetate ([DMEAH][Ac]), respectively, which are much higher than that in commonly used ILs (2–4). This is because the Bronsted acid–base interaction between the protonated nitrogen in the cation and [Ac$^-$] could reduce the affinity of CO$_2$ with [Ac$^-$], and thus decrease the
| absorbent         | $T$ (°C) | $P$ (bar) | $\text{H}_2\text{S}$ solubility (mg $\text{H}_2\text{S}$/g sorbent) | remarks                                                                 | ref  |
|------------------|----------|-----------|---------------------------------------------------------------|-------------------------------------------------------------------------|------|
| [Bmim][PF$_6$]   | 25–130   | up to 96  | [Bmim][PF$_6$] would be useful only for the absorption of $\text{H}_2\text{S}$ with high partial pressure. | 23             |
| [Bmim][BF$_4$]   | 30–70    | up to 10  | The trend in affinity of $\text{H}_2\text{S}$: [Bmim][Tf$_2$N] > [Bmim][BF$_4$] > [Bmim][PF$_6$]. | 63            |
| [Bmim][Tf$_2$N]  | 30–70    | up to 11  | The trend in affinity of $\text{H}_2\text{S}$: [Hmim][BF$_4$] > [Hmim][PF$_6$] ≈ [Hmim][Tf$_2$N]. | 64            |
| [Hmim][PF$_6$]   | 30–80    | up to 18  | The trend in affinity of $\text{H}_2\text{S}$: [HOemim][Tf$_2$N] > [HOemim][Tf$_2$N] > [HOemim][PF$_6$]. | 65            |
| [Hemim][OTf]     | 30–80    | up to 20  | The trend in affinity of $\text{H}_2\text{S}$: [Emim][Tf$_2$N] > [Emim][PF$_6$]. | 66            |
| [Hemim][BF$_4$]  | 30–80    | up to 16  | The diffusion coefficient of $\text{H}_2\text{S}$ in [Emim][EtSO$_4$] is about 2 orders of magnitude as that of CO$_2$. | 102           |
| [Hemim][Tf$_2$N] | 30–80    | up to 11  | The solubility of $\text{H}_2\text{S}$ is higher than CO$_2$ in [Hemim][BF$_4$]. | 103           |
| [C$_4$Py][Tf$_2$N]| 30–80   | up to 20  | The solubility of $\text{H}_2\text{S}$ is about twice as high as that of CO$_2$ in [C$_4$Py][Tf$_2$N]. | 67            |
| [C$_8$Im][BF$_4$]| 30–80    | up to 20  | Solubility of $\text{H}_2\text{S}$ is more than twice that of CO$_2$ at fixed condition; Acid gas solubility increased with the increase of – CF$_3$ group in anion. | 104           |
| [C$_8$Im][PF$_6$]| 30–80    | up to 20  | Both $\text{H}_2\text{S}$ and CO$_2$ solubility increased by increasing the alkyl chain length of cation. | 68            |
| [C$_4$Py][OTf]   | 30–80    | up to 30  | Solubility of $\text{H}_2\text{S}$ is more than four times that of CO$_2$. | 71            |
| [C$_4$Py][Tf$_2$N]| 30–80   | up to 32  | Solubility of $\text{H}_2\text{S}$ is more than four times that of CO$_2$. | 72            |
| [C$_8$Im][SCN]   | 30–60    | up to 6   | H$_2$S solubility: [C$_4$Py][SCN] > [C$_4$Py][SCN] > [C$_4$Py][SCN] > [C$_4$Py][NO$_3$] > [C$_4$Py][BF$_4$]. | 69            |
| [C$_8$Im][Ac]    | 25–45    | up to 1.096| $\text{H}_2\text{S}$ absorption in these ILs is a physical process; $\text{H}_2\text{S}$ solubility increased with the increase of alkyl chain on anion. | 70            |
| [C$_8$Im][Pro]   | 20–60    | up to 3.5 | Solubility of $\text{H}_2\text{S}$ increased with the increase of alkalinity of anions. | 73            |
Table 1. continued

| absorbent | $T$ (°C) | $P$ (bar) | $H_2S$ solubility (mg $H_2S$/g-sorbent) | remarks | ref |
|-----------|----------|-----------|----------------------------------------|---------|-----|
| [Emim][Pro] | 60 | 1 | 106.1 | CO$_2$ solubility in these ILs was quite limited due to the coupling effect of the two Lewis base group. | 24 |
| [Emim][Lac] | 60 | 1 | 48.6 | Protic ILs showed larger solubility for $H_2S$ than for CO$_2$. | 75 |
| [Bmim][Ac] | 60 | 1 | 48.6 | | |
| [N$_{2222}$] [DMG] | 30–60 | up to 1.2 | | Chemical absorption was taken place between [Bmim][Ac] and $H_2S$. | 74 |
| [N$_{2222}$] [IMA] | 30–70 | 1–22 | | Chemical absorption was taken place between [Bmim][Ac] and $H_2S$. | 74 |
| [N$_{2222}$] [NIA] | 25 | 1 | 42.5 | | 77 |
| [Bmim][Ac] | 40 | 1 | 50.4 | The strong interaction between [PhO]$^-$ and $H_2S$ is beneficial for increasing $H_2S$ solubility. | 76 |
| [BDMAE][Tf$_2$N] | 40 | 1 | 50.4 | The strong interaction between [PhO]$^-$ and $H_2S$ is beneficial for increasing $H_2S$ solubility. | 76 |
| [TMHDA][Tf$_2$N] | 40 | 1 | 50.4 | The strong interaction between [PhO]$^-$ and $H_2S$ is beneficial for increasing $H_2S$ solubility. | 76 |
| [TMG][PhO] | 40 | 1 | 42.5 | The strong interaction between $H_2S$ and protic ILs (N$\cdots\cdots$H$^-$S) is responsible for the high $H_2S$ solubility. | 78 |
| [DBU][PhO] | 40 | 1 | 42.5 | The strong interaction between $H_2S$ and protic ILs (N$\cdots\cdots$H$^-$S) is responsible for the high $H_2S$ solubility. | 78 |
| [ TMPDA][Tf$_2$N] | 40 | 1 | 42.5 | The strong interaction between $H_2S$ and protic ILs (N$\cdots\cdots$H$^-$S) is responsible for the high $H_2S$ solubility. | 78 |
| [DBU][Tf$_2$N] | 40 | 1 | 42.5 | The strong interaction between $H_2S$ and protic ILs (N$\cdots\cdots$H$^-$S) is responsible for the high $H_2S$ solubility. | 78 |
| [DBU][Im] | 40 | 1 | 42.5 | The strong interaction between $H_2S$ and protic ILs (N$\cdots\cdots$H$^-$S) is responsible for the high $H_2S$ solubility. | 78 |
| [DBU][Pyr] | 40 | 1 | 42.5 | The strong interaction between $H_2S$ and protic ILs (N$\cdots\cdots$H$^-$S) is responsible for the high $H_2S$ solubility. | 78 |
| [IL-Based Solutions] | 40 | 0.05 | 72.3 | Addition a certain amount of EG could increase both $H_2S$ solubility and absorption rate. | 25 |
| [N$_{2222}$][L-Ala]/EG (1:1)$^a$ | 40 | 0.05 | 72.3 | Addition a certain amount of EG could increase both $H_2S$ solubility and absorption rate. | 25 |
| [N$_{2222}$][β-Ala]/EG (1:1)$^a$ | 40 | 0.05 | 72.3 | Addition a certain amount of EG could increase both $H_2S$ solubility and absorption rate. | 25 |
| [N$_{2222}$][Gly]/EG (1:1)$^a$ | 40 | 0.05 | 72.3 | Addition a certain amount of EG could increase both $H_2S$ solubility and absorption rate. | 25 |
| [N$_{2222}$][L-Pro]/EG (1:1)$^a$ | 40 | 0.05 | 72.3 | Addition a certain amount of EG could increase both $H_2S$ solubility and absorption rate. | 25 |
| MEA/[MEA][Ac] (1:1)$^b$ | 25 | 1 | 80.5 | The high $H_2S$ removal efficiency was attributed to hydramine; ILs increased the stability of blended absorbents. | 80 |
| DEA/[DEA][Ac] (1:1)$^b$ | 25 | 1 | 80.5 | The high $H_2S$ removal efficiency was attributed to hydramine; ILs increased the stability of blended absorbents. | 80 |
| TEA/[TEA][Ac] (1:1)$^b$ | 25 | 1 | 80.5 | The high $H_2S$ removal efficiency was attributed to hydramine; ILs increased the stability of blended absorbents. | 80 |
| MDEA/[MDEA][Ac] (1:1)$^b$ | 25 | 1 | 80.5 | The high $H_2S$ removal efficiency was attributed to hydramine; ILs increased the stability of blended absorbents. | 80 |
| DIPA + [Bmim][Ac] in water with concentration of (50 wt % + 5 wt %), (50 wt % + 10 wt %), (30 wt % + 5 wt %), (30 wt % + 10 wt %), and (50 wt % + 50 wt %) | 40–75 | 2–25 | | | 27 |
The absorption of H₂S.

Addition of a small amount of IL could greatly increase H₂S loading.

The selectivity of H₂S/CO₂ increased with increasing concentration of [C₈mim][BF₄].

Addition of a small amount of IL could greatly increase H₂S loading.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.

The absorption capacity of H₂S is reduced after regeneration due to the loss of peroxo species.
Figure 3. Structures of (a) ILs and (b) DESs.
tris(3-(dimethylamino)propyl)ammonium acetate ([TDMAPAH][Ac]) solution at 40 °C and 1 bar, indicating the advantage of multiple Lewis base group of cation on desulfurization.

Moreover, ILs have also been combined with aqueous alkanolamine solutions. As shown in Figure 5, increasing diisopropanolamine (DIPA) content and [Bmim][Ac] concentration can intensify the selective absorption of H2S in the presence of CO2.27 It was also observed that adding a small amount of tetramethylammonium glycinate ([N1111][Gly]) into aqueous MDEA solution can significantly increase the H2S solubility.83 This observation indicated that the amino group in the anion of [N1111][Gly] not only reacted with H2S, but also promoted the absorption of H2S in aqueous MDEA by increasing the alkalinity of the solution. On the contrary, both H2S absorption capacity and absorption rate decreased with increasing the concentration of MDEA. This is because, at a low partial pressure of H2S, adding more MDEA could not promote the absorption of H2S, but rather increased the viscosity of solutions, and thus limited the absorption and diffusion of H2S.

Sometimes, the temperature of H2S in the industrial gas streams with H2S can reach hundreds of degrees Celsius, while the conventional absorption technologies for H2S removal can only be operated at relatively low temperatures (<80 °C) in order to reduce the solvent loss and increase H2S absorption capacity. As a result, cooling processes are always needed before absorption, which leads to a high energy demand. To achieve H2S absorption at high temperatures, Liu et al.84 dissolved a certain amount of heteropoly compounds (HPCs), such as [Bmim]3PW12‑xMoxO40 and [Bmim]3+PMo12‑xVxO40 into 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]) for H2S removal at 200 °C. It was found that the desulfurization capacity enhanced with the increase in the number of Mo atoms in [Bmim]3PW12‑xMoxO40/[Bmim][Cl], confirming that Mo atoms work better for H2S removal than W atoms do in the anion of HPCs. Meanwhile, HPC was the dominant deriving force for H2S removal, while IL only served as solvent and reaction medium. Among the studied solutions with different amounts of Mo atoms, [Bmim]3PMo10V2O40/[Bmim][Cl] showed the optimal H2S removal performance and good regeneration ability. Later, the same group studied the macroscopic kinetics of the desulfurization in [Bmim]3PMo12O40/[Bmim][Cl] and proved that the absorption was driven by diffusion.85 Moreover, the desulfurization efficiency can still be kept 100% after six times recycle of [Bmim]3PMo12O40/[Bmim][Cl].86 The desulfurization performance was also investigated in several peroxy-heteropoly compound (PHPC)/[Bmim]-based ILs with different anions, including [Cl]−, [TeO4]3−, [PF6]−, [BF4]−, and [HCO3]−.87 and cetyltrimethylammonium peroxyphosphomolybdate (16-
PHPC)/[Bmim][HCO₃] showed the highest H₂S removal efficiency (nearly 100%) for 2 h at 95 °C. All the above-mentioned studies provided a novel method for efficient H₂S removal at high temperatures by using HPCs/ILs and PHPCs/ILs solutions.

