Thermodynamic Validation of 1-Alkyl-3-methylimidazolium Carboxylates as Task-Specific Ionic Liquids for H_2S Absorption

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Solubilities of H_2S in five 1-alkyl-3-methylimidazolium carboxylates ionic liquids (ILs) have been measured at temperatures from 293.15 to 333.15 K and pressures up to 350 kPa. It is shown that these ILs have significantly larger absorption capacities for H_2S than those common ILs reported in the literature. The solubility is found to increase dramatically with the increasing alkalinity of the anions and slightly with the increasing length of the alkyl chains on the cations. It is further demonstrated that the absorption isotherms are typically nonideal. With the assumption of complex formation between H_2S and ILs, a reaction equilibrium thermodynamic model is developed to correlate the experimental solubilities. The model favors a reaction mechanism of AB_2 type that two IL molecules interact with one H_2S molecule. Thermodynamic parameters such as Henry's law constants, reaction equilibrium constants, and heat of complex formation are also calculated to evaluate the absorption process of H_2S in these ILs. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 2227–2235, 2013

Keywords: ionic liquids, H_2S absorption, thermodynamic model, reaction equilibrium, 1-alkyl-3-methylimidazolium carboxylates

Introduction

H_2S, existing usually along with methane in natural gas and other syngas streams, is highly toxic and corrosive. H_2S can also be produced from hydrodesulfurization of crude oils containing sulfur compounds.[1] The aqueous solutions of alkanolamines, for example, monoethanolamine, diethanolamine, and methyldiethanolamine, are widely used in industry as solvents for the removal of H_2S from natural gas (natural gas sweetening), refinery, and syngas steams. However, there exist many disadvantages in these processes including the volatile loss of alkanolamine, transfer of water into the gas steams, intensive energy input to regenerate the absorbents, and degradation of the alkanolamine to form corrosive byproducts, which unfavor the general requirements for the processes to be environmentally benign, energy saving, and highly efficient.

Ionic liquids (ILs) have been paid widespread attention in recent years due to their unique properties, such as extremely low vapor pressure, high thermal stability, designable structure, wide liquid temperature range, and strong solubilization for many compounds.[2–4] Most importantly, ILs can be functionalized to be task-specific ILs (TSILs),[5] which enables highly efficient and selective separation or reaction process according to our requirements. As a consequence, ILs have been regarded as a new type of "green solvents" that exhibit extensive potential of application in many fields such as catalysis,[3,6,7] electrolysis,[8] extraction,[9] membrane separation,[10,11] and gas absorption[5,12–28].

A growing number of articles have been published on CO_2 and SO_2 absorption in various ILs, and a reasonable progress has been achieved in both absorption capacity[14–16,21,29–31] and transfer performance.[16,21,32,33] However, there are only fair efforts focusing on the absorption of H_2S in some common ILs.[28,34–47] Jou and Mather[28] first determined the H_2S solubilities in [bmim][PF_6] at temperatures from 298.15 to 403.15 K and pressures up to 9.6 MPa. Pomelli et al.[34] reported the solubilities of H_2S in $[bmim]^+$-based ILs with different anions and in $[Tf_2N]^-$-based ILs with different cations at 298.15 K and 1.4 MPa. Jalili et al.[36,37,39–41,47] measured and provided a plenty of solubility data of H_2S in a variety of imidazolium-based ILs in a wide temperature and pressure range. Morsi and coworkers[35] published the solubilities and transfer coefficients of H_2S in an ammonium-based IL at temperatures from 300 to 500 K and pressures up to 0.23 MPa. Carvalho and Coutinho[38,44] modeled H_2S solubilities in ILs using Flory–Huggins model and designed ILs for H_2S/CH_4 selective absorption based on the polarity effects. Shiflett et al.[42,43] studied the vapor–liquid–liquid equilibrium phase behavior of H_2S/IL binary mixtures, and a generic Redlich–Kwong equation of state (EoS) was proposed to calculate the obtained experimental data. Instead, Ghotbi et al.[46] performed the calculation of H_2S solubilities in ILs using the modified SAFT-VR and PC-SAFT equations of state.

However, the solubilities of H_2S in the normal ILs remain still at low levels, especially under the condition of low H_2S partial pressures, because they enable only the physical interactions

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

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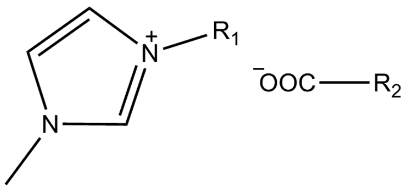

Figure 1. Chemical structures of the ILs prepared in this work.

with H_2S. Therefore, normal ILs are not good candidating solvents for the removal of H_2S. Carboxylate-based ILs are a class of CO_2-philic ILs due to their Lewis base properties.[48–52] It is expected that this class of ILs may also have good affinity with H_2S. In this work, to validate the assumption earlier, the thermodynamic solubilities of H_2S in 1-alkyl-3-methylimdazolium carboxylates ILs were investigated at temperatures from 293.15 to 333.15 K and pressures up to 350 kPa. To examine the effect of cations and anions on the absorption capacities, the length of alkyl chains of the cations were altered from ethyl to hexyl and three anions (e.g., acetate, propionate, and lactate) were chosen for comparison. In addition, a reaction equilibrium thermodynamic model (RETM) was proposed and derived to investigate the interactions between H_2S and ILs.

