Protic Ionic Liquids for the Selective Absorption of H_2S from CO_2: Thermodynamic Analysis

Kuan Huang, Xiao-Min Zhang, Yun Xu, You-Ting Wu, and Xing-Bang Hu
Separation Engineering Research Center, Key Laboratory of Mesoscopic Chemistry of MOE, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, P.R. China

Yun Xu
School of Pharmacy, China Pharmaceutical University, Nanjing 211198, P.R. China

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The solubilities of H_2S and CO_2 in four protic ionic liquids (PILs)—methyldiethanolammonium acetate, methyldiethanolammonium formate, dimethylethanolammonium acetate, and dimethylethanolammonium formate were determined at 303.2–333.2 K and 0–1.2 bar. It is shown PILs have higher absorption capacity for H_2S than normal ionic liquids (ILs) and the Henry's law constants of H_2S in PILs (3.5–11.5 bar at 303.2 K) are much lower than those in normal ILs. In contrast, the solubility of CO_2 in PILs is found to be a magnitude lower than that of H_2S, implying these PILs have both higher absorption capacity for H_2S and higher ideal selectivity of H_2S/CO_2 (8.9–19.5 at 303.2 K) in comparison with normal ILs. The behavior of H_2S and CO_2 absorption in PILs is further demonstrated based on thermodynamic analysis. The results illustrate that PILs are a kind of promising absorbents for the selective separation of H_2S/CO_2 and believed to have potential use in gas sweetening. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 4232–4240, 2014

Keywords: protic ionic liquids, absorption, ideal selectivity, thermodynamics, quantum chemical calculation, H_2S, CO_2

Introduction

Acid gases (e.g., H_2S and CO_2) exist in natural gas should be eliminated to ensure the safety and efficiency of fuel utilization.[1] H_2S is very toxic and corrosive, meanwhile, the presence of CO_2 leads to the decrease of caloric value of natural gas or syngas. One common method adopted in the industry is selective absorption in liquids to capture H_2S and CO_2 from gas streams.[1] There are two types of liquid solvents: physical solvents (e.g., 1-methyl-2-pyrrolidine, sulfolane, propylene carbonate, dimethylsulfoxide, polyethylene glycol dimethyl ethers, etc.), and chemical solvents (e.g., ethanolamine, *N*-methyldiethanolamine, tert-butylaminoethoxyethanol, etc.).[2] Physical solvents can be easily regenerated through pressure or temperature swing, but the absorption capacity is relatively low. In contrast, chemical solvents exhibit high load for sour gases, especially in the low-pressure range. However, the desorption process (regeneration of chemical solvents) is highly energy intensive and the volatilization of organic amines is a significant threat to environment.

As a class of state-of-the-art materials, ionic liquids (ILs) display many fascinating properties including extremely low volatility, high thermal stability, wide liquid range, and good affinity with acid gases.[3–5] Theoretically, there are limitless combinations of cations and anions to construct ILs, which enables researchers to design ILs with specific tasks.[5] Therefore, ILs are promising candidates to replace traditional organic solvents in the purification of natural gas or syngas. Numerous studies have investigated the possibility of using ILs as physical or chemical solvents for the absorption of H_2S and CO_2.[6–52] Although the solubility of CO_2 in ILs has been investigated widely,[13–29] the solubility of H_2S is available in only a few imidazolium-based ILs, such as 1-alkyl-3-methylimidazolium hexafluorophosphate ([Rmim][PF_6]),[31,33,34,39,40,42,50] 1-alkyl-3-methylimidazolium tetrafluoroborate ([Rmim][BF_4]),[33,34,37] 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Rmim]-[Tf_2N]),[33,34,39,40,45] 1-ethyl-3-methylimidazolium ethylsulfate ([emim][$EtSO_4$]),[41] 1-butyl-3-methylimidazolium methylsulfate ([bmim][$MeSO_4$]),[38] and 1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([emim][eFAP])[49].

Although in many cases the simultaneous capture of H_2S and CO_2 is preferred, the selective separation of H_2S from CO_2 is also very important to improve the efficiency of sulfur recovery units in the process of nature gas purification.[51] Aqueous methyldiethanolamine (MDEA) is a commonly used solvent for the selective separation of H_2S from CO_2 while some other physical and chemical solvents are usually used for the simultaneous capture of H_2S and CO_2. It is shown from currently available data in literature that the

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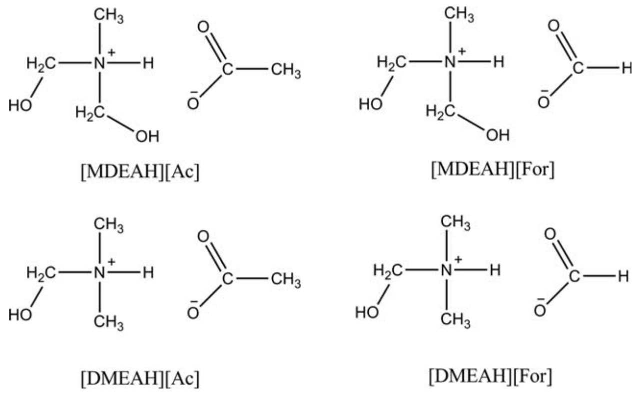
Additional Supporting Information may be found in the online version of this article.

Correspondence concerning this article should be addressed to Y.-T. Wu at ytwu@nju.edu.cn or X.-B. Hu at huxb@nju.edu.cn.