### 3.3. IL-Reinforced Adsorbents and Membranes

Combining ILs with adsorbents or membranes is another potential strategy to overcome the high viscosity of ILs and enhance H₂S adsorption efficiency. Metal–organic frameworks (MOFs) can be ideal supporters owing to their large pore volume, high surface area, and designable structure. When [Bmim][Cl] was immobilized on Cu-TDPAT, a high selectivity of H₂S/CH₄ (611) was obtained compared with the pure Cu-TDPAT (= 141) under the same conditions. This phenomenon can be explained by the “like dissolves like” principle, which means polar H₂S is easier to dissolve into polar IL compared with CH₄.

Ishak et al. compared the stability of choline (Chl)-based ILs/isoreticular MOF (IRMOF-1) composites with different anions of ILs, such as [SCN]⁻, [OTf]⁻, and methyl sulfate ([MeSO₄]⁻). They found that a smaller-sized anion of IL contributed to a better stability since it could easily diffuse inside the pores of IRMOF-1. Solubilities of H₂S and CH₄ in [Chl][SCN], calculated from the solvation free energy by using the Bennet acceptance ratio (BAR) method, showed that both H₂S solubility and H₂S/CH₄ selectivity were significantly increased compared with pure IL and IRMOF-1, owing to the low affinity of IRMOF-1 toward H₂S as well as the strong interaction between the cation and anion in [Chl][SCN] and also its high viscosity. Later, the same research group studied [Chl][Ala]/IRMOF-1 for selective H₂S/CO₂ capture. One H₂S molecule could combine with two molecules through carbohydrate groups (−COO⁻) in [Ala]− anion via hydrogen bonds, while one molecule of CO₂ was only hydrogen bonded with one molecule of amino group (−NH₂) in the [Ala]− anion. The stronger interaction between H₂S and the [Ala]− anion resulted in a higher H₂S adsorption capacity. All these research studies indicate that IL/MOF composites are promising adsorbents for H₂S separation from CH₄ and CO₂.

Ma et al. prepared a novel metal-based IL, triethylamine hydrochloride copper chloride (Et₃NHCl-CuCl₂), and compared the adsorption performance of H₂S in pure zeolite, cyclodextrin-grafted zeolite (CDGZ), zeolite-supported IL (IL-zeolite), and cyclodextrin-modified zeolite-supported IL (IL-CDGZ). The order of H₂S removal capacity is CDGZ < zeolite < IL-zeolite < IL-CDGZ. Introducing cyclodextrin (CD) to zeolite decreased H₂S removal capacity due to its inappropriate cavity size. The chemically active species of IL, including amines and Cu²⁺, could associate with H₂S, and thus increase H₂S capacity of IL-zeolite. In the system of IL-CDGZ, some IL-cations filled the cavity of CD and enlarged the pore size. The combined effect of CD, zeolite, and IL achieves a good H₂S removal performance of CDGZ. Later, the H₂S adsorption performance of metal-based IL immobilized sol–gel derived silica (IL/silica gel) was also investigated by the same group.

The use of conventional polymeric membranes is limited by their competitive relationship between permeability and selectivity. Combining ILs with polymeric membranes gives many opportunities for designing novel membranes with both high H₂S permeability and selectivity. Zhang et al. prepared several supported ionic liquid membranes (SILMs) composed of polyvinylidene difluoride (PVDF) with neutral [Bmim]-based ILs containing the anions of [PF₆]⁻, [BF₄]⁻, [Tf₂N]⁻, [OTf]⁻, and a basic [Bmim][Ac]. The H₂S permeability in these SILMs with neutral ILs increased with an increase of the basicity of the anion. H₂S permeability in [Bmim][OTf]/PVDF membrane could reach 4303 barrers. The selectivity of CO₂/CH₄ was 50.7, while that for H₂S/CO₂ was only 4.0, at 0.1 bar and 40 °C. For [Bmim][Ac]/PVDF, the H₂S permeability was 7304 barrers, whereas the selectivities of H₂S/CH₄ and H₂S/CO₂ were 136 and 11.7, respectively, under the same condition. This means that [Bmim][OTf]/PVDF can be used for simultaneous removal of CO₂ and H₂S, while [Bmim][Ac]/PVDF is beneficial to the selective separation of H₂S from CO₂ and CH₄.

Akhmetshina et al. prepared another kind of SILMs using [Bmim][BF₄] and a microfiltration tetrafluoroterephthaloylvinylene fluoride composite membrane (MFFK-1). H₂S achieved the highest permeability (∼380 barrers), followed by CO₂ (∼80 barrers) and CH₄ (∼12 barrers). Bhattacharya et al. studied the permeabilities of H₂S, CO₂, air, and CH₄, respectively, in a mixed matrix membrane synthesized with [Emin]EtSO₄ and poly(ether-block-amide) (PEBA). The observed trend for different gases follows H₂S > CO₂ > air > CH₄. These studies further confirmed that SILMs are promising candidates for selective H₂S removal.

### 3.4. DESs

Recently, DESs have been widely studied owing to their benign characteristics, such as low cost, low environmental impact, easy preparation, without purification process, and no byproduct generation. Considering the unique properties of DESs and the observed promising absorption performance for weak acidic CO₂, the application of DESs for acidic H₂S removal should provide great potential, although the number of current studies is still very low.

Choline chloride (ChCl)/urea is one of the most common DESs for gases separation. The measurement of H₂S, CO₂, and CH₄ solubilities in ChCl/urea with the molar ratios of 1:1.5, 1:2.0, and 1:2.5 showed that H₂S solubility decreased with the decrease of ChCl/urea ratio, which is different for CO₂ and CH₄ showing the highest value in ChCl/urea (1:2). This is because the Cl of ChCl could form a strong hydrogen bond with the H atom of H₂S during the absorption of H₂S in the ChCl/urea systems, and the decrease of the molar ratio weakened the strength of interaction, which caused the decrease of H₂S solubility. However, the solubilities of CO₂ and CH₄ were affected by the free volume of solvents. ChCl/urea (1:2.0) has the lowest melting point, exhibiting the biggest free volume, and in turn, showed the highest absorption performance for CO₂ and CH₄ among the studied ChCl/urea. Recently, [Bmim][Cl]/imidazole (2:1) was proven to be a promising candidate for the selective separation of H₂S from CO₂ in various processes as it has ultrahigh selectivities (up to 30.9 at 25 °C) and high stability of removal performance in moisture environment with low water content.
hydrogen-bonding networks in ChCl-based DESs and decreases the overall space to absorb H$_2$S. Moreover, H$_2$S solubility increases with the decrease of temperature and increase of pressure, behaving like a typical physical absorption.

Inspired by functionalized ILs, novel functionalized DESs (FDESs) were prepared by adding polyethylenimine (PEI) to the ChCl-based DESs, including ChCl/Gly (1:2), ChCl/EG (1:2), ChCl/propylene glycol (PG) (1:2), and ChCl/urea (1:2), to enhance H$_2$S removal efficiency. The combination of PEI and ChCl/EG (1:2) (PEI/FDES@EG) was identified as the most promising desulfurizer owing to its optimal H$_2$S removal efficiency. For PEI/FDES@EG with 25% PEI, H$_2$S removal efficiency could maintain above 95% at least 80 min at 30 °C due to the strong interaction between the N of amine group in PEI and the H of H$_2$S, while it dropped sharply at the beginning for ChCl/EG (1:2). Very recently, a novel kind of task-specific DESs using quaternary ammonium salts as HBAs and azoles as HBDs were prepared by Shi et al., which showed the highest H$_2$S absorption capacity and H$_2$S/CO$_2$ selectivity compared with the reported DESs. Moreover, both alkalinity and free volume could influence the solubility of H$_2$S, as the larger is the alkalinity and free volume the higher is the H$_2$S absorption capacity, which is in agreement with the results obtained from the ILs.

Liu et al. prepared an ETA/DES solution by dissolving ethanolamine (ETA) into ChCl/EG (1:2, molar ratio) with a weight concentration of 20%. Then the DES-based nanofluid (NF) systems (NF@Cu-x%) were further prepared by suspending Cu nanoparticles into the ETA/DES solution with different weight concentrations (x) of Cu. The DES-based NF systems showed quite low H$_2$S removal efficiency in the absence of ETA, indicating that Cu$_3$S removal performance of the NF systems is attributed to the effect of ETA. Meanwhile, Cu nanoparticles were served as the promoter for the interaction of H$_2$S and ETA, and thus the H$_2$S removal efficiency increased with the increasing concentration of Cu.

Considering the great potential and advantages of supported ILs, the study on the H$_2$S removal performance of supported DESs (SDESs) should be meaningful for a wider application of DESs. Mao et al. prepared a novel kind of SDESs using fumed silica (FS) as the supporting material, and TAE$_3$CuCl$_{2-x}$ with various molar ratios of triethylamine hydrochloride (TEACl) and cupric chloride (CuCl$_2$$_3$) as the loading substance. SDES with 10 wt % loading of TAE$_3$CuCl$_3$ (TAE$_3$CuCl$_3$@FS/10 wt %) has the optimum desulfurization performance at 30 °C with the highest adsorption efficiency (molar ratio of Cu to absorbed H$_2$S, H$_2$S$_{abs}$/H$_2$S$_{Cu}$ is 0.87), which is about 3.56 times higher than the pure TAE$_3$CuCl$_3$ under the same condition. This is because the interaction between FS and DES could reduce the size of surface TAE$_3$CuCl$_3$ microclusters and thus promote the transformation of metal active sites. After adsorption, a small amount of H$_2$S was oxidized to sulfur and sulfate ions, and most of the H$_2$S was transferred to Cu$_3$S. This study suggests that SDESs are potential sorbents for an efficient removal of H$_2$S.

3.5. Summary and Outlook of ILs and DESs for H$_2$S Removal. Some conclusions regarding H$_2$S removal in ILs and DESs are summarized in Figure 6. H$_2$S absorption in physical ILs has been widely studied due to the favorable properties of ILs. On the basis of the analysis presented above, both cation and anion of ILs have a great influence on H$_2$S absorption performance. The cation with a longer alkyl chain has higher molar volume, which could weaken the interaction between the cation and anion of ILs, and thus increase H$_2$S solubility. Physical ILs are only suitable for the removal of H$_2$S when its partial pressure is high. Developing functionalized ILs is a promising way to improve H$_2$S absorption capacity and H$_2$S/CO$_2$ selectivity at low pressures. Protic ILs have been proven to be favorable absorbents for the separation of H$_2$S from CO$_2$. The strong interactions between H$_2$S and the anion of carboxylate, azole-based, and dual Lewis base functionalized ILs are the main causes of high H$_2$S absorption capacity in these ILs. Nevertheless, the high viscosities are the main bottleneck of most functionalized ILs, which limit their large-scale applications. Mixing ILs with low viscous aqueous and organic solvents reduces the viscosity of ILs and promotes the absorption kinetics of H$_2$S. Water and EG were often selected to increase the absorption rate of H$_2$S in ILs due to their low viscosities. ILs can be also mixed with alkanolamines, where ILs play the roles to stabilize absorbents, and/or to promote the absorption of H$_2$S in alkanolamines. Besides, the development of HPCs/ILs and PHPCs/ILs realized efficient H$_2$S absorption at high temperatures. The combination of ILs with absorbents and membranes is another potential strategy to overcome the high viscosity of ILs and improve H$_2$S sorption performance. MOFs, modified...
zeolites, and sol–gel derived silica are all promising supporters of ILs due to their porous structure and high surface area.