Experimental

Materials

H_2S (99.99%) was supplied from Nanjing Messer Gas. Acetic acid (AR grade, 99.5%), propanoic acid (AR grade, 99.5%), lactic acid (AR grade, 90%), and silver oxide (AR grade, 99.5%) were all purchased from Sinopharm Chemical Reagent. Acetic acid, propanoic acid, and silver oxide were used without further purification. Lactic acid was purified under reduced pressure before use, and the concentration was calibrated through titration using the standard NaOH solution. 1-Ethyl-3-methylimidazolium bromide ([emim]Br), 1-butyl-3-methylimidazolium bromide ([bmim]Br), and 1-hexyl-3-methylimidazolium bromide ([hmim]Br), used as the cation-containing halide precursors (purity $>$ 99%) in the preparation of ILs, were obtained from Shanghai Chengjie Chemical and were dried and degassed at 80°C in vacuum for 24 h before use.

Preparation and characterization of ILs

The five ILs used in this work are 1-ethyl-3-methylimidazolium acetate ([emim][Ace]), 1-ethyl-3-methylimidazolium propionate ([emim][Pro]), 1-ethyl-3-methylimidazolium lactate ([emim][Lac]), 1-butyl-3-methylimidazolium acetate ([bmim][Ace]), and 1-hexyl-3-methylimidazolium acetate ([hmim][Ace]). Their chemical structures are shown in Figure 1. All of them were prepared using the established method according to the literature.[50] In brief, the silver salts of target anions were prepared through the neutralization of silver oxide with the corresponding acids in the first step, followed by the equimolar metathesis reaction with the cation-containing halide salts to generate the crude products. After filtration, the solvents were removed by evaporation under reduced pressure to obtain the target ILs. The IL samples were kept in vacuum at 80°C for at least 3 days to remove traces of water before use. The molecular structures of the ILs prepared in this study were verified using ^1H NMR spectra, ^{13}C NMR spectra, elemental analysis, and mass spectrometry. ^1H NMR and ^{13}C NMR spectra were determined on a Bruker DPX 300 MHz spectrometer, using $CDCl_3$ or DMSO-d_6 as solvents with TMS as the internal standard. Elemental analysis was taken on an Elementar vario EL II. Mass spectrometry was performed on a Shimadazu LC-MS 2020. The water mass fraction in the ILs was examined by a 787KF Titrino to be less than 0.1%. The halogen mass fraction was checked to be less than 100 ppm using the Mohr titration. The characterization results are available in the Supporting Information.

Absorption of H_2S

Apparatus for measuring H_2S absorption is very similar to that in our previous work used for CO_2 absorption.[53] The whole device consists of two 316L stainless steel chambers whose volumes are 121.025 cm^3 (V_1) and 47.073 cm^3 (V_2). The bigger chamber, named as gas reservoir, isolates H_2S, before it contacts with the IL samples in the smaller chamber. The smaller chamber used as equilibrium cell is equipped with a magnetic stirrer. The temperatures (T) of both chambers are controlled by 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) of $\pm 0.2\%$ 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 pressure changes online. In a typical run, a known mass (w) of IL sample was placed into the equilibrium cell, and the air in the two chambers was evacuated ($<$10 Pa). The pressure in the equilibrium cell was recorded to be P_0. H_2S from its gas cylinder was then fed into the gas reservoir to a pressure of P_1. The needle valve between the two chambers was turned on to let H_2S 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 reservoir. The H_2S partial pressure in the equilibrium cell was $P_S = P_2 - P_0$. The H_2S uptake, $n(P_S)$, can, thus, be calculated using the following equation

$$n(P_s) = \rho_g(P_1,T)V_1 - \rho_g(P'_1,T)V_1 - \rho_g(P_s,T)(V_2 - w/\rho_{IL}) \tag{1}$$

where $\rho_g(P_i,T)$ represents the density of H_2S in mol/cm^3 at P_i (i = 1,S) and T and is calculated according to Ref. 54. ρ_{IL} is the density of the ILs in g/cm^3 at T. V_1 and V_2 represent the volumes in cm^3 of the two chambers. Continual determinations of solubility data at elevated pressures were performed by introducing more H_2S into the equilibrium cell to reach new equilibrium. After determinations, H_2S left in the chambers should be introduced to an off-gas absorber containing aqueous solution of NaOH in case of H_2S leaking into the atmosphere. Duplicate experiments were run for each IL system to obtain averaged values of H_2S absorption. The averaged uncertainty of the absorption data in this work was well within $\pm 1\%$.[53]

Results and Discussion

Absorption of H_2S

The temperature and pressure dependence of the solubilities of H_2S in [emim][Ace], [emim][Pro], [emim][Lac],