Scheme 1. Chemical structures of the four protic ionic liquids investigated in this work.

absorption selectivities of H_2S/CO_2 in most ILs are poor (with the values ranging from 2 to 4),[1] although some researchers tried to predict the best solvents for the selective separation of H_2S/CO_2 using theoretical tools.[46] Most ILs are even inferior to normal organic solvents in the selective absorption of H_2S from CO_2. Although the incorporation of functional groups (e.g., tertiary amine group) to the framework of ILs can improve the solubility of H_2S and selectivity of H_2S/CO_2,[51] the high cost and viscosity of functionalized ILs disfavor their applications in industry. The major purpose of our work is to find potential ILs with both high absorption capacity of H_2S and high selectivity of H_2S/CO_2 as physical solvents for gas sweetening.

Protic ionic liquid (PILs)[53] are a class of ILs with low cost. They can be easily prepared from simple materials through the direct neutralization between corresponding acid and base. As far as we know, the ability of PILs for the selective absorption of H_2S still remains unknown. To evaluate the potential application of PILs in the selective separation of H_2S/CO_2, the solubilities of individual H_2S and CO_2 in four hydroxylammonium carboxylates-based PILs, methyldiethanolammonium acetate ([MDEAH][Ac]), methyldiethanolammonium formate ([MDEAH][For]), dimethylethanolammonium acetate ([DMEAH][Ac]), and dimethylethanolammonium formate ([DMEAH][For]), were determined systematically in this work. Their chemical structures are graphically shown in Scheme 1. The Henry's law constants of H_2S and CO_2 as well as the ideal selectivities of H_2S/CO_2 in these PILs were calculated from the solubility data. Comparison of PILs with other normal ILs and organic solvents were also done to demonstrate the advantages of PILs. The interaction between PILs and H_2S or CO_2 was illustrated on the basis of thermodynamic analysis.

Experimental Section

Materials

H_2S (99.99 mol %) and CO_2 (99.99 mol %) were supplied from Nanjing Messer Gas Co. (Nanjing, China). MDEA (99 wt %), dimethylethanolamine (99 wt %), acetic acid (AR grade, 99.5 wt %), and formic acid (99 wt %) were purchased from Aladdin Chemical Reagent Co., and used without further purification.

Preparation of PILs

The four PILs investigated in this work ([MDEAH][Ac], [MDEAH][For], [DMEAH][Ac], and [DMEAH][For]) were all prepared in our laboratory according to the literature.[54] In brief, the ethanol solution of equimolar acid was added dropwisely to the ethanol solution of base. The reaction was stirred for 24 h in ice bath. Ethanol was then removed by evaporation under reduced pressure. The resulting crude product was washed for several times with dimethyl ether to remove unreacted reactants. The obtained liquid was dried under vacuum at 333.2 K for 48 h to remove trace of solvent to offer yellow or pale yellow liquid. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX 300 MHz spectrometer using $CDCl_3$ as the solvent with TMS as the internal standard to confirm the structures of the PILs. No impurities were observed in the NMR spectra. Karl Fisher titration revealed that water contents in the four PILs were all below 1000 $\mu g\ g^{-1}$. TG traces were recorded on a PerkinElmer Pyris 1 TGA from room temperature to 400°C at a scanning rate of 10°C/min under N_2 atmosphere to determine the decomposition temperatures of PILs. The spectra data of the four PILs are given as follows:

- **[MDEAH][Ac]:** ^1H NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 1.81 ppm(3H, s), 2.53 ppm(3H, s), 2.87 ppm(4H, t), 3.67 ppm(4H, t); ^{13}C NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 23.45, 41.47, 57.08, 58.96, 178.54 ppm;
- **[MDEAH][For]:** ^1H NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 2.60 ppm(3H, s), 2.90 ppm(4H, t), 3.81 ppm(4H, t), 8.53 ppm(1H, s); ^{13}C NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 41.97, 57.87, 59.87, 169.95 ppm;
- **[DMEAH][Ac]:** ^1H NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 1.90 ppm(3H, s), 2.69 ppm(6H, s), 2.99 ppm(2H, t), 3.80 ppm(2H, t); ^{13}C NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 22.34, 43.28, 56.33, 60.14, 176.96 ppm;
- **[DMEAH][For]:** ^1H NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 2.75 ppm(6H, s), 3.06 ppm(2H, t), 3.80 ppm(2H, t), 8.32 ppm(1H, s); ^{13}C NMR(300 MHz, $CDCl_3$, 25°C, TMS), δ: 43.23, 56.03, 59.83, 167.79 ppm;

Determination of physical properties

The densities were determined using an Anton Paar DMA 5000 type automatic densiometer with a precision of 0.00001 g/cm^3. The apparatus was calibrated using distilled water. The viscosities were measured on a Brookfield LVDV-II+Pro viscometer with an uncertainty of ±1% in relation to the full scale.