DESs have been considered as one of the most desirable solvents for the selective removal of H2S because of their benign properties. However, most reported DESs to date, especially functionalized DESs, have high viscosity due to the strong hydrogen-bond network in DESs, which are unadaptable for industrial H2S removal. Developing aqueous and supported DESs is an alternative way to minimize unfavorable effects of the high viscosity of DESs, but related research is still limited; thus further investigation is required to gain an in-depth understanding of the roles of DESs, and to screen more appropriate DESs for efficient H2S removal. It should be noted that even supported ILs/DESs exhibit attractive performance, they are only suitable for the gas streams with low H2S concentrations, while IL/DES-based liquid sorbents can be used for bulk H2S removal.

On the basis of the discussions presented above, the development of ILs/DESs-based sorbents is still one of the most potential directions for H2S removal. Therefore, the following aspects deserve further investigations: (1) Computational chemistry should be carried out to understand the mechanism of action between H2S and different ILs/DESs, and provide guidelines for the optimization of the structural design of task-specific ILs and DESs with high H2S absorption capacity and selectivity. (2) Carry out relevant research on the evaluation of technology and economy of IL/DES-based H2S removal processes, such as detailed analysis on energy requirement and total cost of a process, for commercial-scale adaptation of IL/DES-based technologies. (3) Explore the developing potentials of ILs and DESs for the utilization of H2S to widen the application of ILs and DESs, and to build a more sustainable H2S removal and utilization process.

4. THEORETICAL STUDIES

A large part of studies have been experiments to investigate H2S removal performance with ILs and DESs as sorbents, such as absorption capacity and selectivity, as described in the above sections. Meanwhile, theoretical studies, including quantum chemical calculations, Molecular Dynamics simulations, thermodynamic models, and Machine learning approaches for the prediction of H2S solubility, are very important to clarify mechanisms and provide valuable information for designing and screening novel IL-based and DES-based sorbents, even if such research is still limited.

4.1. Quantum Chemical Calculations. Quantum chemical calculations are highly useful tools to calculate the geometry structures and analyze the interaction mechanisms of H2S in ILs and DESs, and in general, they are often combined with experimental studies for a verification of the theory but also to better understand the measurements. Quantum chemical calculations are mainly used to analyze the nature of H2S capture in ILs/DESs and provide guidelines for designing and screening suitable ILs/DESs. The density functional theory (DFT) method combined with hybrid Becke 3-Lee–Yang–Parr (B3LYP) exchange-correlation function has been widely applied in quantum chemical calculations of ILs, in which electron correlation is well considered. For example, a computational study at the density functional theory DFT/B3LYP level with the basis sets of 6-311+G(d) and 6-311++G(2d,2p) was performed by Jalili et al. to understand the nature of H2S and CO2 in [Cmim][Tf2N]. The binding energy of anion–cation complexes calculated in the basis set of 6-311+G(d) decreases from the cations of [Cmim]+ to [Cmim]+, and then increases for [Cmim]+. However, a decreasing trend was observed from [Cmim]+ to [Cmim]+ by using 6-311+G(2d,2p). Moreover, an excellent linear correlation between the calculated absolute value of the energies of [Cmim][Tf2N]− at the B3LYP/6-311++G(2d,2p) level and Henry’s constant of H2S and CO2 were observed, which confirmed that a more polarized and diffused basis set 6-311++G(2d,2p) provides more accurate results, and the increase of alkyl chain decreased the interaction energy of anion and cation, promoting the interaction of IL and H2S. This observation could also explain the gradually increased H2S solubility with increasing alkyl chain of [PF6]−-based ILs as reported by Safavi et al. It was also found that the molecules of H2S and CO2 are directed toward the less electronegative N atom, rather than the most electronegative F atom of the [Tf2N]− anion, as shown in Figure 7. Quantum chemical calculations on the H2S-anion by Pomelli et al. and those on the CO2-anion by Bhargava et al. confirmed the conclusion.

Handy et al. reported that the higher H2S solubility compared with that of CO2 in [Bmim][Br] is attributed to the much shorter H-bond of the H2S-cation (2.38 Å) than that of the CO2-cation (3.18 Å) by using the B3LYP/6-311G(2d,p) level. To reveal how the structures of cations and anions of ILs affect H2S solubility, Zhou et al. calculated the interaction of H2S with different ILs, including 4-bis(2-hydroxypropyl)-1,1,3,3-tetramethyl guanidinium tetrafluoroborate ([TMGHPO2][BF4]), tetramethyl guanidinolactate (TMGL), etc.
and [Bmim]-based ILs with the anions of [Cl]−, [BF4]−, [PF6]−, [OTf]−, and [Tf2N]− by using B3LYP/6-311+G(d,p) level. The orders of the hydrogen bond strength and interaction energy of H2S-IL were consistent with that for the H2S solubility determined experimentally, revealing that hydrogen bonds are the main driving force of H2S absorption in these ILs, which is also in agreement with other experimental and calculation investigations.107,108

Different from the absorption mechanism of H2S in the ILs with common anions, the active protons of H2S are ionizable in the anion-functionalized ILs. For instance, DFT calculations for the phenolic ([PhO]−) IL-H2S complexes verified that the active proton of H2S was transferred to the oxygen atom of [PhO]− and formed a solid O−H bond during H2S absorption.78 Similar results were obtained by Zhang et al.77 in their calculations of the interaction between the azole-based protic IL and H2S. They stated that the extremely high H2S absorption capacity is attributed to the chemical combination of the H atom in the H2S molecule and the N atom in the anion of ILs.

Quantum chemical calculations were also used to understand the different behavior of H2S, CO2, and CH4 in DESs.75 In the system of H2S + ChCl/urea (1:2.0), Cl and H of ChCl formed strong hydrogen bonds with H and S of H2S, respectively. For CO2- ChCl/urea (1:2.0), hydrogen bonds were also formed between the Cl of ChCl with C of CO2 and H of urea with O of CO2. While only van der Waals interactions were observed in the system containing CH4 and ChCl/urea (1:2.0). As mentioned in section 3.4, the combination of PEI and ChCl/EG could greatly increase the H2S removal efficiency. Quantum chemical calculations on the complexes of H2S-PEI, H2S-ChCl, and H2S-EG confirmed that the interaction between PEI and H2S was the dominant driving force of high H2S removal performance, while DES (ChCl/EG) only played a role of solvent.98

4.2. Molecular Dynamics Simulations. Molecular Dynamics (MD) simulations have been used as an important method to understand the structural and energetic phenomena, as well as the thermodynamic and transport properties of ILs at the molecular level.110–113 The solubility of H2S can be obtained through MD simulations by calculating the solvation free energy using free energy perturbation (FEP), Bennett acceptance ratio methods (BAR), and so on. Sanchez-Badillo et al.114 performed MD simulations to obtain the Henry’s constant and solvation thermodynamic properties of H2S in [Bmim][Cl], [Bmim]-[BF4]−, and [Bmim][PF6] using the FEP method with united-atom force fields. The order of the predicted Henry’s constants in these three ILs is [Bmim][Cl] < [Bmim][BF4] < [Bmim][PF6], which is in agreement with the experimental results reported by Pomelli et al.106 The radial distribution functions (RDFs) indicated that the H atoms of H2S are oriented toward anions, while the S atom of H2S is surrounded by cations. The shortest distance between the H atoms in H2S and the [Cl]− anion resulted in the highest H2S solubility of [Bmim][Cl]. Moreover, the contribution of solvation enthalpy to free energy is twice of entropy, and, therefore, the H2S absorption in ILs is an enthalpy-driven process.

Salehin et al.115 calculated the solvation free energy and thermodynamics properties of H2S in five cholinium ([Chl])-based amino acid ILs using the BAR method with Optimized Potentials for Liquids Simulations (OPLS) force field. It showed that the free energy of H2S in IL is more negative compared with that in the aqueous system, indicating H2S can be more easily solvated in ILs. The radial and spatial distribution functions displayed that the H atoms of H2S are more aligned toward the anion, while the S atom of H2S is surrounded by cations, which agreed with the results from the literature.114 Moreover, the IL with the lowest Henry’s constant has the weakest interaction energy between anion and cation, which would lead to an increase of free volume for H2S to occupy and thus improve H2S solubility. Amhamed et al.116 performed all-atom MD simulations to study the absorption of H2S, CO2, and CH4 in choline benzololate ([Chl][BE]) and choline lactate ([Chl]-[Lac]). The selectivities of H2S/CH4 and CO2/CH4 were estimated to be more than 105 and 104, respectively, which indicated that [Chl]-based ILs are potential candidates for acid gas removal.

RDFs between H2S with CH4 and the components of caprolactam (CPL)-based DES (CPL/TBABr with a molar ratio of 1:1) were computed by Karibayev et al.,117 to explore the interactions within the DES, and to examine the interactions between the DES with H2S and CH4 in natural gas. As shown in Figure 8, the highest peak at a distance of 3.9 Å indicated the strong interaction between the H2S molecule and the Br of the DES. Moreover, the peaks of H2S-TBA and H2S-CPL were slightly higher than that of H2S-CH Br thus favoring the selective removal of H2S from CH4. Besides, the strength of the interactions (peak height) within the DES was marginally

Figure 8. (A) RDFs between H2S with CH4 and the components of DES, and (B) RDFs between the components of DES before and after mixing with natural gas. Figure reprinted from ref 117. Copyright 2020 American Chemical Society.
found that the interactions formed between H(H2S)/C(CO2) ILs. But Amhamed et al.116 found that the GROMOS 53A6 all-mixtures, and thus has been widely used to predict H2S solubility MD simulations can also predict H2S solubility in ILs and DESs, in ILs. The calculating the H2S solubility in ILs, which are discussed in equation of state (EoS) and conductor-like screening model for ILs and DESs theoretically. A variety of theoretical tools, such as calculation of solvation free energy, the force fields, and the structure of ILs/DESs. For example, Sanchez-Badillo et al.114 evaluated united-atom and different all-atom force field types for [Bmim]-based ILs with the anions of [PF6]-, [BF4]-, and [Cl]-, and found that some all-atom force fields are unsuitable for these ILs. But Amhamed et al.116 found that the GROMOS 53A6 all-atom force field is suitable to predict selectivity in [Chl]-based ILs. Overall, MD simulations are mainly used to calculate the solubility trend of H2S in ILs and DESs, while thermodynamic properties of pure ILs and the H2S+IL mixtures. It was found that the predictions of VLE are reliable with an AAD of 3.40%.

As mentioned above, MD simulations have been used to understand the interaction of anion—cation, and H2S-ILs/DESs. MD simulations can also predict H2S solubility in ILs and DESs, but the precision strongly depends on the methods used for the calculation of solvation free energy, the force fields, and the structure of ILs/DESs. For example, Sanchez-Badillo et al.114 evaluated united-atom and different all-atom force field types for [Bmim]-based ILs with the anions of [PF6]-, [BF4]-, and [Cl]-, and found that some all-atom force fields are unsuitable for these ILs. But Amhamed et al.116 found that the GROMOS 53A6 all-atom force field is suitable to predict selectivity in [Chl]-based ILs. Overall, MD simulations are mainly used to calculate the solubility trend of H2S in ILs and DESs, while thermodynamic models will be used to predict H2S solubility with high precision.

4.3. Thermodynamic Modeling of H2S Solubility

Experimental measurements can be time-consuming and dangerous because of the high toxicity of H2S, and even expensive. Therefore, it is desirable to obtain H2S solubility in ILs and DESs theoretically. A variety of theoretical tools, such as equation of state (EoS) and conductor-like screening model for real solvents (COSMO-RS) have been established for calculating the H2S solubility in ILs, which are discussed in this section and summarized in Figure 9.

4.3.1. Cubic EoS. EoS is a powerful tool in representing thermodynamic properties of pure ILs and the H2S + IL mixtures, and thus has been widely used to predict H2S solubility in ILs. The first prediction for H2S + IL mixtures was done by using relatively simple cubic EoS, including Peng-Robinson (PR) and EoS Redlich-Kwong (RK). In these cases, the IL was modeled as a whole molecule without specification about its structure and consideration of the association effect.