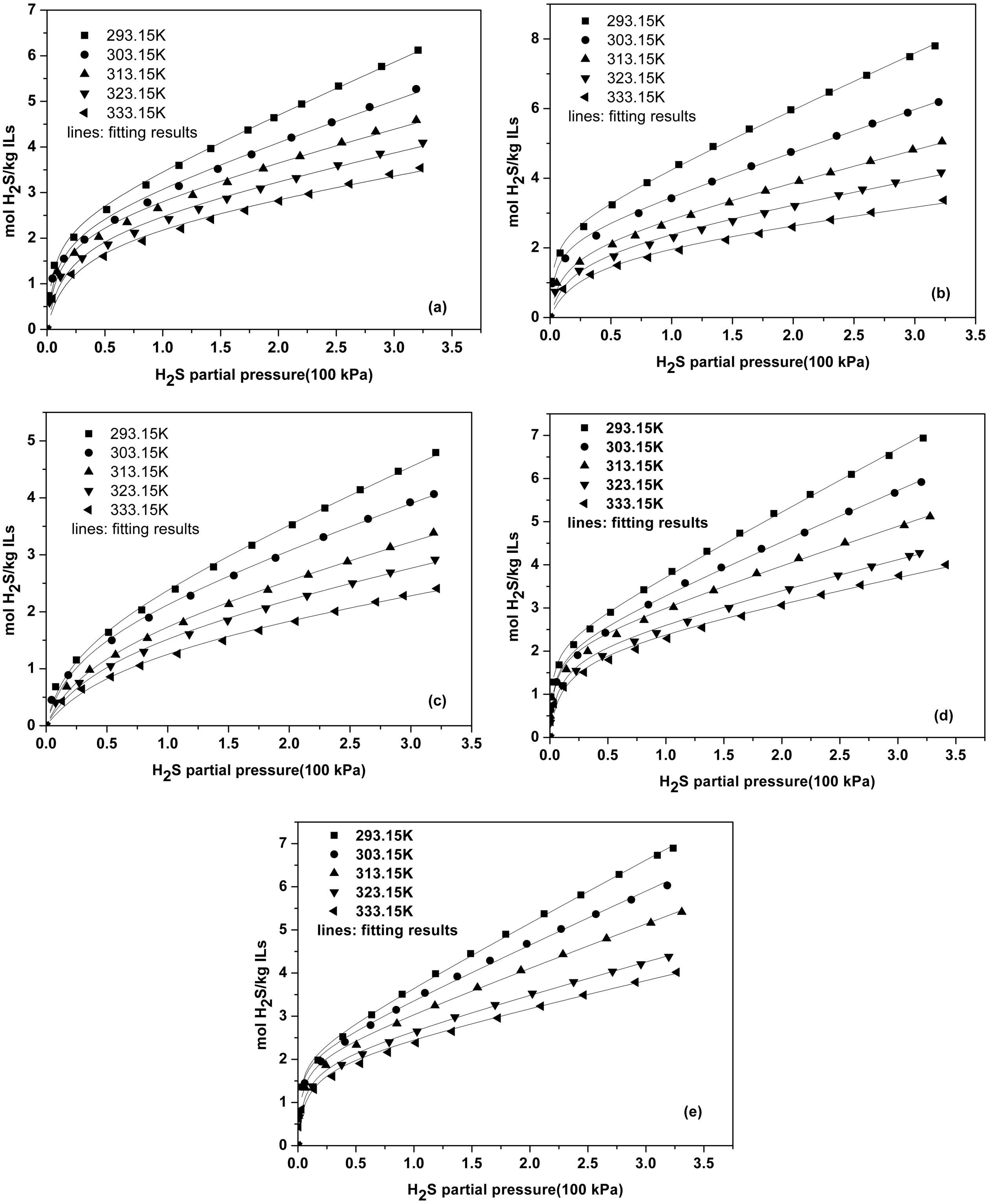

Figure 2. Solubilities of H_2S in five carboxylate-based ILs at different temperatures.

(a) [emim][Ace]; (b) [emim][Pro]; (c) [emim][Lac]; (d) [bmim][Ace]; and (e) [hmim][Ace].

[bmim][Ace], and [hmim][Ace] are graphically shown in Figure 2. (The corresponding solubility data are available in Supporting Information.) It is found that the solubility of H_2S increases with the increasing pressure and decreases with the increasing temperature, which shows a similar behavior as most acid gases or ordinary gases do.[12,13,18]

However, the absorption isotherms of H_2S in all the five carboxylate-based ILs show typically nonideal profiles. The solubility rises dramatically with pressure in the low-pressure region. However, it increases only gradually and almost linearly in the high-pressure region. It implies that H_2S is strongly (or chemically) trapped by the carboxylate-based