Determination of gas absorption

The apparatus for the determination of gas absorption in PILs is the same as that in our previous work.[48] The whole device consists of two 316L stainless steel chambers whose volumes are 120.802 cm^3 (V_1) and 47.368 cm^3 (V_2), respectively. The bigger chamber, used as gas reservior, isolates the gas before it contacts with the PIL in the smaller chamber. The smaller chamber named as the equilibrium cell is equipped with a magnetic stirrer. The temperatures (T) of both chambers are controlled using a water bath with an uncertainty of ±0.1 K. The pressures in the two chambers are monitored using two pressure transducers (Wideplus Precision Instruments Co.) of ±0.2% uncertainty (in relation to the full scale). The pressure transducers are connected to a numeric instrument (WP-D821-200-1212-N-2P) to record the

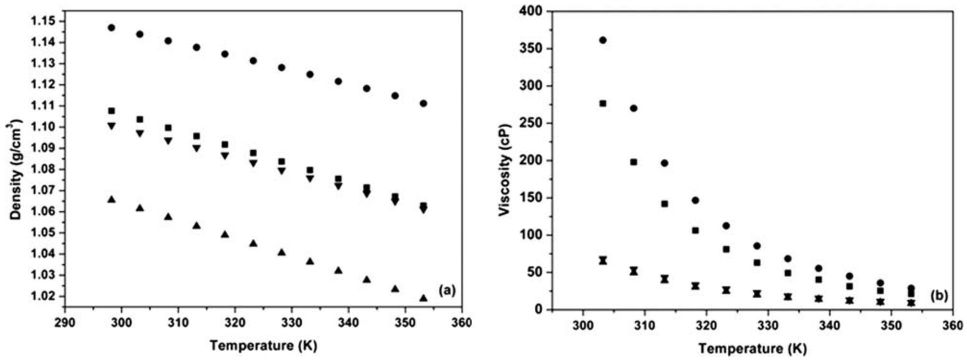


Figure 1. Density (a) and viscosity (b) of [MDEAH][Ac] (■), [MDEAH][For] (•), [DMEAH][Ac] (▲), and [DMEAH][For] (▼) at different temperatures.

pressure changes online. In a typical run, a known mass (w) of a PIL was placed into the equilibrium cell, and the air in the two chambers was evacuated. The remaining pressure in the equilibrium cell was recorded to be P_0 (<10 Pa). Gas from cylinder was then fed into the gas reservior to a pressure of P_1. The needle valve between the two chambers was turned on to let the gas be introduced to the equilibrium cell. Absorption equilibrium was thought to be reached when the pressures of the two chambers remained constant for at least 2 h. The equilibrium pressures were denoted as P_2 for the equilibrium cell and P_1' for the gas reservior. The gas partial pressure in the equilibrium cell was $P_g = P_2 - P_0$. The gas uptake, $n(P_g)$, can thus be calculated using the following equation

$$n\left(P_g\right)=\rho_g(P_1,T)V_1-\rho_g\left(P_1',T\right)V_1-\rho_g\left(P_g,T\right)(V_2-w/\rho_{IL}) \quad (1)$$

where ρ_g (P_i,T) represents the density of gas in mol/cm^3 at P_i ($i = 1$,g) and T. ρ_{IL} is the density of PIL in g/cm^3 at T. V_1 and V_2 represent the volumes in cm^3 of the two chambers, respectively. Continual determinations of solubility data at elevated pressures were performed by introducing more gas into the equilibrium cell to reach new equilibrium. The solubility of gases was defined in terms of molar fraction in this work. After determinations, the gas remaining in the chambers were introduced to an off-gas absorber containing aqueous solution of NaOH to prevent gas leakage into atmosphere. Duplicate experiments were run for each PIL to obtain averaged values of gas solubility. The reproducibility of solubility data in this work was well within ±1%.

Thermodynamic analysis

The thermodynamic equation of temperature-dependent Krichevsky–Kasarnovsky (K–K equation)[55] was used to correlate the solubility data

$$\ln\frac{f_2}{x_2}\approx\ln\frac{P_2}{x_2}=\ln H_{21}(T_1)+\frac{\Delta H_{sol}}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)+\frac{V_2{}^{\infty}P_2}{RT} \quad (2)$$

where f_2 and P_2 are the fugacity and pressure of gas solute (H_2S or CO_2) in the gas phase, respectively. As the solubilities of gases were determined at low pressures (0–1.2 bar), the fugacity f_2 was approximately equal to the pressure P_2. x_2 is the molar fraction of gas solute in the liquid phase, $H_{21}(T_1)$ is the Henry's law constant of gas solute in the liquid solvent at the temperature T_1, ΔH_{sol} is the enthalpy change of H_2S or CO_2 absorption in the PILs, V_2^{∞} is the partial molar volume of gas solute at infinite dilution, R is the universal gas constant, and T is the absolute temperature. The ideal selectivity of H_2S/CO_2 in PILs can thus be defined as the ratio of the Henry's law constant of H_2S to that of CO_2 at the same temperature

$$S=H_{21}(CO_2)/H_{21}(H_2S) \quad (3)$$

Results and Discussions

Physical properties

The density and viscosity of liquid solvents are fundamental data for the process design of gas separation. These physical properties can also influence the absorption of gas in liquid. However, the detailed density and viscosity data of the four PILs are absent in the open resource. Therefore, we measured the density and viscosity in the temperature range of 298.2–353.2 K (Figure 1). It is found that the density of PILs decreases linearly with the increase of temperature, whereas the viscosity of PILs decreases in an exponential manner. If anion is kept the same, the PILs with [MDEAH] cation have larger density than those with [DMEAH] cation. Similarly, the PILs with [For] anion exhibit larger density than those with [Ac] anion if cation is the same. The effect of cation or anion on the viscosity of PILs follows the same sequence as that on the density, that is, [MDEAH] > [DMEAH] and [For] > [Ac]. However, anion is of less influence on the viscosity than on the density, especially in case of PILs with [DMEAH] cation. The PILs with [DMEAH] cation have low viscosity (<75 mPa s at 303.2 K), which is helpful to the mass transfer of H_2S or CO_2.