Fainéndez et al.118 used a modified PR EoS to correlate the solubilities of H2S and SO2 in ILs, and found that the model results are acceptable in all cases with the absolute average deviations (AAD) below 7.6% for H2S/IL mixtures and 2.6% for SO2/IL mixtures. Shojaeian et al.119 applied the Peng-Robinson two-state (PR-TS) EoS model to predict the solubility of H2S in the imidazolium-based ILs with the assumption that cross-association or self-association interaction is presented in binary mixtures. It was found that the predictions of VLE are reliable with an AAD of 3.40%.

Shiflet et al.120,121 developed a generic RK EoS to evaluate the vapor—liquid—liquid equilibrium (VLL) of H2S/[Bmim]-[PF6], CO2/[Bmim][PF6], H2S/[Bmim][MeSO4] and CO2/[Bmim][MeSO4]. The calculated results showed that [Bmim]-[MeSO4] has higher H2S/CO2 selectivity compared with [Bmim][PF6], which is inconsistent with the experimental results. Jallili et al.67 used this model to determine the solubilities of H2S and CO2 in [Ommim][TF2N] at 30–80 °C and the pressures up to 20 bar. The Krchekvsky-Kasarnovsky (KK) equation, the model comprising the extended Henry’s law and the Pitzer’s virial expansion, and the generic RK EoS were used to correlate the experimental values, and the RK model showed the best correlation with the experimental data for IL/CO2/H2S ternary mixtures. Same results were also obtained by Safavi et al.58 when correlating the measured data for [Ommim][PF6]/CO2/H2S ternary mixtures.

4.3.2. CPA EoS. The cubic plus association (CPA) EoS, which combines both cubic and association terms, has also been applied successfully to predict H2S solubility in different imidazolium-based ILs. Haghtalab et al.74 modeled the simultaneous solubilities of H2S and CO2 in [Bmim][Ac] by applying CPA and the reaction equilibrium thermodynamic model. The calculated AADs for the ternary H2S/CO2/IL system were estimated to be 18.8% for H2S and 13.7% for CO2, respectively. Panah et al.122 used CPA to calculate H2S solubilities in 14 imidazolium-based ILs, and the values of AAD were lower than 10% for all the cases. Moreover, modeling H2S solubility in [Ommim][TF2N],123 [Bmim][MeSO4],124 [Emim][PF6],125 [Ommim][PF6],126 [Emim][Ac], and [Hmim][Ac]127 verified that CPA is able to provide acceptable results for the binary H2S/imidazolium-IL mixtures. Sousa et al.128 used CPA to model the solubilities of H2S in 2-hydroxyethylammonium acetate ([2-HEA][Ac]), bis(2-hydroxyethyl)-ammonium acetate ([B-2-HEA][Ac]), and 2-hydroxyethylthiylammnonium hydrogen diacetate ([2-HEDEA][H(Ac)2]) at
temperatures of 25–45 °C and atmospheric pressure, by considering the 4-sites association scheme for the H$_2$S and 2-sites association scheme for the ILs. The AADs for the H$_2$S/IL mixtures in the three ammonium-based ILs were 6.5%, 6.9%, and 8.9%, respectively.

4.3.3. SAFT EoS. Statistical associating fluid theory (SAFT) EoS is a method for investigating the phase behavior of both nonassociating and associating fluids, in which the Helmholtz free energy is given as the sum of different contributions. Several versions of SAFT have been proposed to represent the H$_2$S solubility in ILs, such as SAFT-VR (variable range), perturbed-chain SAFT (PC-SAFT), and soft-SAFT. Rahmati-Rostami et al. calculated H$_2$S solubilities in six imidazolium-based ILs using the SAFT-VR and PC-SAFT models, and both showed good agreement with the experimental data. Moreover, by studying the effect of self-association of the H$_2$S molecules, they made a conclusion that self-association plays an important role in modeling the systems. Baramaki et al. modeled H$_2$S solubility in various ILs using PC-SAFT, and acceptable results were obtained in most of the cases with the AAD lower than 10%. PC-SAFT has been developed to predict the properties of ILs and gas solubilities (e.g., H$_2$S, CO$_2$, and CH$_4$) in ILs. Ji et al. studied the solubilities of H$_2$S, O$_2$, CO, and H$_2$ in [C$_n$ mim]-based ILs (2 ≤ n ≤ 8) with the anion of [Tf$_2$N]$^-$, [PF$_6$]$^-$, and [BF$_4$]$^-$ using ePC-SAFT. The results indicated that ePC-SAFT could predict quantitatively the solubility of H$_2$S under temperatures of 30–80 °C and pressures up to 20 bar. Later, the work was extended to other commonly used ILs (composed of the IL-cations of [C$_n$ mim]$^+$, [C$_n$ py]$^+$, [C$_n$ mpy]$^+$, [THTDP]$^+$, and the IL-anions of [Tf$_2$N]$^-$, [PF$_6$]$^-$, [BF$_4$]$^-$, [OTf]$^-$, [DCA]$^-$, [SCN]$^-$, [C$_2$ SO$_4$]$^-$, [C$_2$ SO$_3$]$^-$, [eFAP]$^-$, [Cl]$^-$, [Ac]$^-$, and Br$^-$), making it possible to predict gas solubility in a wide variety of ILs. Al-Fnaish et al. used PC-SAFT to investigate the solubilities of H$_2$S and CO$_2$ in [C$_n$ mim][Tf$_2$N] (n = 2, 4, 6, and 8). In their work, two strategies that (1) ILs were treated as neutral molecules, and (2) ILs were modeled as two charged ions, were examined. For the second strategy, four self-association schemes, including nonassociating, 2-sites (hydrogen ions, were examined. For the second strategy, four self-neutral molecules, and (2) ILs were modeled as two charged

![Figure 10. Illustrative example of hydrogen bonding between cation and anion of [Hmim][Tf$_2$N]. Figure reprinted with permission from ref 132. Copyright 2017 Elsevier.](image)
predictive EoS models to reduce the amount of experimental work in predicting H$_2$S solubility. The group contribution equation of state (GC-EoS) derived by the combination of four well-known theories (van der Waals EoS, Carnahan-Starling expression for hard spheres, NRTL, and group contribution principle), has been successfully applied to model gas + IL systems. This model takes into account the interactions between different functional groups of the molecules instead of different chemical structures of ILs, temperature, and pressure.

In this case, several ILs containing similar functional groups do not need to estimate new interaction parameters, and less amount of experimental data will be required, which makes this model easily applicable to various ILs. Breure et al. were the first to model binary systems of CO$_2$ and imidazolium-based ILs with the anions of [PF$_6$]$^-$ and [BF$_4$]$^-$ using GC-EoS. Good agreement between experimental and calculated solubilities was obtained for pressures up to 100 MPa. Subsequently, application of GC-EoS to model the binary systems, including ILs with the anions of [Tf$_2$N]$^-$, [NO$_3$]$^-$, and tetracyanoborate [TCB]$^-$, with gases such as SO$_2$, alkanes, H$_2$, and CO, was also reported and obtained satisfactory results. Even the research related to H$_2$S + CO$_2$ and H$_2$S + imidazolium-based ILs. A low ADD of 4.58% for 465 experimental data points was obtained. Sedghamiz et al. predicted the solubilities of H$_2$S in ILs using the feed-forward neural network (FFNN), and the modeling results were compared with empirical correlations and PR. The accuracy of FFNN is higher than both empirical correlations and PR. Moreover, multi-layer perceptron ANN (MLP-ANN) was proposed by the research groups of Amedi, Faúndez, and Hosseini, to investigate H$_2$S solubility in ternary mixtures containing CO$_2$. Desirable predictions by using the MLP-ANN method indicate that MLP-ANN is a good alternative method for the estimation of H$_2$S solubility in ILs.

4.4. Machine Learning Approaches for Predicting H$_2$S Solubility. Machine learning (ML) approaches also offer predictions for H$_2$S-IL systems. Examples of these models include the artificial neural network (ANN), gene expression programming (GEP), least square support vector machine (LSSVM), stochastic gradient boosting (SGB), extreme learning machine (ELM), Predictions of H$_2$S solubility in different ILs with ML approaches are discussed below and summarized in Table 2.

ANN is a nonlinear mathematical model with the advantages of high uniformity of analysis, nonlinearity, parallelism, and capability to challenge fuzzy and imprecise data. Shaheen et al. employed the acetic factor ($\omega$), critical temperature ($T_c$), and critical pressure ($P_c$) of ILs as input parameters to build a multilayer feed-forward neural network (MLFFNN) model to predict the H$_2$S solubility in various imidazolium-based ILs. A low ADD of 4.58% for 465 experimental data points was obtained. Sedghamiz et al. predicted the solubilities of CO$_2$ and H$_2$S in ILs using the feed-forward neural network (FFNN), and the modeling results were compared with empirical correlations and PR. The accuracy of FFNN is higher than both empirical correlations and PR. Moreover, multi-layer perceptron ANN (MLP-ANN) was proposed by the research groups of Amedi, Faúndez, and Hosseini, to investigate H$_2$S solubility in ternary mixtures containing CO$_2$. Desirable predictions by using the MLP-ANN method indicate that MLP-ANN is a good alternative method for the estimation of H$_2$S solubility in ILs.

GEP, as a full-fledged genotype-phenotype system, is inspired by genetic algorithms and genetic programming. Ahmadi et al. evaluated the performance of the GEP model in estimating the solubility of H$_2$S in ILs with the input variables of $\omega$, $T_c$, and $P_c$ accompanied by temperature and pressure. A quite high coefficient of determination ($R^2 = 0.9902$) and extremely low mean absolute relative error (MARE = 0.0438%) were obtained.

| ML approach | no. of data points | no. of ILs | input parameters | model performance | ref |
|-------------|-------------------|------------|------------------|-------------------|----|
| MLFFNN-ANN  | Total: 465; Training: 372; Test: 93 | 11 | Acentric factor, critical temperature and pressure of ILs, temperature | $R^2$: 0.9922 | 155 |
| FFNN-ANN    | Total: 664; Training: 70%; Validation: 15%; Test: 15% | 14 | Acentric factor, critical temperature and pressure of ILs, temperature | $R^2$: 0.9987 | 156 |
| MLP-ANN     | Total: 664; Training: 554; Test: 110 | 13 | Critical temperature, pressure and molecular weight of ILs, pressure, and temperature | $R^2$: 0.9995 (for H$_2$S/IL) | 157 |

Table 2. Summary of the Research Work on the Prediction of H$_2$S Solubility in ILs Using ML Approaches
Support vector machine (SVM) is an intelligent method, which converts the nonlinear input space to a high-dimensional feature space and discovers a hyperplane by the means of nonlinear mapping.\textsuperscript{169} LSSVM is the variant of SVM. It has the ability to handle large-scale data sets with a higher convergence rate and less complexity.\textsuperscript{170} H$_2$S solubility in 11 imidazolium-based ILs has been estimated by Ahmadi et al.\textsuperscript{161} through the LSSVM model with a genetic algorithm as an optimization scheme. The obtained results agree well with the experimental data, and the corresponding $R^2$ and mean squared error (MSE) are 0.9976 and 0.00006651, respectively. Baghban et al.\textsuperscript{162} also employed LSSVM to predict H$_2$S solubility in 27 different ILs. In this proposed model, only 15 different chemical structures of ILs were used as input parameters, while previously reported models required many input parameters, such as $\omega$, $T_c$, and $P_c$ for each IL.