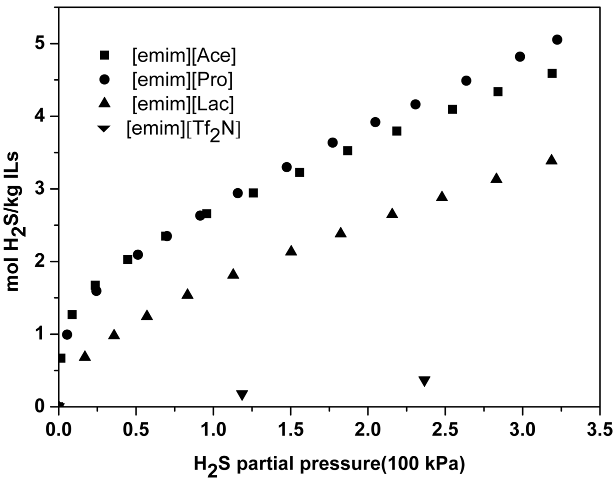

Figure 3. Effect of anions on the absorption of H_2S in the 1-methy-3-ethylimidazolium-based ILs at 313.15 K.

ILs through strong attractive interactions (or complex formation). The equilibrium absorption capacities of H_2S in these ILs are also incredibly large. For example, the solubility of H_2S in [emim][Ace] at 333.15 K is about 2 mol/kg (more than 0.3 mol of H_2S per mole of IL) at 100 kPa and approaches 3.5 mol/kg (almost 0.6 mol of H_2S per mole of IL) when the H_2S partial pressure exceeds 300 kPa. On the contrary, the data of H_2S absorption in the common IL [emim][PF_6] are 0.11 and 0.34 mol/kg under the same conditions,[40] being only one-fifteenth of the former case. Such a large difference in solubility justifies the advantage of carboxylate-based ILs over the common ILs. The carboxylate-based ILs can, thus, be reasonably regarded as a kind of TSILs for H_2S absorption. In fact, although the carboxylate-based ILs are very weak bases, they can still interact strongly with H_2S that has acidic and active protons through acid–base interactions as well as the formation of hydrogen bonds.

Comparing the H_2S solubilities in the ILs with different anions (e.g., [emim][Ace], [emim][Pro], and [emim][Lac]) at 313.15 K, as shown in Figure 3, it is found that [emim][Pro] exhibits the largest H_2S absorption capacity. It is obvious that the effect of anions on the H_2S absorption capacity follows the sequence [emim][Pro] > [emim][Ace] > [emim][Lac], which is consistent with the order of the alkalinity of the three anions. According to the conjugated acid–base theory, a weak acidity of carboxylic acid corresponds to a strong alkalinity of the corresponding carboxylate. The pK_a values of acetic acid, propanoic acid and lactic acid are 4.75, 4.87, and 3.86, respectively. Although the anions of ILs are not alkaline enough to deprotonate H_2S ($pK_{a1} = 6.89$), they can still interact with the H_2S molecule through acid–base complex and hydrogen bonds formation, and the interactions should be stronger if the anions were more alkaline. This accounts for the strongest affinity of H_2S with [emim][Pro] and the weakest with [emim][Lac]. In addition, the absorption capacity difference between [emim][Pro] and [emim][Ace] is much smaller than that between [emim][Ace] and [emim][Lac]. This is identical to the difference in pK_a values.

The H_2S absorption isotherm of [emim][Tf_2N],[40] a typical normal IL investigated in the literature, is also presented in Figure 3 for comparison. It is demonstrated that the absorption of H_2S in all the three carboxylate-based ILs is an order of magnitude larger than that in [emim][Tf_2N], especially at low H_2S partial pressures. This is because the anion [Tf_2N] has negligible alkalinity to interact chemically with the hydrogen donor. It is clear from the comparison that the alkaline nature of the carboxylate anions is the primary factor that influences the absorption of H_2S.

As for the effect of cations on the absorption of H_2S, it can be seen from the comparison of the solubility data in [emim][Ace], [bmim][Ace], and [hmim][Ace] at 313.15 K, as shown in Figure 4. These three ILs have the same anion [Ace], and their cations are all based on the imidazolium ring. The experiments reveal that lengthening the alkyl chain of the cation can lead to a slight increase in the absorption capacity of H_2S at pressures higher than 100 kPa. It may be caused by the fact that ILs with longer alkyl chains possess larger free volumes to accommodate more H_2S molecules, which has been confirmed via modeling by Bara and coworkers recently.[55] The cationic structure has little influence on the absorption of H_2S at pressures lower than 100 kPa, primarily due to the dominative chemical absorption in this region. With the fade-out of the chemical absorption at elevated pressures, physical absorption prevails so that the large free volume begins to function. Nevertheless, the cation has a quite inferior effect on the absorption of H_2S compared to the anion.

The absorption/desorption recyclability of an IL for gas separation is a critical property that determines the process cost. [emim][Pro] is selected as an example to investigate the reusability of ILs for H_2S absorption. Four absorption/desorption cycles are shown in Figure 5. In the experiments, the absorption of H_2S was carried out at 293.15 K, and the desorption was performed at 363.15 K with sweeping N_2 for 4 h. It is obvious that the H_2S absorption capacity of the IL changes only within ±2.6% during the four cycles, indicating the complete reversibility of [emim][Pro] in the absorption of H_2S. Other four carboxylate-based ILs in this work that have a similar or less affinity with H_2S are also believed to be reversible absorbents for H_2S.