Absorption of H_2S and CO_2

The solubilities of H_2S and CO_2 in the four PILs, [MDEAH][Ac], [MDEAH][For], [DMEAH][Ac] and, [DMEAH][For], were measured at temperatures from 303.2 to 333.2 K and elevated pressures up to 1.2 bar. The solubility data are graphically shown in Figures 2 and 3 and tabulatedly given in details in the Supporting Information. It can be seen that the absorption behavior of H_2S and CO_2 in these PILs deviate only slightly from the ideality. Therefore, the temperature-dependent K–K equation is believed to be a suitable model for this situation.

The fitting results from the K–K equation are compared with the experiments in Figures 2 and 3 and in the Supporting Information, and the calculated thermodynamic parameters such as H_{21}, V_2^{∞}, and ΔH_{sol} are summarized in Tables 1 and 2. The K–K equation is found to be accurate in

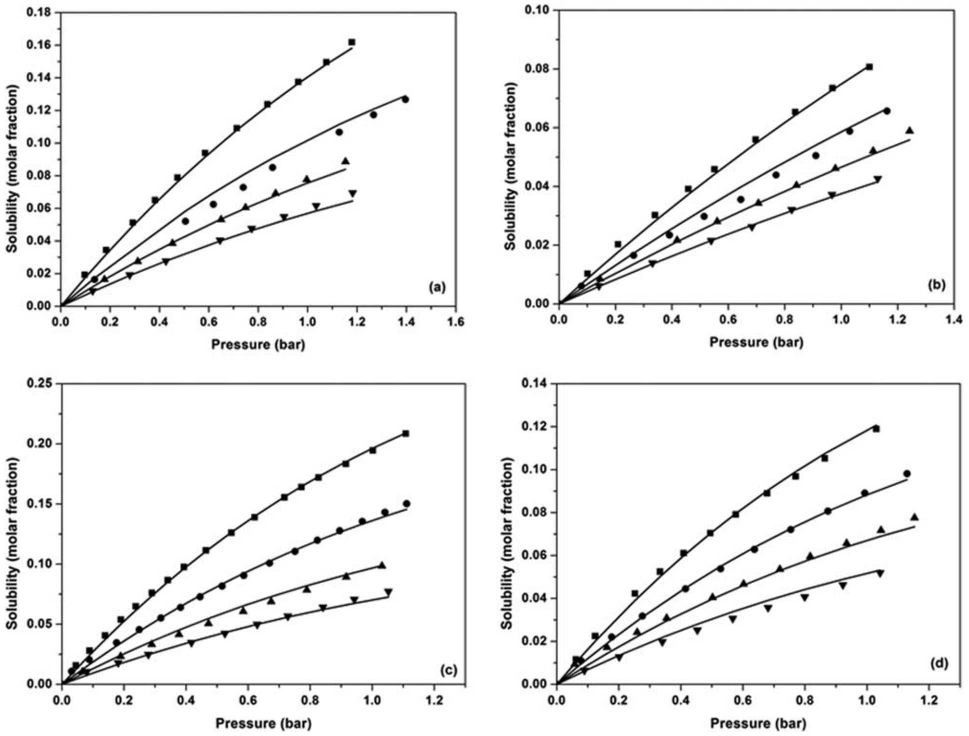


Figure 2. Solubility of H_2S in [MDEAH][Ac] (a), [MDEAH][For] (b), [DMEAH][Ac] (c), and [DMEAH][For] (d) at 303.2 K (■), 313.2 K (•), 323.2 K (▲), and 333.2 K (▼); lines: fitting results from K–K equation.

correlating the solubility data of H_2S and CO_2 in these PILs as the overall average relative deviations are about 5% (see Supporting Information Table S5). The Henry's law constants of H_2S in the four PILs at 303.2 K varies from 3.5 to 11.5 bar, with the lowest for [DMEAH][Ac] and the largest for [MDEAH][For]. However, the Henry's law constants of CO_2 in the four PILs (49–117 bar) are of a magnitude larger than that of H_2S, implying that the PILs exhibit much larger absorption capacity for H_2S than for CO_2. Therefore, these PILs enable selective separation of H_2S from CO_2.

It is noted that the solubility of CO_2 in the two acetate-based protic ILs is much lower than that in aprotic ILs with the same anion. For example, 1-ethyl-3-methylimidazolium acetate ([emim][Ac]) can absorb CO_2 with a solubility of