In the SGB method, randomness is introduced into its sequential fitting using subsamples of the training data for each iteration to improve the performance of gradient boosting.\textsuperscript{171} The application of SGB for the prediction of H$_2$S solubility in ILs was first reported by Soleimani et al.\textsuperscript{163} with the input variables of $\omega$, $T_c$, and $P_c$ of ILs, accompanied by operating temperature and pressure. It was found that SGB has desirable performance with a quite high correlation coefficient ($R$) of 0.9995, and low MARE of 0.0222.\textsuperscript{165} The comparative studies with EoS, GEP, and LSSVM indicated that SGB is more efficient and reliable than other models due to its higher accuracy and robustness. Figure 11 illustrates an example for the prediction of H$_2$S solubility in [Hmim][Tf$_2$N] with different models. The above mentioned models are able to predict H$_2$S solubility with a high precision. However, they still meet some obstacles as experimental data need to be employed as the input. To overcome this problem, Zhao et al.\textsuperscript{164} reported an ELM algorithm for predicting H$_2$S solubility in ILs with the number of fragments as the input parameters, in which 1282 pieces of data for 27 ILs were included. The $R^2$, average absolute relative deviation (AARD) and root-mean-square error (RMSE) for the whole set were 0.997, 4.12%, and 0.0168, respectively, indicating that ELM can be used to estimate H$_2$S solubility in ILs over wide ranges of temperatures and pressures. Later, a new type of molecular descriptors, electrostatic potential surface (SEP), was proposed by the same group to obtain information at the electron level for the prediction of H$_2$S solubility in ILs using ELM.\textsuperscript{166} In this work, two new quantitative models were established based on the SEP parameters of isolated cation and anion (ELM$_c$), or ion pair structure of each IL (ELM$_i$). The ELM$_i$ model showed better prediction ability since the effect of the corresponding opposite charge of ILs was included in the calculation. All the aforementioned results proved that ML methods have great potential to estimate the H$_2$S solubility in ILs. It should be noted that a high number of experimental data is usually needed to get high prediction accuracy when using ML methods, and a small number of experimental data will result in erroneous predictions.

5. PROCESS SIMULATION OF H$_2$S REMOVAL IN ILS AND DESS

Evaluation of the technologies are always required for a large-scale adaptation of any process. A combination of experimental and computational methods is the most common and powerful way to carry out process analysis. For H$_2$S removal, physical absorption using methanol and the mixture of dimethyl ether and polyethylene glycol is applied in industrial processes, which are called Rectisol\textsuperscript{172} and Selexol.\textsuperscript{173} However, Rectisol shows high volatility and low H$_2$S selectivity in the presence of CO$_2$; the high viscosity of Selexol results in low absorption kinetics.\textsuperscript{174} Chemical amine-based processes show the drawbacks of high solvent loss and energy usage. As mentioned above, recent developments have demonstrated that IL/DES-based sorbents are promising and offer desirable performance for desulfurization from different gas streams owing to their unique properties compared with conventional physical and chemical absorbents. Therefore, there is a pressing demand for evaluating the feasibility and implementation in industrial desulfurization.

Santiago et al.\textsuperscript{175} combined predictive model and process simulations to select promising ILs for H$_2$S capture. Specifically,
COSMO-RS was used to select promising ILs according to thermodynamic criteria. Then Aspen Plus was applied to test the absorption performance of H₂S in the industrial absorption column. It showed that the ILs that exhibited desirable H₂S absorption performance in the thermodynamic aspect may present a weak operating performance because of their limited transport properties. Wang et al.176 developed a multilevel screening method for simultaneous removal of H₂S and CO₂ from natural gas. First, potential ILs were prescreened based on the Henry’s law constant-based absorption-selectivity-desorption index (ASDI) at infinite dilution conditions. Then, their simultaneous H₂S and CO₂ removal performance was further evaluated based on vapor−liquid equilibrium (VLE) of ILs + gas mixture (H₂S, CO₂ and CH₄). Following this, several key physical properties of selected ILs, including melting point, viscosity, and thermal and chemical stability, were assessed by the group contribution methods to find out suitable ILs for industrial applications. Finally, IL-based acid gases removal processes were simulated with Aspen Plus to evaluate the feasibility. After evaluation, phosphate [BeMPYO][H₂PO₄] and [EMIM][H₂PO₄] were identified as the two best absorbents. This work provides a comprehensive method for evaluating the potential of ILs in industrial H₂S removal processes.

Wang et al.21 designed a novel IL-based process for simultaneous removal of H₂S and CO₂ from syngas at room temperature using Aspen Plus. By comparing the physical properties of different ILs, [Bmim][Tf₂N] was selected for further investigation because of its high solubility of acid gases and low viscosity. The process flow diagram based on [Bmim][Tf₂N]-based syngas purification was shown in Figure 12. In this case, the removal ratios of CO₂ and H₂S could reach 97.6% and 95.3%, respectively, whereas in the Rectisol process as reported by Liu et al.,177 the removal ratios of CO₂ and H₂S were 89.7% and 99.89%, respectively. Besides, the recovery ratio of IL was high, up to 99.91%. Later, Taheri et al.178 compared the removal efficiency, energy usage, and total direct capital cost of [Bmim][Tf₂N]-based purification process with the Rectisol process as a reference. The electricity used to capture 1 kg of CO₂ was estimated to be 1.150 and 1.176 MJ using the [Bmim][Tf₂N]-based and Rectisol processes, respectively, meaning that the IL-based process is more energy-efficient. However, the total direct capital cost of the IL-based process is higher than that of Rectisol process due to the high selling price and still expensive recovery cost of IL.

Kazmi et al.179 studied the removal of acid gases from natural gas through an amine-based process with an imidazolium-based cationic IL, such as [Bmim][PF₆], as absorbent. They found that the removal efficiency can go up to 99% in the IL-based process, and 99.77% IL could be recovered. The estimated energy demand and total annualized cost were reduced by 85.6% and 50.7% compared to the amine-based process. This indicated that the IL-based process has a great potential for industrial applications.

The similar characteristics as ILs and the lower price make DESs more attractive for large-scale H₂S removal. Haider et al.180 did use Aspen Plus to evaluate the performance of aqueous ChCl/urea for biogas upgrading at 36 bar. The upgraded biogas was further liquefied for economical and safe transportation. During this process, the biogas is upgraded by selective absorption of H₂S (≤10 ppm) and CO₂ (99% removal), with biomethane recovery (≥97 wt %) with a purity of 99 wt %. For the process with the DES of 70% concentration, the savings in the overall capital cost, overall operating cost, and total annualized costs were 2.80%, 25.82%, and 14.26%, respectively, compared with MEA-based process, and 1.41%, 16.85%, and 8.71% were saved compared with the [Bmim][PF₆]-based process. This study concludes that DESs have the potential to replace conventional solvents and provide feasible solutions for cost-related issues of ILs.

6. EVALUATION OF ILS AND DESS FOR H₂S REMOVAL

6.1. Viscosity and H₂S Absorption Capacity. Viscosity and H₂S absorption capacity provide important references for the screening of candidate ILs and DESs since they are the main influential factors for H₂S removal efficiency. Besides, H₂S removal conditions (high pressure or low pressure) and removal types (selective or simultaneous removal of H₂S and CO₂) will also affect the selection of ILs and DESs. In this part, different
ILs and DESs will be evaluated based on their viscosity and H₂S absorption capacity, as well as the H₂S removal conditions and removal types.

For H₂S removal at high pressures, physical ILs are suitable absorbents considering their low regeneration energy due to the weak interaction between ILs and H₂S. Figure 13 summarized the viscosities and Henry's constant of different physical ILs. Since high viscosity could result in low mass transfer, only ILs with low viscosity (less than 70 mPa·s at 30 °C) were selected for further evaluation, which include [Emim][Tf₂N], [Emim]-[OTf], [Bmim][Tf₂N], [Emim][eFAP], [Hmim][Tf₂N], [Bmim][OTf], [Hemim][Tf₂N], [C₄Py][Tf₂N], and [C₄Py]-[SCN]. As shown in Figure 13b, ILs with a longer alkyl chain of cation, and with the anion of [Tf₂N]⁻, [OTf]⁻, and [SCN]⁻ have a lower Henry's constant. Ideal ILs should have low viscosity and a low Henry's constant of H₂S. To meet this requirement, ILs with the viscosity lower than 70 mPa·s and the Henry's constant below 15 bar at 30 °C were chosen. These ILs were then divided into two groups for selective (H₂S/CO₂ selectivity > 4) and simultaneous (H₂S/CO₂ selectivity < 3) removal of H₂S and CO₂.

Functionalized ILs can be used as attractive absorbents for low pressure H₂S removal. As can be seen in Figure 14a, most reported functionalized ILs for H₂S removal are protic ILs due to their advantages of simple synthetic routes and good affinity with H₂S. Similar to the evaluation criteria of physical ILs, functionalized ILs with viscosities less than 60 mPa·s at 35 °C or 50 mPa·s at 40 °C were first selected for further discussion. [NEMH]-based ILs with the anion of [Pro]⁻, [Bu]⁻, and [Ac]⁻ exhibited high H₂S removal capacities at 1 bar, and their viscosities were lower than 6 mPa·s at 35 °C, indicating a great application potential for industrial H₂S removal processes. However, experimental data about CO₂ absorption capacity in these ILs have not been reported yet, and thus it is still unclear what kind of H₂S removal (selective or simultaneous removal of H₂S and CO₂) that [NEMH]-based ILs applies. [DBNH][Pry], [DBNH][Im], [DBUH][Pry], [DBUH][Im], [DBNH][1,2,4-Triaz], [DMEAH][Ac], and [DMEAH][For] also showed low viscosities. Since all these functionalized ILs showed satisfied H₂S absorption capacity, only H₂S/CO₂ selectivity was compared as shown in Figure 14b. The last three ILs are potential candidates for selective H₂S absorption because of their high H₂S/CO₂ selectivities (>4). Especially, the H₂S/CO₂ selectivity of [DMEAH][For] is higher than 10. [DBNH][Pry], [DBNH][Im], [DBUH][Pry], [DBUH][Im] are promising absorbents for simultaneous removal of H₂S and CO₂ considering their low H₂S/CO₂ selectivities.

The viscosity data of most DESs used for H₂S removal are lacking, and thus we cannot make an evaluation of DESs based on their viscosity directly. In fact, most reported DESs to date have very high viscosity at room temperature, which is attributed to the strong hydrogen-bond network between HBAs and HBDs.
of DESs. Therefore, finding a way to use high viscous DESs is also important since some of them have excellent H$_2$S removal performance. Since ChCl/urea shows good biodegradability, and mixing DESs with low viscous solvents is a simple and feasible method to reduce viscosity, aqueous ChCl/urea should be a promising candidate for H$_2$S removal at high pressure. It is reported that the viscosity of pure ChCl/urea (1:2) is 1571 mPa·s at 25 °C, which reduces to 45.06 mPa·s when 36.47% (molar fraction) water exists in ChCl/urea (1:2).\(^{195}\)

6.2. Thermal Stability. Thermal stability of ILs/DESs is another important factor for deciding their suitability for gas separation processes. The decomposition temperatures of [Emim][Tf$_2$N], [Bmim][Tf$_2$N], [Hmim][Tf$_2$N], [Emim][OTf], [Bmim][OTf] are up to 400 °C,\(^{196,−198}\) and [C$_3$Py][SCN] is 220 °C.\(^{69}\) The decomposition temperature of ChCl/urea (1:2) is 172 °C.\(^{199}\) The high stability of these physical ILs and ChCl/urea (1:2) verify that the selected ILs and DES can be used for H$_2$S removal without decomposition during the regeneration. For functionalized ILs, [DBNH][Pr$_y$], [DBNH]-[Im], [DBUH][Pr$_y$], [DBUH][Im], and [DBNH][1,2,4-Triaz] are unsuitable for industrial H$_2$S removal due to their low decomposition temperatures (<80 °C).\(^{78,79}\) The decomposition temperatures of [DMEA/H][Ac] and [DMEA/H][For] are about 120 °C,\(^{78,79}\) and these two ILs can be used in industry when the operation temperature is lower than 120 °C.