Thermodynamic analysis of H_2S absorption in the carboxylate-based ILs

As discussed in the previous sections, the absorption profiles of H_2S in the carboxylate-based ILs stray away strongly

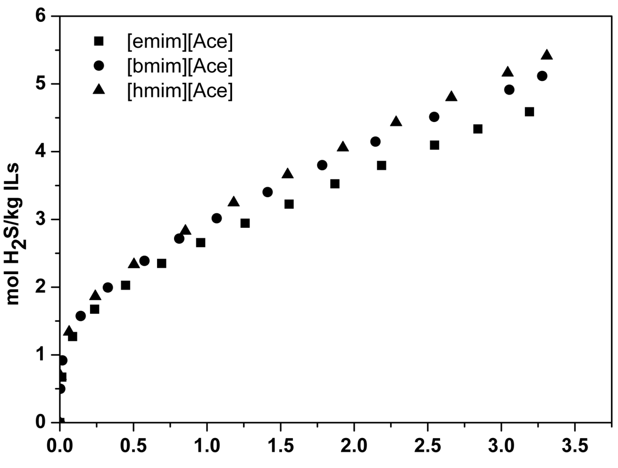

Figure 4. Influence of cations on the absorption of H_2S in the acetate-based ILs at 313.15 K.

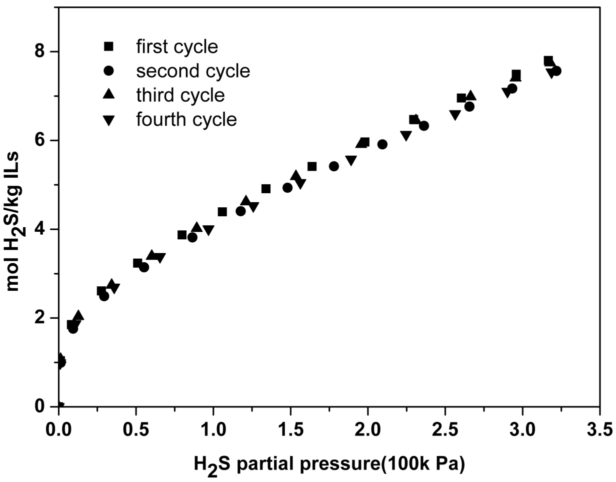

Figure 5. Cycles of H_2S absorption in [emim][Pro] for the investigation of ILs' reversibility.

from the ideality, especially in the low-pressure region. Chemical reactions are thought to take place between H_2S and ILs to form acid–base complexes. To obtain more information about the interactions between H_2S and ILs, a RETM is derived on the basis of Henry's law and reaction equilibrium to correlate the experimental solubility data.

Because there are two active hydrogen protons in H_2S, the H_2S–IL complexes should have at least two possible forms (AB and AB_2), where species A is designated for H_2S and B stands for an IL. The reactions taking place in the system can, thus, be written as

$$A(g) + B(1) \rightarrow AB(1) \tag{2}$$

$$A(g) + 2B(1) \rightarrow AB_2(1) \tag{3}$$

where g and l in Eqs. 2 and 3 represent the existing states (gas and liquid, respectively) of a species.

The Henry's law, reaction equilibrium, and mass balance are the three basic relations existing in the system. They can be expressed into the following equations

$$\text{Henry's law equation: } P = H\gamma_A \frac{m_A}{m^o} \tag{4}$$

$$\text{Reaction equilibrium equation 1: } K_1^\circ = \frac{\gamma_{AB}\frac{m_{AB}}{m^\circ}}{\frac{P}{P^\circ}\cdot\gamma_B\frac{m_B}{m^\circ}} \tag{5}$$

$$\text{Reaction equilibrium equation 2: } K_2^\circ = \frac{\gamma_{AB_2}\frac{m_{AB_2}}{m^\circ}}{\frac{P}{P^\circ}\cdot\left(\gamma_B\frac{m_B}{m^\circ}\right)^2} \tag{6}$$

$$\text{Material balance equation 1: } m_{B0} = m_B + m_{AB} + 2m_{AB_2} \tag{7}$$

$$\text{Material balance equation 2: } m_{A0} = m_A + m_{AB} + m_{AB_2} \tag{8}$$

where P is the partial pressure of H_2S in kPa, and H is the Henry's law constant in kPa. m_A, m_B, m_{AB}, and m_{AB_2} are the molalities of free H_2S dissolved in the liquid, free IL, complex AB, and complex AB_2 in mol/kg, respectively. γ_A, γ_B, γ_{AB}, and γ_{AB_2} are the corresponding activity coefficients of the species mentioned earlier in the liquid phase. K_1° and K_2° are the equilibrium constants of Reactions (2) and (3), respectively. m° is the standard molality (1 mol/kg), and P° is the standard pressure (100 kPa). m_{A0} is the total solubility of H_2S in ILs, and m_{B0} is the initial molality of ILs in the liquid phase in mol/kg.