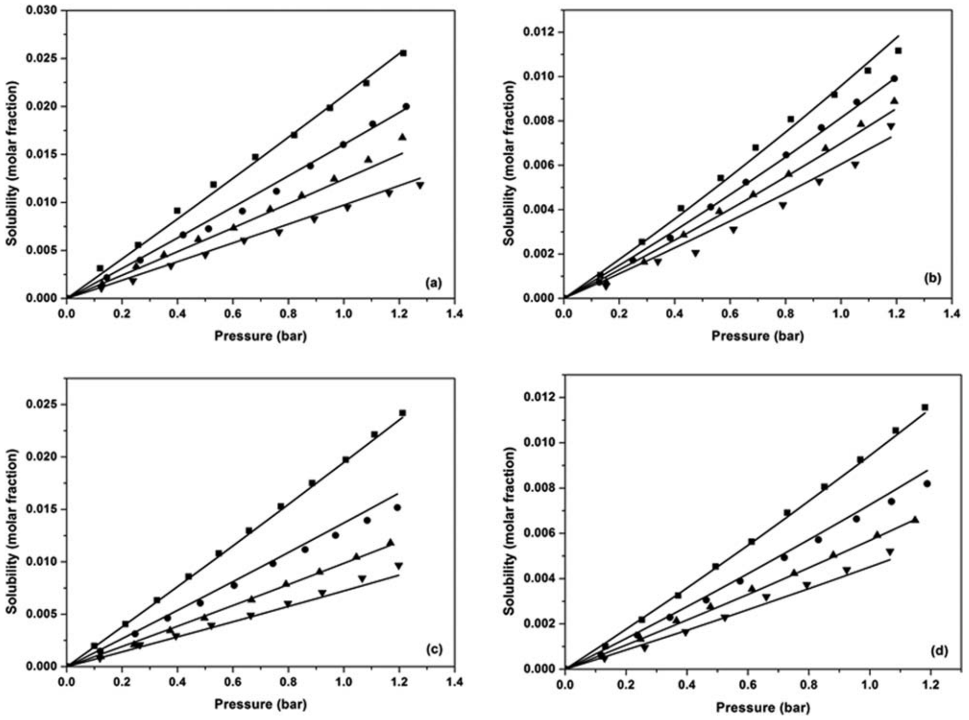


Figure 3. Solubility of CO_2 in [MDEAH][Ac] (a), [MDEAH][For] (b), [DMEAH][Ac] (c), and [DMEAH][For] (d) at 303.2 K (■), 313.2 K (•), 323.2 K (▲), and 333.2 K (▼); lines: fitting results from K–K equation.

Table 1. Thermodynamic Parameters of H_2S Absorption in PILs

T (K)	H_{21} (bar)	V_2^{∞} (cm^3 mol^{-1})	ΔH_{sol} (kJ mol^{-1})	ΔG_{sol} (kJ mol^{-1})	ΔS_{sol} (J mol^{-1} K^{-1})
[MDEAH][Ac]					
303.2	5.5 ± 0.1	654 ± 64	−25.9 ± 0.6	4.3 ± 0.1	−100 ± 2
313.2	7.6 ± 0.2			5.3 ± 0.1	−100 ± 2
323.2	10.4 ± 0.3			6.3 ± 0.1	−100 ± 2
333.2	13.9 ± 0.4			7.3 ± 0.1	−100 ± 2
[MDEAH][For]					
303.2	11.5 ± 0.3	387 ± 77	−19.7 ± 0.6	6.2 ± 0.1	−85 ± 2
313.2	14.7 ± 0.4			7.0 ± 0.1	−85 ± 2
323.2	18.6 ± 0.5			7.9 ± 0.1	−85 ± 2
333.2	23.2 ± 0.7			8.7 ± 0.1	−85 ± 2
[DMEAH][Ac]					
303.2	3.5 ± 0.1	921 ± 38	−29.7 ± 0.4	3.2 ± 0.1	−108 ± 2
313.2	5.2 ± 0.1			4.3 ± 0.1	−109 ± 1
323.2	7.3 ± 0.1			5.3 ± 0.1	−108 ± 1
333.2	10.2 ± 0.2			6.4 ± 0.1	−108 ± 1
[DMEAH][For]					
303.2	5.9 ± 0.1	907 ± 61	−24.1 ± 0.5	4.5 ± 0.1	−94 ± 2
313.2	8.0 ± 0.2			5.4 ± 0.1	−94 ± 2
323.2	10.6 ± 0.2			6.3 ± 0.1	−94 ± 2
333.2	13.9 ± 0.3			7.3 ± 0.1	−94 ± 2

0.267 in molar fraction at 298.1 K and 1 bar.[10] One possible explanation for this result is the different structures of protic ILs and aprotic ILs. In protic ILs, the protonated nitrogen in ammonium cation is weakly acidic. It can form Brønsted acid–base interaction (or hydrogen bond) with the alkaline acetate anion, thus reduces the affinity with CO_2 for acetate anion. However, in aprotic ILs, such interaction does not exist and the acetate anion can attract CO_2 freely through Lewis acid–base interaction.

Similarly, Brønsted acid–base interaction between protonated nitrogen and acetate anion can also reduce the dissolution of H_2S in protic ILs in comparison with aprotic ILs with the same anion. For instance, the solubility of H_2S in [emim][Ac] is 0.334 in molar fraction at 303.15 K and 1 bar.[48] However, unlike CO_2 molecule, there exist active protons in H_2S molecule. As a result, H_2S molecule still has the possibility of interacting with the electron-donating groups in protic ILs (e.g., hydroxyl and carboxylate groups). Therefore, H_2S is more favorable to be absorbed by protic ILs than CO_2. More work should be expanded with the assistance of theoretical calculations or spectrum study to demonstrate the different absorption behavior of H_2S and CO_2 in protic ILs.

The partial molar volume of gas solute at infinite dilution (V_2^{∞}) is a useful parameter to distinguish the absorption behavior of H_2S and CO_2 in PILs. H_2S in PILs has a positive V_2^{∞}, indicating that PILs have more free volume to accommodate H_2S. On the contrary, the negative V_2^{∞} implies that CO_2 in PILs is compressed to exist in a thermodynamically unfavorable state when PILs receive more CO_2 molecules. PILs are thus good solvents for H_2S and poor for CO_2. This is consistent with the finding from experimental solubility. Similar phenomenon was observed for the absorption of H_2S and CO_2 in 1-(2-hydroxylethyl)−3-methylimidazolium tetrafluoroborate ([hemim][BF_4]).[37] It should be noted that as the simplified K–K equation neglects the effect of activity coefficients, the fitted values of V_2^{∞} usually exhibit large errors.