6.3. Cost. The high price of ILs compared with conventional solvents results in a high investment cost of ILs. But the use of ILs may also increase the removal performance of H$_2$S and reduce the energy usage of the processes. Therefore, economic evaluation is always needed before using these ILs in pilot-scale application. Taheri et al.\(^{178}\) compared [Emim][Tf$_2$N] with the reference Rectisol process for H$_2$S removal, and it was found that the direct capital cost of [Emim][Tf$_2$N] is four times higher than the Rectisol process due to the high price of IL. However, ILs as green solvent can be easily recycled, for example, the recovery ratio of [Emim][Tf$_2$N] can be as high as 99.91%,\(^{21}\) so its advantages are obvious for long-term applications. In fact, the complicated synthetic route is one of the main reasons for the high price of ILs, and simplifying the synthetic routes could reduce cost. [DMEA/H][Ac] and [DMEA/H][For] can be synthesized using a one-step method, and the price of raw material is low. Therefore, these two functionalized ILs are promising for industrial H$_2$S removal. Economic evaluation of a DESs-based process is also performed, and 14.26% total annualized cost saving was obtained for aqueous ChCl/urea (1:2) of 70% concentration compared with the amine-based technology, indicating the high economic feasibility of ChCl/urea.\(^{80}\)

7. ILS AND DESS FOR UTILIZATION OF H$_2$S

7.1. Recovery of Sulfur and Hydrogen. Sulfur is one of the important chemicals for sulfuric acid (H$_2$SO$_4$) production in the industry. Therefore, the recovery of sulfur from H$_2$S-contained gas streams is an attractive way to reuse resources and achieve sustainable development. The Claus process is the most mature technology for sulfur recovery through a two-step reaction (eqs 1 and 2). In the thermal step, H$_2$S is oxidized to SO$_2$ in the furnace at 1000−1200 °C, and then elemental sulfur is produced from the reaction of H$_2$S and SO$_2$ in the presence of catalysts at 200−350 °C.\(^{200}\) For this process, reasonable efficient conversion of H$_2$S is difficult because of the thermodynamic limitations, and the high-temperature results in large energy requirements. The liquid-phase Claus reaction has shown great progress for the recovery of sulfur under relatively mild conditions. However, the main obstacles include the volatile and toxic nature of organic solutions and other challenges, such as the operating temperature should be above the melting point of sulfur (112.8 °C), which is still high and needs to be further optimized.

\[
\text{thermal-step: } \text{H}_2\text{S} + \frac{3}{2}\text{O}_2 = \text{SO}_2 + \text{H}_2\text{O} \tag{1}
\]

\[
\text{catalytic-step: } 2\text{H}_2\text{S} + \text{SO}_2 = \frac{3}{8}\text{S}_8 + 2\text{H}_2\text{O} \tag{2}
\]

It has been found that ILs can be highly appropriate solvents for the absorption of H$_2$S. This fact promotes the investigation of ILs as alternative media for the capture and oxidation of H$_2$S. Huang et al.\(^{201}\) reported an IL-mediated Claus reaction under mild conditions without the addition of any catalysts. Among the ILs with different cations and anions, [Hmim][Cl] was found to be the most effective reaction media for the oxidation of H$_2$S, in which the oxidation of H$_2$S to S$_8$ was almost complete within 3 min with a high conversion ratio of 96.4% at 40 °C, which is quite higher than that in the organic solvent—diglycol monomethyl ether (81.0%) under the same condition. The desirable performance of ILs as reaction media was attributed to the strong affinity of ILs with H$_2$S and SO$_2$.

Sulfur o xo-acid salts would also be formed as byproducts during the Claus reaction, even in the IL-based reaction medium. To prevent the side-reaction, He et al.\(^{202}\) synthesized a type of hydrophobic iron-based IL (Fe(III)-IL) for the oxidation of H$_2$S to sulfur. It was found that the removal efficiency of H$_2$S...
conversion of H$_2$S is only 20% at 1010 °C. Such a high temperature makes the thermal decomposition method not a good choice for industrial hydrogen recovery from H$_2$S since it is very energy-intensive. Reducing reaction temperature and using electrical energy originated from renewable sources are two main strategies to reduce energy usage and enhance the economic feasibility of the H$_2$S conversion process. At present, electrolysis has been used for hydrogen and sulfur recovery from H$_2$S by direct and indirect routes. Direct transformation of H$_2$S is preferred, but the aggregation of sulfur formed on the anode causes the serious passivation of the anode. Indirect electrolysis could avoid the problem of anode passivation, but the separation of flocculent sulfur is usually difficult. Therefore, no commercial-scale research has been reported for H$_2$S conversion to produce hydrogen and sulfur based on electrolysis. Inspired by the successful application of ILs in enhancing the performance of sulfur recovery from H$_2$S and the great potential of electrolysis, Guo et al. 210 established a new nonaqueous desulfurization system (Fe(III/II)–IL/DMF), in which the controlled-potential electrolysis method was used for the regeneration of the desulfurizer. It was found that a quite high desulfurization efficiency of 99.96% can be obtained in Fe(III/II)–IL/DMF, but the method to separate sulfur from the electrolytes is not mentioned. More recently, Ma et al. 211 established an effective method for direct H$_2$S electrolysis at 50 °C in the IL-TGDE-MEA electrolyte using hydroxy-functionalized IL [C$_3$OHmim][BF$_4$] as the supporting electrolyte, tetraethylene glycol dimethyl ether (TGDE) as the solvent, and MEA as the absorbent of H$_2$S. No sulfur was attached on the surface of the anode after 7 h due to its quite high solubility in electrolyte at 50 °C, indicating that direct electrolysis of H$_2$S in this IL-based solvent did not result in problems linked to anodic passivation. Sulfur was precipitated when the temperature was reduced to 20 °C, which makes it easy to recover sulfur and reuse the electrolyte. Besides, the mild reaction condition could reduce the volatilization and degradation of MEA. Therefore, this process is also environmentally friendly. This study provides a promising method for the efficient recovery of hydrogen and sulfur from the direct electrolysis of H$_2$S, even if only lab-scale tests are performed.

### 7.2. Synthesis of Value-Added Chemicals.

Conversion of H$_2$S to value-added chemicals is another feasible way to use H$_2$S. Mishra et al. 215 used the IL of trihexyltetradecyl- phosphonium chloride (THTDPC) as the catalyst for the utilization of H$_2$S to synthesize bis(2-phenylethyl) sulfochloride (PES). More specifically, H$_2$S was first absorbed into aqueous MDEA, which was followed by the reaction of H$_2$S-enriched MDEA with 2-bromoethylbenzene (2-BEB) to produce PES in the presence of THTDPC. The initial reaction rate in the system with the IL concentration of 0.03 kmol/m$^3$ is three times higher than that in the system without IL. The final selectively of PBS could reach 100%.

The above studies verify that Fe(III)-based ILs and metal-based DESs have great potential for sulfur recovery. However, their regeneration rate by air or O$_2$ is very slow due to the low solubility of O$_2$ and the low reaction kinetics in ILs and DESs. Besides, hydrogen, as a clean energy source with high energy density, was not recovered during the regeneration process of H$_2$S.

The thermal decomposition of H$_2$S at high temperature (>1000 °C) is the most direct way for H$_2$S splitting to obtain hydrogen and sulfur. However, the highly endothermic nature of this reaction results in unsatisfactory low values of conversion even at high temperatures. It was reported that the
attractive for H$_2$S conversion to highly valuable products. Xiong et al.\textsuperscript{213} developed a novel mild method for H$_2$S conversion to produce mercaptan alcohol with tertiary amine-functionalized protic ILs serving as both solvents and catalysts. [BDMAEEH]-[MeOAc] showed the highest conversion of 99% with the highest selectivity of 74%. These methods will open new opportunities for the utilization of H$_2$S.

8. CONCLUSIONS AND FUTURE PROSPECTS

In this work, recent developments of conventional chemical absorption and adsorption, including their challenges, are reviewed. Fundamental research on H$_2$S removal using pure ILs, IL-based solvents, IL-reinforced adsorbents/membranes, and DESs are summarized and discussed. ILs and DESs presented advantages in the desulfurization process compared with conventional absorption and adsorption technologies. Theoretical studies, including quantum chemical calculations, MD simulations, and thermodynamic models, and machine learning approaches for predicting H$_2$S solubility are summarized to analyze the interaction mechanism between H$_2$S and IL/DES, and to screen suitable ILs with high H$_2$S solubility. From process simulation, the lower energy usage and total annualized cost evidenced the feasibility of IL-based and DES-based processes to replace conventional Rectisol and amine-based processes for industrial desulfurization. Moreover, several ILs and DES are selected from the choices based on their viscosity, H$_2$S removal capacity, thermal stability, and cost. Finally, the application of ILs and DESs in the conversion of H$_2$S provides an effective way for resource reutilization. However, a number of issues still exist and need to be addressed in the future as illustrated in Figure 15.

First, from the viewpoint of IL selection, the complicated synthetic routes, large viscosity, and still high price of most ILs potentially increasing the total running cost are still unfavorable factors for the scale-up of an IL-based process for H$_2$S removal. To simplify the synthetic step, protic ILs are getting more attention in research. The development of IL-based solvents and IL-reinforced adsorbents/membranes could overcome the negative effect of viscosity and thus lower capital cost. DESs have shown specific advantages of the simple synthetic process, biodegradable capability, and cheap raw material cost, which may bring about a breakthrough in the near future.

Second, with respect to experimental research related to H$_2$S removal, current work with ILs/DESs is still relatively new, and lots of effects have not been deeply studied and understood. Studies on H$_2$S absorption using ILs/DESs in mixed gases are scarce and need to be complemented, to provide fundamental knowledge for conducting the practical processes, since H$_2$S solubility may be more or less influenced by the presence of other gases.

Third, combining quantum chemical calculations and MD simulations with experimental studies are important methods to understand the relationship of ILs/DESs-properties–H$_2$S removal performance, and thus to design task-specific ILs/DESs. However, related work is not yet rewarding enough. Various thermodynamic models have been used for estimating H$_2$S solubility in ILs. Nevertheless, most of the EoS models are limited to the specific system and need to be advanced to reduce the amount of experimental work in predicting H$_2$S solubility due to numerous combinations of anions and cations of ILs and extreme operating conditions. COSMO-RS could predict the thermodynamic properties independent of experimental data, but it is often not sufficient to accurately predict H$_2$S solubility, which needs to be further modified. Machine learning approaches are promising models due to their simplicity, flexibility, and high precision, but they are not adequately rich in molecular information. However, they can be used to find hidden correlations in large data sets and also to provide more

---

Figure 15. Challenges and future prospects for H$_2$S removal and utilization in ILs/DESs.
accurate force field models for molecular simulations from quantum chemistry calculations. This has not been done yet in the context of H₂S removal but will most likely be seen in the near future.

Fourthly, although a large amount of experimental studies on the absorption of H₂S using ILs and DESs have been reported, pilot scale research related to H₂S removal in pure ILs, IL-based solvents, and DESs is still lacking. Therefore, future studies should focus more on the process design to analyze the technical, economic, and environmental aspects, and to evaluate the feasibility of IL/DES-based desulfurization processes in industrial applications. Moreover, the potential issues during the use of ILs/DESs, for example, corrosion, toxicity, environmental impact, and long-term stability should be addressed and studied.

Finally, developing H₂S utilization technologies in ILs/DESs systems is an efficient way to reuse H₂S. However, only a limited number of ILs and DESs have been used for the conversion of H₂S. In the future, more efforts should be put into the investigation of functionalized ILs and DESs. Quantum chemistry calculations and MD simulations can also be used to further in-depth understanding of the roles of ILs and DESs in H₂S conversion. Additionally, the evaluation of techno-economic-environmental impacts for H₂S utilization processes should also be conducted to judge their industrial feasibility in ILs/DESs-based systems.

□ AUTHOR INFORMATION

Corresponding Authors
Xiangping Zhang — CAS Key Laboratory of Green Process and Engineering, Beijing Key Laboratory of Ionic Liquids Clean Process, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China; School of Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China; orcid.org/0000-0002-1431-0873; Email: xpzhang@ipe.ac.cn
Xiaoyan Ji — Energy Engineering, Division of Energy Science, Luleå University of Technology, 97187 Luleå, Sweden; Email: xiaoyan.ji@ltu.se

Authors
Fangfang Li — Energy Engineering, Division of Energy Science, Luleå University of Technology, 97187 Luleå, Sweden; orcid.org/0000-0001-9841-8285

Aatto Laaksonen — Energy Engineering, Division of Energy Science, Luleå University of Technology, 97187 Luleå, Sweden; Division of Physical Chemistry, Department of Materials and Environmental Chemistry, Århenius Laboratory, Stockholm University, Stockholm 10691, Sweden; Center of Advanced Research in Biomacromolecules and Biopolymers, “Petru Poni” Institute of Macromolecular Chemistry, Iaşi 700469, Romania; State Key Laboratory of Materials-Oriented and Chemical Engineering, Nanjing Tech University, Nanjing 211816, China; orcid.org/0000-0001-9783-4535

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.iecr.1c04142

Notes
The authors declare no competing financial interest.