It is not easy to calculate the activity coefficients of the four species A, B, AB, and AB_2 in the liquid phase of the reaction system. However, the ideal diluted solution can be easily fulfilled, and all the activity coefficients tend to be unity when the concentration of free H_2S in the liquid is low. In fact, only the products of activity coefficients are required in the calculation of K_1° and K_2° as shown in Eqs. 5 and 6, respectively. Therefore, it is reasonable to assume that the products of activity coefficients in Eqs. 5 and 6 are constant during the whole absorption process to avoid the calculation of activity coefficients. After simple deduction, the following RETM equation is obtained to relate the total solubility of H_2S in ILs to the partial pressure of H_2S

$$m_{A0} = \frac{4K_2Pm_{B0} + (1-K_1^2P^2)\left[1-\sqrt{\frac{8m_{B0}K_2P}{(1+K_1P)^2}+1}\right]}{8K_2P} + \frac{P}{H} \tag{9}$$

where K_1 and K_2 are the reaction equilibrium constants based on the concentrations of species but not on the activities as in Eqs. 5 and 6, respectively.

There are three unknown parameters in Eq. 9, H, K_1, and K_2. These three important parameters can be obtained by fitting the experimental solubilities to evaluate the gas absorption process. The fitting curves for the five systems studied in this work are also shown in Figure 2. It is clear that the experimental solubilities of H_2S in ILs can be excellently correlated using Eq. 9. The fitted parameters H, K_1, and K_2, as well as the correlation coefficient R^2, are summarized in Table 1. It is found that all the correlation coefficients R^2 are larger than 0.99, indicating the accuracy of the model.

It is surprisingly found that the equilibrium constants of Reaction (2) (K_1) is 0 for most of the systems. Exceptions occur only at 293.15 K for the systems of H_2S + [emim][Pro], H_2S + [bmim][Ace], and H_2S + [hmim][Ace]. The much smaller K_1 in comparison with K_2 implies that the complex AB may exist only when the temperature is low. In particular, although the uncertainty of K_1 is large, for example, 1.11 ± 0.28 for H_2S + [emim][Pro] system, 0.13 ± 0.42 for H_2S + [bmim][Ace] system, and 0.53 ± 0.41 for H_2S + [hmim][Ace] system at 293.15 K, it does not affect the overall accuracy of the RETM model, because the correlation coefficients R^2 are better than 0.99 in all cases. As for the standard errors of K_1 (i.e., ±0.42 for H_2S + [bmim][Ace] system) being larger than the fitted values (i.e., 0.13 for this system), it can be explained that the randomicity of K_1 is too large to justify the formation of AB-type complex. In fact, if the values of K_1 at 293.15 K are fixed to be 0, the model with only two parameters (K_2 and H) can still be used to calculate the experimental data accurately (R^2 is still better than 0.99), and the refitted values of K_2 and H are almost the same as those given in Table 1. For example, for H_2S + [bmim][Ace] system at 293.15 K, the refitted K_2 and H are 7.79 ± 0.93 and 69 ± 1, respectively, being comparable to 7.54 ± 1.18 and 70 ± 4 that are obtained using K_1 as an additional parameter. Therefore, the model correlation favors a reaction mechanism that two IL molecules react chemically with one H_2S molecule to form the complex of AB_2 type even when the temperature is as low as 293.15 K. This seems in contradiction with the activity difference of the two

Table 1. Thermodynamic Parameters of H_2S–IL Systems Calculated from the RETM Model

	T (K)				
	293.15	303.15	313.15	323.15	333.15
[emim][Ace]					
K_1	0	0	0	0	0
K_2	1.76 ± 0.16	1.12 ± 0.17	0.87 ± 0.12	0.50 ± 0.06	0.34 ± 0.04
H (kPa)	92 ± 1	120 ± 4	155 ± 7	193 ± 10	259 ± 16
R^2	0.998	0.992	0.991	0.990	0.991
[emim][Pro]					
K_1	1.11 ± 0.28	0	0	0	0
K_2	5.43 ± 0.83	2.95 ± 0.38	0.86 ± 0.15	0.49 ± 0.07	0.29 ± 0.03
H (kPa)	67 ± 3	85 ± 1	117 ± 8	163 ± 7	249 ± 14
R^2	0.999	0.998	0.997	0.992	0.992
[emim][Lac]					
K_1	0	0	0	0	0
K_2	0.35 ± 0.03	0.31 ± 0.01	0.18 ± 0.01	0.15 ± 0.01	0.10 ± 0.01
H (kPa)	111 ± 2	143 ± 3	187 ± 5	248 ± 12	350 ± 21
R^2	0.998	0.998	0.998	0.995	0.995
[bmim][Ace]					
K_1	0.13 ± 0.42	0	0	0	0
K_2	7.54 ± 1.18	3.56 ± 0.96	3.27 ± 0.62	1.48 ± 0.40	0.99 ± 0.12
H (kPa)	70 ± 4	87 ± 9	115 ± 3	154 ± 3	188 ± 7
R^2	0.998	0.996	0.994	0.993	0.993
[hmim][Ace]					
K_1	0.53 ± 0.41	0	0	0	0
K_2	9.19 ± 1.69	8.28 ± 1.81	5.16 ± 0.83	2.59 ± 0.46	1.82 ± 0.26
H (kPa)	72 ± 3	83 ± 6	101 ± 2	139 ± 14	170 ± 6
R^2	0.999	0.997	0.997	0.997	0.993