Subsequently, the changes of Gibbs free energy and entropy of H_2S and CO_2 absorption in the PILs at different temperatures can be calculated from the following two equations

Table 2. Thermodynamic Parameters of CO_2 Absorption in PILs

T (K)	H_{21} (bar)	V_2^{∞} (cm^3 mol^{-1})	ΔH_{sol} (kJ mol^{-1})	ΔG_{sol} (kJ mol^{-1})	ΔS_{sol} (J mol^{-1} K^{-1})
[MDEAH][Ac]					
303.2	49 ± 2	−75 ± 78	−21.6 ± 0.6	9.8 ± 0.1	−104 ± 2
313.2	64 ± 2			10.8 ± 0.1	−104 ± 2
323.2	83 ± 3			11.9 ± 0.1	−104 ± 2
333.2	105 ± 3			12.9 ± 0.1	−104 ± 2
[MDEAH][For]					
303.2	117 ± 5	−278 ± 100	−12.6 ± 0.7	12.0 ± 0.1	−81 ± 3
313.2	138 ± 5			12.8 ± 0.1	−81 ± 3
323.2	159 ± 6			13.6 ± 0.1	−81 ± 3
333.2	183 ± 7			14.4 ± 0.1	−81 ± 2
[DMEAH][Ac]					
303.2	53 ± 2	−88 ± 72	−27.7 ± 0.6	10.0 ± 0.1	−124 ± 2
313.2	75 ± 2			11.2 ± 0.1	−124 ± 2
323.2	105 ± 3			12.5 ± 0.1	−124 ± 2
333.2	143 ± 4			13.7 ± 0.1	−124 ± 2
[DMEAH][For]					
303.2	115 ± 3	−209 ± 73	−20.4 ± 0.6	12.0 ± 0.1	−107 ± 2
313.2	149 ± 4			13.0 ± 0.1	−107 ± 2
323.2	190 ± 5			14.1 ± 0.1	−107 ± 2
333.2	239 ± 7			15.2 ± 0.1	−107 ± 2

Table 3. Ideal Selectivities of H_2S/CO_2 in PILs

T (K)	[MDEAH][Ac]	[MDEAH][For]	[DMEAH][Ac]	[DMEAH][For]
303.2	8.9 ± 0.5	10.2 ± 0.7	15.1 ± 1.0	19.5 ± 0.8
313.2	8.4 ± 0.5	9.4 ± 0.6	14.4 ± 0.7	18.6 ± 1.0
323.2	8.0 ± 0.5	8.5 ± 0.6	14.4 ± 0.6	17.9 ± 0.8
333.2	7.6 ± 0.4	7.9 ± 0.5	14.0 ± 0.7	17.2 ± 0.9

$$\Delta G_{\text{sol}} = -RT \ln H_{21} \tag{4}$$

$$\Delta S_{\text{sol}} = (\Delta H_{\text{sol}} - \Delta G_{\text{sol}})/T \tag{5}$$

ΔG_{sol} and ΔS_{sol} are calculated and summarized in Tables 1 and 2.

[MDEAH][Ac]+H_2S and [MDEAH][Ac]+CO_2 systems are found to have very close values of ΔS_{sol} (-100 vs. -104 J mol^{-1} K^{-1}), although the absorption of H_2S differs largely in capacity from that of CO_2 ($H_{21} = 5.5$ vs. 49 bar at 303.2 K). Similar phenomenon is also observed in the absorption of H_2S and CO_2 in [MDEAH][For]. However, the absorption of H_2S in the two [MDEAH]-based PILs has less negative values of ΔH_{sol} than that of CO_2. It is, therefore, concluded that the effect of enthalpy rather than entropy contributes primarily to the different absorption behavior of H_2S and CO_2 in the two [MDEAH]-based PILs. As more negative ΔH_{sol} leads to smaller ΔG_{sol} in the absorption, the dissolution of H_2S in the two [MDEAH]-based PILs is thermodynamically more favorable than that of CO_2. As for the absorption of the two gases in [DMEAH][Ac] and [DMEAH][For], both the enthalpy and entropy effects contribute to the different dissolution behavior of H_2S and CO_2 in these two [DMEAH]-based PILs, because ΔH_{sol} of H_2S systems are more negative than those of CO_2 systems (-29.7 vs. -27.7 kJ/mol and -24.1 vs. -20.4 kJ/mol) while ΔS_{sol} of H_2S systems are less negative than those of CO_2 systems (-108 vs. -124 J mol^{-1} K^{-1} and -94 vs. -107 J mol^{-1} K^{-1}). These two effects are superimposed to result in even low ΔG_{sol}, so that [DMEAH]-based PILs are more preferred for the selective absorption of H_2S from CO_2 than [MDEAH]-based ones.

It is of interest to note that both the cation and anion of PILs have influence on the change of enthalpy during the absorption of H_2S and CO_2. Such phenomenon comes from the fact that both the cation and anion of PILs have electron donors (—OH and —COO$^-$ groups) to attract the acidic H_2S and CO_2. ΔG_{sol} is found to be influenced in a similar way as in the case of ΔH_{sol}. In general, for either H_2S or CO_2, large absorption capacity leads to large negative ΔH_{sol} and small positive ΔG_{sol}.