□ ACKNOWLEDGMENTS

This work was supported by the Swedish Energy Agency (P47500-1), the Swedish Research Council, and partial support from a grant from Ministry of Research and Innovation of Romania (CNCS-UEFISCDI, Project No. PN-III-P4-ID-PCCF-2016-0050, within PNCDI III).

□ REFERENCES

(1) Wiheeb, A. D.; Shamsudin, I. K.; Ahmad, M. A.; Murat, M. N.; Kim, J.; Othman, M. R. Present technologies for hydrogen sulfide removal from gaseous mixtures. Rev. Chem. Eng. 2013, 29 (6), 449–470.
(2) García-Arriaga, V.; Álvarez-Ramírez, J.; Amaya, M.; Sosa, E. H₂S and O₂ influence on the corrosion of carbon steel immersed in a solution containing 3 M diethanolamine. Corros. Sci. 2010, 52 (7), 2268–2279.
(3) Dou, X. M.; Veksha, A.; Chan, W. P.; Oh, W. D.; Liang, Y. N.; Teoh, F.; Mohamed, D. K. B.; Giannis, A.; Lisak, G.; Lim, T. T. Poisoning effects of H₂S and HCl on the naphthenalene steam reforming and water-gas shift activities of Ni and Fe catalysts. Fuel 2019, 241, 1008–1018.
(4) Fazlollahi, F.; Asadizadeh, S.; Khoshrcehooei, M. A.; Birjandi, M. R. S.; Sarkari, M. Investigating efficiency improvement in sulfur recovery unit using process simulation and numerical modeling. Oil Gas Sci. Technol. 2021, 76, 18–26.
(5) Li, J. P.; Wang, R.; Dou, S. Y. Electrolytic cell-assisted polyoxometalate based redox mediator for H₂S conversion to elemental sulphur and hydrogen. Chem. Eng. J. 2021, 404, 127090–127098.
(6) Mishra, P.; Kumar, S.; Sen, S. Kinetic modeling onionic liquid mediated bi-liquid phase transfer catalyzed synthesis of bis-(2-phenylthio) sulphide with H₂S-rich methyldiethanolamine. J. Mol. Liq. 2018, 271, 580–588.
(7) Wang, Y.; Liu, Y. X.; Wang, Y. Oxidation absorption of hydrogen sulfide from gas stream using vacuum ultraviolet/H₂O₂/urea wet scrubbing system. Process Saf. Environ. Prot. 2020, 140, 348–355.
(8) Kapoor, R.; Ghosh, P.; Kumar, M.; Vijay, V. K. Evaluation of biogas upgrading technologies and future perspectives: a review. Environ. Sci. Pollut. Res. 2019, 26 (12), 11631–11661.
(9) Shoukat, U.; Pinto, D. D. D.; Knuttila, H. K. Study of various aqueous and non-aqueous amine blends for hydrogen sulfide removal from natural gas. Processes 2019, 7 (3), 160–174.
(10) Uresin, E.; Sarac, H. I.; Sarioğlan, A.; Ay, S.; Akgun, F. An experimental study for H₂S and CO₂ removal via caustic scrubbing system. Process Saf. Environ. Prot. 2015, 94, 196–202.
(11) Liu, D. J.; Li, B.; Wu, J.; Liu, Y. X. Sorbents for hydrogen sulfide capture from biogas at low temperature: a review. Environ. Chem. Lett. 2020, 18 (1), 113–128.
(12) Zhao, L.; Wang, Y.; Li, X.; Wang, A. J.; Song, C. S.; Hu, Y. K. Hydrogen production via decomposition of hydrogen sulfide by synergism of non-thermal plasma and semiconductor catalysis. Int. J. Hydrogen Energy 2013, 38 (34), 14415–14423.
(13) Traus, I.; Suhr, H.; Harry, J. E.; Evans, D. R. Application of a rotating high-pressure glow discharge for the dissociation of hydrogen sulfide. Plasma Chem. Plasma Process. 1993, 13 (1), 77–91.
(14) Xueqian, W.; Ke, X.; Xing, M.; Ping, N.; Chen, C.; Langlang, W.; Jinhuang, C. Simultaneous removal of H₂S and dust in the tail gas by DC corona plasma. Plasma Chem. Plasma Process. 2016, 36 (6), 1545–1558.
(15) Zhang, Q.-Z.; Wang, W.; Thille, C.; Bogaerts, A. H₂S decomposition into H₂ and S₂ by plasma technology: Comparison of gliding arc and microwave plasma. Plasma Chem. Plasma Process. 2020, 40 (5), 1163–1187.
(16) Sassi, M.; Amira, N. Chemical reactor network modeling of a microwave plasma thermal decomposition of H₂S into hydrogen and sulfur. Int. J. Hydrogen Energy 2012, 37 (13), 10010–10019.
(17) Dan, M.; Yu, S.; Li, Y.; Wei, S.; Xiang, J.; Zhou, Y. Hydrogen sulfide conversion: How to capture hydrogen and sulfur by photocatalysis. J. Photochem. Photobiol., C 2020, 42, 100339–100363.
(18) Mizuta, S.; Kondo, W.; Fujii, K.; Iida, H.; Ishikii, S.; Noguchi, H.; Kikuchi, T.; Sue, H.; Sakai, K. Hydrogen production from hydrogen

https://doi.org/10.1021/acs.iecr.1c04142
Ind. Eng. Chem. Res. 2022, 61, 2643–2671
sulfide by the iron-chlorine hybrid process. *Ind. Eng. Chem. Res.* 1991, 30 (7), 1601–1608.

(19) Pieplu, A.; Saur, O.; Lavallée, J. C.; Legendre, O.; Nedez, C. Claus catalysis and H₂S selective oxidation. *Catal. Rev. - Sci. Eng.* 1998, 40 (4), 409–450.

(20) Valencia-Marquez, D.; Flores-Tlacuahuac, A.; Ricardez-Sandoval, L. A controllability analysis of a pilot-scale CO₂ capture plant using ionic liquids. *AIChE J.* 2016, 62 (9), 3298–3309.

(21) Wang, Y. L.; Liu, X. B.; Kraslawski, A.; Gao, J. C.; Cui, P. Z. A novel process design for CO₂ capture and H₂S removal from the syngas using ionic liquid. *J. Cleaner Prod.* 2019, 213, 480–490.

(22) Zhang, L. H.; Zhang, Z. J.; Sun, Y. L.; Jiang, B.; Li, X. G.; Ge, X. H.; Wang, J. T. Ether-functionalized ionic liquids with low viscosity for efficient SO₂ capture. *Ind. Eng. Chem. Res.* 2013, 52 (46), 16335–16340.

(23) Jou, F. Y.; Mather, A. E. Solubility of hydrogen sulfide in 1mM HCl. *Int. J. Thermophys.* 2007, 28 (2), 490–495.

(24) Huang, K.; Cai, D. N.; Chen, Y. L.; Wu, Y. T.; Hu, X. B.; Zhang, Z. B. Dual Lewis base functionalization of ionic liquids for highly efficient and selective capture of H₂S. *ChemPlusChem.* 2014, 79 (2), 241–249.

(25) Wang, B.; Zhang, K.; Ren, S. H.; Hou, Y. C.; Wu, W. Z. Efficient capture of low partial pressure H₂S by tetraethyl ammonium amino acid ionic liquids with absorption-promoted solvents. *RSC Adv.* 2016, 6 (103), 101462–101469.

(26) Huang, K.; Zhang, J. Y.; Hu, X. B.; We, Y. T. Absorption of H₂S and CO₂ in aqueous solutions of tertiary-amine functionalized protic ionic liquids. *Energy Fuels* 2017, 31 (12), 14060–14069.

(27) Afsahrour, A.; Haghtalab, A. Simultaneous measurement absorption of CO₂ and H₂S mixture into aqueous solutions containing Diisopropanolamine blended with 1-butyl-3-methylimidazolium acetate ionic liquid. *Int. J. Greenh. Gas Control.* 2017, 58, 71–80.

(28) Li, Z. J.; Xiao, Y. L.; Xue, W. J.; Yang, Q. Y.; Zhong, C. L. Ionic liquid/metal-organic framework composite for H₂S removal from natural gas: A computational exploration. *J. Phys. Chem. C* 2015, 119 (7), 3674–3683.

(29) Zhang, X. M.; Tu, Z. H.; Li, H.; Huang, K.; Hu, X. B.; Wu, Y. T.; MacFarlane, D. R. Selective separation of H₂S and CO₂ from CH₄ by supported ionic liquid membranes. *J. Membr. Sci.* 2017, 543, 282–287.

(30) Wazeer, I.; Hadj-Kali, M. K.; Al-Nashef, I. M. Utilization of deep eutectic solvents to reduce the release of hazardous gases to the atmosphere: A critical review. *Molecules* 2021, 26 (1), 75–108.

(31) Li, M.; Guan, J.; Han, J.; Li, X.; Wang, K. K.; Duan, E. H.; Gao, B. Absorption and oxidation of H₂S in triethylamine hydrochloride center dot ferric chloride ionic liquids. *J. Mol. Liq.* 2015, 209, 58–61.

(32) Wang, J. H.; Zhang, W. D. Oxidative absorption of hydrogen sulfide by iron-containing ionic liquids. *Energy Fuels* 2014, 28 (9), 5930–5935.

(33) Shah, M. S.; Tsapatsis, M.; Siepmann, J. I. Hydrogen sulfide capture: From absorption in polar liquids to oxide, zeolite, and metal-organic framework adsorbents and membranes. *Chem. Rev.* 2017, 117 (14), 9755–9803.

(34) Chiappe, C.; Pomelli, C. S. Hydrogen sulfide and ionic liquids: Absorption, separation, and oxidation. *Top. Curr. Chem.* 2017, 375 (3), 52–76.

(35) Wang, L. Y.; Xu, Y. L.; Li, Z. D.; Wei, Y. N.; Wei, J. P. CO₂/CH₄ and H₂/S/CO₂ selectivity by ionic liquids in natural gas sweetening. *Energy Fuels* 2018, 32 (1), 10–23.

(36) Haider, J.; Saeed, S.; Qayyum, M. A.; Kazmi, B.; Ahmad, R.; Muhammad, A.; Lee, M. Simultaneous capture of acid gases from natural gas adopting ionic liquids: Challenges, recent developments, and prospects. *Renew. Sust. Energy Rev.* 2020, 123, 109771–109791.

(37) Kumar, S.; Cho, J. H.; Moon, I. Ionic liquid-amine blends and CO₂/BOCs: Prospective solvents for natural gas sweetening and CO₂ capture technology—A review. *Int. J. Greenh. Gas Control.* 2014, 20, 87–116.
(57) Mohammadi, A.; Saadati, Z.; Joohari, S. Comparison of the adsorption of H2S by ZnO-TiO2 and Ni-ZnO-TiO2 nanoparticles: An adsorption isotherm and thermodynamic study. *Environ. Prog. Sustain. Energy* 2019, 38 (6), 13258–13266.

(58) Yang, C.; Yang, S.; Fan, H.-L.; Wang, J.; Wang, H.; Shangguan, J.; Hau, C. A sustainable design of ZnO-based adsorbent for robust H2S uptake and secondary utilization as hydrogenation catalyst. *Chem. Eng. J.* 2020, 382, 122892–122902.

(59) Yang, C.; Wang, J.; Fan, H.-L.; Shangguan, J.; Mi, J.; Hau, C. Contributions of tailored oxygen vacancies in ZnO/Al2O3 composites to the enhanced ability for H2S removal at room temperature. *Fuel* 2018, 215, 695–703.

(60) Bajji, B.; Joh, H. L.; Jo, S. M.; Park, J. H.; Yi, K. B.; Lee, S. Enhanced reactive H2S adsorption using carbon nanofibers supported with Cu/Cu2O nanoparticles. *Appl. Surf. Sci.* 2018, 429, 253–257.