All the parameters H, K_1, and K_2 are essentially non-negative according to the physical meaning.

protons in the H_2S molecule ($pK_{a1} = 6.89$ and $pK_{a2} = 19$). It is argued that without ionization the two protons in H_2S are indistinguishable and have the same opportunity to interact with the IL. The three-body interaction (two IL molecules complexing with one H_2S molecule) can reduce more efficiently the fugacity of H_2S, thus making the system more stable.

Similar results are found in the case of CO_2 absorption in 1-alkyl-3-methylimidazolium carboxylates ILs where only the AB_2 complex formation (A represents for CO_2 and B represents for IL) exists according to Shiflett et al.'s calculation based on an EoS.[50] To examine further the reliability of the RETM model proposed in this work, the correlation of solubility data of CO_2 in [emim][Ace] from the literature[49] using Eq. 9 is performed to calculate H, K_1, K_2, and ΔH_2 (heat of AB_2 complex formation). The calculated values of these parameters, as well as the results obtained using the EoS model by Shiflett et al.,[50] are presented in Table 2 for comparison. Similar to the case of H_2S interacting with ILs, the K_1 value calculated from the RETM model is also found to be 0, indicating that the formation of AB_2 complex dominates in CO_2 + IL system. This is consistent with the result from the EoS method by Shiflett et al.[50] It is also noted that the values of H and K_2 calculated from the RETM method differ in order of magnitude from those in the EoS method. This cannot be well explained from the difference in concentration scales adopted in the two models (molality scale in the RETM model vs. mole fraction scale in the EoS model), especially in the case of H value. The too small H value in the EoS model is out of the range for the Henry's law constant of a gas dissolving in a solvent, so that its physical meaning is obscure. In contrast, the H value in our model is located in the normal range, standing exactly for its physical meaning. Nevertheless, the ΔH_2 values calculated from the two models are comparable (−33.2 vs. −30.8 kJ/mol), showing the reliability of both models in analyzing the interaction between H_2S and ILs.

Table 2. Thermodynamic Parameters of CO_2 + [emim][Ace] System Calculated from the RETM and EoS Models for Comparison

Model	T (K)	H (kPa)	K_1	K_2	$-\Delta H_2$ (kJ/mol)
RETM*	298.1	1310	0	0.92	33.2
EoS†	298.1	5.12	0	220	30.8

*Based on the molality scale.
†Based on the scale of mole fraction (data obtained from Ref. 36).

It is clearly demonstrated from the model that H_2S can be absorbed both chemically and physically in the carboxylate-based ILs. The physical absorption is related to the Henry's law constant H, whereas the reaction equilibrium constant K_2 accounts for the chemical absorption. To compare the data from different systems, K_2 and H are plotted using histograms in Figures 6 and 7, respectively. The equilibrium constant K_2 is a measure that indicates the reactivity of the carboxylate-based ILs with H_2S. The larger the K_2 value is, the more actively the ILs react with H_2S. All the K_2 values are found to be in a range from 0.35 to 9.19 at 293.15 K, showing a weak to moderate combination of H_2S with ILs. In all five H_2S–IL systems studied in the article, K_2 varies negatively and dramatically with the temperature, implying that the increasing temperature weakens the complexation of H_2S with the ILs. K_2 is also found to increase with the increasing alkalinity of the anion and the lengthening alkyl chain of the cation, which is similar to the case of solubility variation. As for the Henry's law constant H, in contrast to the variation of K_2, it increases remarkably with the temperature. The alkyl chain of the ILs' cation is shown to have a slightly positive effect on the lowering of H value. The H data of H_2S in the carboxylate-based ILs, ranging from 67 to 360 kPa at temperatures from 293.15 to 333.15 K, are much lower than that of CO_2 in [emim][Ace] (1310 kPa, see Table 2). It means that the physical absorption of H_2S into the carboxylate-based ILs is also better than that of CO_2. In

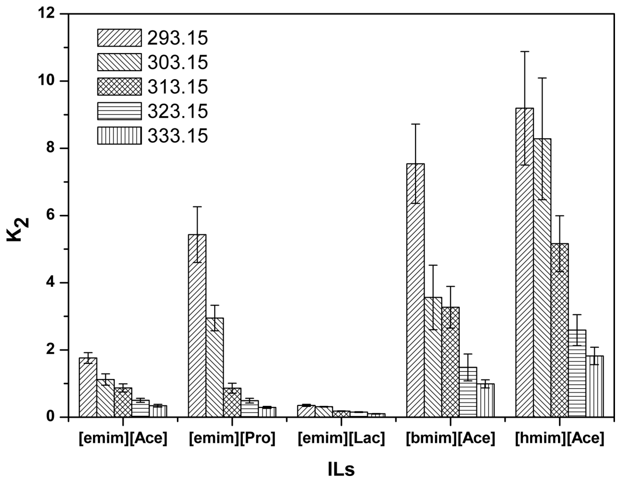

Figure 6. K_2 values of H_2S reacting with the five ILs at different temperatures.

addition, H varies negligibly with the alkalinity of the anions, which is in accordance with the experimental observations.