Ideal selectivity of H_2S/CO_2

The ideal selectivities of H_2S/CO_2 (S_{H_2S/CO_2}) in the four PILs are calculated according to Eq. 3 and shown in Table 3. S_{H_2S/CO_2} in the four PILs ranges from 8.9–19.5 at 303.2 K, almost a magnitude larger than that (2–4) in normal ILs.[1] This implies that these PILs enable the selective absorption of H_2S from CO_2 more efficiently than normal ILs. S_{H_2S/CO_2} is found to vary insensibly with temperature in all four PILs, primarily due to the fact that ΔG_{sol} of H_2S+PIL systems has a nearly constant difference with ΔG_{sol} of CO_2 + PIL systems at different temperatures. For example, the difference of ΔG_{sol} between H_2S + [DMEAH][For] and CO_2 + [DMEAH][For] is around -7.8 kJ/mol at all four temperatures, leading to the narrow variation of S_{H_2S/CO_2} from 19.5 to 17.2. In addition, both the cation and anion of PILs are also found to have apparent influence on S_{H_2S/CO_2}. The order of S_{H_2S/CO_2} follows the sequences of [For] > [Ac] and [DMEAH] > [MDEAH].

Ideal solvents for the selective separation of H_2S from CO_2 should have not only large absorption capacity for H_2S but also high selectivity of H_2S/CO_2. To search ideal solvents for the selective absorption of H_2S, the Henry's law constants of H_2S and the ideal selectivities of H_2S/CO_2 in different ILs[14,15,17,29,33–35,37,39–41,45,49,50,56] as well as in organic solvents[57–60] at ambient temperature are summarized in Table 4 and plotted in Figure 4 for legible comparison. The parameter of $1/H_{21}(H_2S)$ in Figure 4 represents the absorption capacity of H_2S in a liquid. The comparison shows that normal ILs have not only lower absorption capacity but also smaller selectivity of H_2S/CO_2 than most of organic solvents. On the contrary, the four PILs investigated in this work are even superior to most of organic solvents both in the absorption capacity and in the selectivity, especially for the [DMEAH]-based PILs. The points of S_{H_2S/CO_2} vs. $1/H_{21}(H_2S)$ for the two [DMEAH]-based PILs fall far beyond the range of organic solvents while those for the two [MDEAH]-based PILs are located at the vicinity of some organic solvents of high performance. Obviously, the two [DMEAH]-based PILs is justified from the comparison to have the best performance in the selective absorption of H_2S from CO_2 among all the screened solvents.

Aqueous MDEA is a commonly used chemical solvent for the selective absorption of H_2S in industry. Due to the strong alkalinity of organic amine, its absorption capacity for H_2S is much higher than the PILs investigated in this work, especially under low pressure range, and it can achieve almost equimolar absorption for H_2S. However, according to literature,[61] the equilibrium solubility of H_2S in aqueous MDEA is only slightly higher than that of CO_2, with a value of 1–2 times as that of CO_2. Nonetheless, the dissolution of CO_2 in aqueous MDEA is different from that of H_2S. Due to the absence of active protons in CO_2 molecule, CO_2 can not react directly with MDEA. CO_2 should be hydrated to produce carbonic acid and then the active proton of carbonic acid transfers to alkaline MDEA to form bicarbonate. In contrast, there exist active protons in H_2S molecule and it can react directly with MDEA through the transfer of proton. As a result, the absorption rate of CO_2 in aqueous MDEA is much slower than that of H_2S. Therefore, the high selectivity for H_2S/CO_2 in aqueous MDEA is mainly from kinetics while not thermodynamics.

As is well known, the cost and viscosity of ILs are two major disadvantages that influence their practical applications in industry. Normal imidazolium-based ILs are generally prepared from nucleophilic substitution of imidazole and anion exchange, where expensive reactants and tedious reaction/separation steps are usually required. However, the four PILs in this work can be easily produced in one step through the direct neutralization of organic acids with organic bases, not to mention the fact that all the materials used in the

Table 4. A Summary of the Henry's Law Constants of H_2S and Ideal Selectivities of H_2S/CO_2 in Different ILs and Organic Solvents at Ambient Temperature

Solvents	T (K)	$H_{21}(H_2S)$ (bar)	S_{H_2S/CO_2}	Ref.
[MDEAH][Ac]	303.2	5.5	8.9	This work
[MDEAH][For]	303.2	11.5	10.2	This work
[DMEAH][Ac]	303.2	3.5	15.1	This work
[DMEAH][For]	303.2	5.9	19.5	This work
TEGO IL K5	300.0	23.5	1.2	35
[emim][Tf_2N]	303.2	14.8	2.6	15,37
[bmim][Tf_2N]	303.2	13.7	2.0	27,32
[bmim][PF_6]	303.2	18.6	3.2	15,34
[bmim][BF_4]	303.2	15.5	3.8	17,34
[hmim][Tf_2N]	303.2	17.4	2.1	14,33
[emim][$EtSO_4$]	303.2	60.7	1.6	41
[hemim][BF_4]	303.2	31.3	3.5	37
[hemim][PF_6]	303.2	27.7	3.2	40,56
[hemim][Tf_2N]	303.2	18.9	2.3	40,56
[hemim][TfO]	303.2	19.3	3.2	40,56
[omim][Tf_2N]	303.2	9.9	2.6	45
[omim][PF_6]	303.2	64.4	1.5	50
[emim][eFAP]	303.2	15.3	1.9	49
Sulfolane	298.2	17.4	5.0	57
Glycol	298.2	52.9	4.9	58
Proplene carbonate	298.2	23.4	3.7	59
Methyl cyanoacetate	298.2	28.5	3.1	59
Selexol	298.2	4.4	8.1	59
Diglyme	298.2	6.4	5.8	60
Triglyme	298.2	5.1	6.6	60
Tetraglyme	298.2	4.2	7.1	60
Aniline	298.2	15.1	8.4	58
Benzyl alcohol	298.2	24.0	5.3	58
Dimethylsulfoxide	298.2	10.9	9.7	58
Hexadecane	298.2	18.7	3.3	58
1-methyl-2-pyrrolidine	298.2	5.6	10.6	58
Tripropylphosphate	298.2	4.2	6.7	58