(61) Basina, G.; Guber, D. A.; Al Yafei, S.; Tzitzios, V.; Guber, S. A.; Ismail, I.; Vathiilangim, B. V.; Polychronopoulou, K.; Al Hashimi, S.; Al Abdurrahman, M.; Jumbri, K. Choline-based ionic liquids-incorporated porphyrin mesoporous layered double hydroxide for hot coal gas desulfurization. *Ind. Eng. Chem. Res.* pubs.acs.org/IECR 2019, 58 (9), 391–401.

(57) Mohammadi, A.; Saadati, Z.; Joohari, S. Comparison of the adsorption of H2S by ZnO-TiO2 and Ni-ZnO-TiO2 nanoparticles: An adsorption isotherm and thermodynamic study. *Environ. Prog. Sustain. Energy* 2019, 38 (6), 13258–13266.

(58) Yang, C.; Yang, S.; Fan, H.-L.; Wang, J.; Wang, H.; Shangguan, J.; Hau, C. A sustainable design of ZnO-based adsorbent for robust H2S uptake and secondary utilization as hydrogenation catalyst. *Chem. Eng. J.* 2020, 382, 122892–122902.

(59) Yang, C.; Wang, J.; Fan, H.-L.; Shangguan, J.; Mi, J.; Hau, C. Contributions of tailored oxygen vacancies in ZnO/Al2O3 composites to the enhanced ability for H2S removal at room temperature. *Fuel* 2018, 215, 695–703.

(60) Bajji, B.; Joh, H. L.; Jo, S. M.; Park, J. H.; Yi, K. B.; Lee, S. Enhanced reactive H2S adsorption using carbon nanofibers supported with Cu/Cu2O nanoparticles. *Appl. Surf. Sci.* 2018, 429, 253–257.

(61) Basina, G.; Guber, D. A.; Al Yafei, S.; Tzitzios, V.; Guber, S. A.; Ismail, I.; Vathiilangim, B. V.; Polychronopoulou, K.; Al Hashimi, S.; Al Abdurrahman, M.; Jumbri, K. Choline-based ionic liquids-incorporated porphyrin mesoporous layered double hydroxide for hot coal gas desulfurization. *Ind. Eng. Chem. Res.* pubs.acs.org/IECR 2019, 58 (9), 391–401.

(57) Mohammadi, A.; Saadati, Z.; Joohari, S. Comparison of the adsorption of H2S by ZnO-TiO2 and Ni-ZnO-TiO2 nanoparticles: An adsorption isotherm and thermodynamic study. *Environ. Prog. Sustain. Energy* 2019, 38 (6), 13258–13266.

(58) Yang, C.; Yang, S.; Fan, H.-L.; Wang, J.; Wang, H.; Shangguan, J.; Hau, C. A sustainable design of ZnO-based adsorbent for robust H2S uptake and secondary utilization as hydrogenation catalyst. *Chem. Eng. J.* 2020, 382, 122892–122902.

(59) Yang, C.; Wang, J.; Fan, H.-L.; Shangguan, J.; Mi, J.; Hau, C. Contributions of tailored oxygen vacancies in ZnO/Al2O3 composites to the enhanced ability for H2S removal at room temperature. *Fuel* 2018, 215, 695–703.

(60) Bajji, B.; Joh, H. L.; Jo, S. M.; Park, J. H.; Yi, K. B.; Lee, S. Enhanced reactive H2S adsorption using carbon nanofibers supported with Cu/Cu2O nanoparticles. *Appl. Surf. Sci.* 2018, 429, 253–257.
liquids with the Peng-Robinson and the PC-SAFT models. *Pet. Sci. Technol.* 2019, 37 (1), 110–117.

(131) Ji, X. Y.; Held, C.; Sadowski, G. Modeling imidazolium-based ionic liquids with ePC-SAFT. Part II. Application to H₂S and synthesis-gas components. *Fluid Phase Equilib.* 2014, 363, 59–65.

(132) Al-Fnaish, H.; Lue, L. Modelling the solubility of H₂S and CO₂ in ionic liquids using PC-SAFT equation of state. *Fluid Phase Equilib.* 2017, 450, 30–41.

(133) Llovel, F.; Marcos, R. M.; MacDowell, N.; Vega, L. F. Modeling the absorption of weak electrolytes and acid gases with ionic liquids using the Soft-SAFT approach. *J. Phys. Chem. B* 2012, 116 (26), 7709–7718.

(134) Llovel, F.; Oliveira, M. B.; Coutinho, J. A. P.; Vega, L. F. Solubility of greenhouse and acid gases on the [C₅ mim][MeSO₃] ionic liquid for gas separation and CO₂ conversion. *Catal. Today* 2015, 255, 87–96.

(135) Ji, X. Y.; Held, C.; Sadowski, G. Modeling imidazolium-based ionic liquids with ePC-SAFT. *Fluid Phase Equilib.* 2012, 335, 64–73.

(136) Ji, X. Y.; Held, C. Modeling the density of ionic liquids with ePC-SAFT. *Fluid Phase Equilib.* 2016, 410, 9–22.

(137) Sun, Y. H.; Zuo, Z. D.; Laaksonen, A.; Lu, X. H.; Ji, X. Y. How to detect possible pitfalls in ePC-SAFT modelling: Extension to ionic liquids. *Fluid Phase Equilib.* 2020, 519, 112641–112651.

(138) Sun, Y. H.; Schemann, A.; Held, C.; Lu, X. H.; Shen, G. L.; Ji, X. Y. Modeling thermodynamic derivative properties and gas solubility of ionic liquids with ePC-SAFT. *Ind. Eng. Chem. Res.* 2019, 58 (19), 8401–8417.

(139) Sun, Y. H.; Laaksonen, A.; Lu, X. H.; Ji, X. Y. How to detect possible Pitfalls in ePC-SAFT modeling 2. Extension to binary mixtures of 96 ionic liquids with CO₂, H₂S, CO, O₂, CH₄, N₂, and H₂. *Ind. Eng. Chem. Res.* 2020, 59 (49), 21579–21591.

(140) Andreu, J. S.; Vega, L. F. Capturing the solubility Behavior of CO₂ in ionic liquids by a simple model, *J. Phys. Chem. C* 2007, 111 (43), 16028–16034.

(141) Baramaki, Z.; Arab Aboosadi, Z.; Esfandiar, N. Thermodynamic modeling of ternary systems containing imidazolium-based ionic liquids and acid gases using SRK, Peng-Robinson, CPA and PC-SAFT equations of state. *Pet. Sci. Technol.* 2019, 37 (24), 2420–2428.

(142) Kamgar, A; Esmaeilzadeh, F. Prediction of H₂S solubility in [hmim][PF₆] and [hmim][BF₄] using UNIQUAC, NRTL and COSMO-RS. *J. Mol. Liq.* 2016, 220, 631–634.

(143) Taheri, M.; Zhu, R. S.; Yu, G. Q.; Lei, Z. G. Ionic liquid screening for CO₂ capture and H₂S removal from gases: The syngas purification case. *Chem. Eng. Sci.* 2021, 230, 230.

(144) Mechergui, A.; Akhmetschina, A. I.; Kazarnia, O. V.; Atlaskina, M. E.; Petukhov, A. N.; Vorotyntsev, I. V. Acidic gases solubility in bis(2-Ethylhexyl) sulfosuccinate based ionic liquids using the predictive thermodynamic model. *Membranes* 2020, 10 (12), 429–439.

(145) Mortazavi-Manesh, S.; Satyro, M. A.; Marriott, R. A. Screening for CO₂ capture and H₂S removal from gases using artificial neural networks. *Journal of Environmental Chemical Engineering* 2016, 4 (1), 211–218.

(146) Hosseini, M.; Rahimi, R.; Ghaedi, M. Hydrogen sulfide solubility in different ionic liquids: an updated database and intelligent modeling. *J. Mol. Liq.* 2020, 317, 113984–113991.

(147) Ahmadi, M. A.; Haghbaksh, R.; Soleimani, R.; Hajighazvini, M. B. Estimation of H2S solubility in ionic liquids using a rigorous method. *J. Supercrit. Fluids* 2014, 92, 60–69.

(148) Ahmadi, M. A.; Pourali, B.; Javvi, Y.; Alkhani, S.; Soleimani, R. Connectionist technique estimates H2S solubility in ionic liquids through a low parameter approach. *J. Supercrit. Fluids* 2015, 97, 81–87.

(149) Baghban, A.; Sasanipour, J.; Habibzadeh, S.; Zhang, Z. E. Estimating solubility of supercritical H₂S in ionic liquids through a hybrid LSSVM chemical structure model. *Chinese Journal of Chemical Engineering* 2019, 27 (3), 620–627.

(150) Soleimani, R.; Saeedi Dehaghi, A. H.; Bahadori, A. A new decision tree based algorithm for prediction of hydrogen sulfide solubility in various ionic liquids. *J. Mol. Liq.* 2017, 242, 701–713.

(151) Zhao, Y. S.; Gao, H. S.; Zhang, X. P.; Huang, Y.; Bao, D.; Zhang, J. S. Hydrogen Sulphide Solubility in Ionic Liquids (ILs): An Extensive Database and a New ELM Model Mainly Established by Imidazolium-Based ILs. *J. Chem. Eng. Data* 2016, 61 (12), 3970–3978.

(152) Zhao, Y. S.; Gao, J. B.; Huang, Y.; Aftai, R. M.; Zhang, X. P.; Zhang, S. J. Predicting H2S solubility in ionic liquids by the quantitative structure-property relationship method using a sigma-profile molecular descriptors. *RSC Adv.* 2016, 6 (74), 70405–70413.

(153) Kang, X. J.; Qian, J. G.; Deng, J.; Lutfi, U.; Zhao, Y. S. Novel molecular descriptors for prediction of H2S solubility in ionic liquids. *J. Mol. Liq.* 2018, 265, 756–764.

(154) Lashkarbolooki, M.; Shafipour, Z. S.; Hezave, A. Z.; Farmani, H. Use of artificial neural networks for prediction of phase equilibria in the binary system containing carbon dioxide. *J. Supercrit. Fluids* 2013, 75, 144–151.

(155) Ferreira, C. J. A. Gene expression programming: A new adaptive algorithm for solving problems. 2001 csAI/0102027.
(208) Adesina, A. A.; Meeyoo, V.; Foulds, G. Thermolysis of hydrogen sulphide in an open tubular reactor. *Int. J. Hydrogen Energy* 1995, 20 (10), 777−783.

(209) Zaman, J.; Chakma, A. Production of hydrogen and sulfur from hydrogen sulfide. *Fuel Process. Technol.* 1995, 41 (2), 159−198.

(210) Guo, Z. H.; Zhang, T. T.; Liu, T. T.; Du, J.; Jia, B.; Gao, S. J.; Yu, J. Nonaqueous system of iron-based ionic liquid and DMF for the oxidation of hydrogen sulfide and regeneration by electrolysis. *Environ. Sci. Technol.* 2015, 49 (9), 5697−5703.

(211) Ma, Y. J.; Jin, X. B.; Hu, Y.; Huang, Q.; Wang, Z. Y. Recovery of hydrogen and sulfur by electrolysis of ionized H₂S in an amine-containing organic electrolyte with highly temperature-dependent sulfur solubility. *Energy Fuels* 2020, 34 (6), 7756−7762.

(212) Zhang, X. M.; Xiong, W. J.; Shi, M. Z.; Wu, Y. T.; Hu, X. B. Task-specific ionic liquids as absorbents and catalysts for efficient capture and conversion of H₂S into value-added mercaptan acids. *Chem. Eng. J.* 2021, 408, 127866−127872.

(213) Xiong, W. J.; Shi, M. Z.; Zhang, X. M.; Tu, Z. H.; Hu, X. B.; Wu, Y. T. The efficient conversion of H₂S into mercaptan alcohols mediated in protic ionic liquids under mild conditions. *Green Chem.* 2021, 23 (20), 7969−7975.