preparation are very cheap and easily available in large quantity from industry. As for the consideration of mass transfer in practical applications, the two [DMEAH]-based PILs still have low viscosities (63.9 and 68.4 cP at 303.2 K) and are comparable with most of imidazolium-based ILs. Owing to the low cost and viscosity, and to the excellent performance in the selective absorption, the two [DMEAH]-based PILs are believed to be potential absorbents in the selective sweetening of natural gas, even though more work should be done before practical application. We will focus on this issue in our future work.

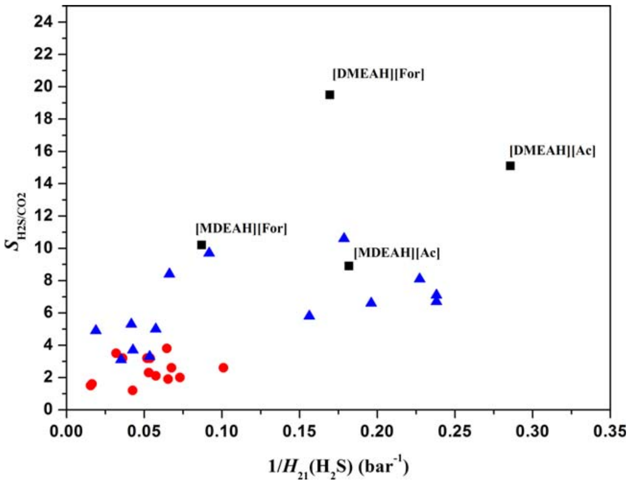


Figure 4. Plot of S_{H_2S/CO_2} vs. $1/H_{21}(H_2S)$ for PILs (■), normal ILs (•), and organic solvents (▲).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Recycling of PILs

To evaluate the recyclability of PILs during H_2S absorption, H_2S-saturated [DMEAH][For] was heated to 353.2 K under a vacuum of 0.1 kPa for 1 h and then reused for the determination of gas solubility. The absorption–desorption experiments were performed for five cycles and Figure 5 shows the solubility of H_2S in [DMEAH][For] at 303.2 K and 1 bar during the five cycles. It is revealed that the absorption of H_2S in [DMEAH][For] is totally reversible and the solubility of H_2S remains almost unchanged after five cycles. Generally speaking, the thermal stability of PILs is relatively lower than that of aprotic ILs. According to the TG traces of the four PILs (see Supporting Information Figure S1), the onset decomposition temperatures of the four PILs are above 393.2 K, which is higher than the desorption temperature. Therefore, the thermal stability of PILs is enough to ensure gas desorption.

Conclusions

In summary, to find highly effective ILs for the selective absorption of H_2S from CO_2, the absorption of H_2S and CO_2 in four PILs: [MDEAH][Ac], [MDEAH][For], [DMEAH][Ac], and [DMEAH][For] were measured. Temperature-dependent Krichevsky–Kasarnovsky (K–K) equation was used to correlate the data, and quantum chemical calculations were performed to analyze the underlying mechanism in the article. It is found that these PILs exhibit not only

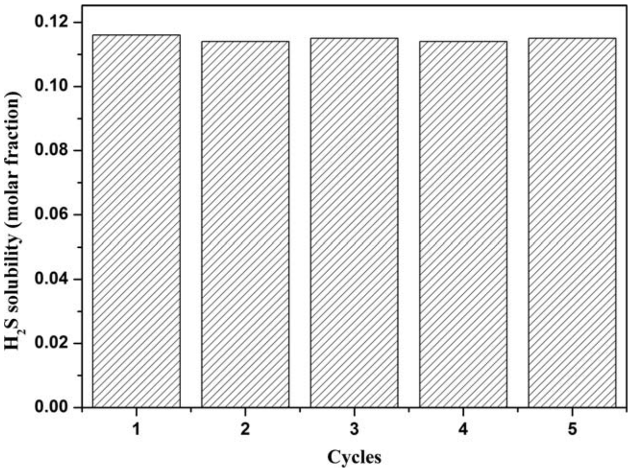


Figure 5. Recycling of [DMEAH][For] for the absorption of H_2S (absorption condition: 303.2 K and 1 bar; desorption condition: 353.2 K and 0.1 kPa).

higher absorption capacity for H_2S but also higher ideal selectivity of H_2S/CO_2 than normal imidazolium-based ILs and organic liquids. It is further illustrated that the dissolution of H_2S in these PILs is thermodynamically more favorable than that of CO_2. This article provides new insights into the exploration of ideal ILs for the selective absorption of H_2S from CO_2, and the PILs investigated in the article is verified to be potential absorbents of large capacity and high selectivity for the separation of H_2S from CO_2.

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