To examine the relative contributions of chemical solubility (m_{AB} + m_{AB_2}) and physical solubility (m_A) to the total solubility (m_{A0}), the chemical and physical absorption profiles for H_2S + [emim][Ace] at 293.15 K are calculated and shown in Figure 8 (see Supporting Information for the calculation results of other H_2S + IL systems). The chemical absorption capacity levels off at pressures larger than 50 kPa, due to the stoichiometric limitation of equilibrium reaction. On the contrary, the physical absorption capacity increases almost linearly with the increasing H_2S pressure. There exists a boundary pressure (P_b = 230 kPa) where the chemical and physical absorptions contribute to the total solubility equally. The chemical absorption dominates in the system at pressures lower than P_b, whereas the physical one is the governing mechanism at high pressures.

A deep insight into the interactions of H_2S with ILs can be achieved by calculating the molar enthalpy (ΔH_2) of Reaction (3) from the van't Hoff equation

$$\frac{\partial \ln K_2}{\partial T} = \frac{\Delta H_2}{RT^2} \tag{10}$$

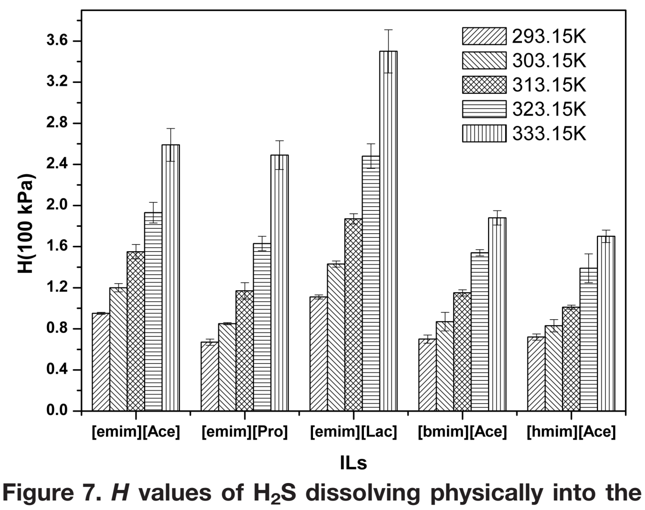

Figure 7. H values of H_2S dissolving physically into the five ILs at different temperatures.

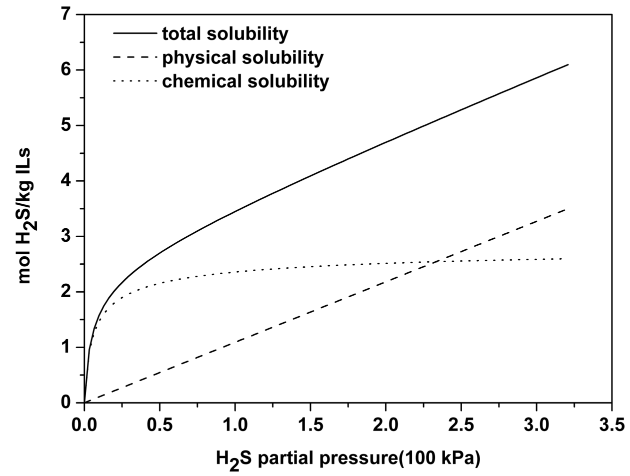

Figure 8. Chemical and physical solubility of H_2S in [emim][Ace] calculated using the RETM model.

The calculated results are shown and compared in Figure 9. ΔH_2 is found to range from −25 to −40 kJ/mol for the four systems, H_2S + [emim][Ace], H_2S + [emim][Lac], H_2S + [bmim][Ace], and H_2S + [hmim][Ace], being only about twice of the hydrogen bonding energy (−10 to −20 kJ/mol). It implies that the H_2S–IL complexation is weak to moderate, and the absorption can be easily reversed by heating. This is in consistence with our experimental observations in the regeneration of the ILs. However, a large negative value of ΔH_2 (−62.3 kJ/mol) is obtained for the system H_2S + [emim][Pro]. It can be explained from the largest alkalinity of [emim][Pro] among the five ILs. In addition, as ΔH_2 is very sensitive to the K_2 values at different temperatures, large deviations of ΔH_2 may result from the small error in the determination of the absorption data. Nevertheless, the calculated ΔH_2 is a useful thermodynamic parameter for the evaluation of the complexing strength of an IL with H_2S, as well as the evaluation of the energy involved in the absorption/desorption process.

Similarly, the enthalpy of solution,ΔH_{sol}, that reflects the thermal effect of physical dissolution of H_2S in ILs, can be calculated using Eq. 11

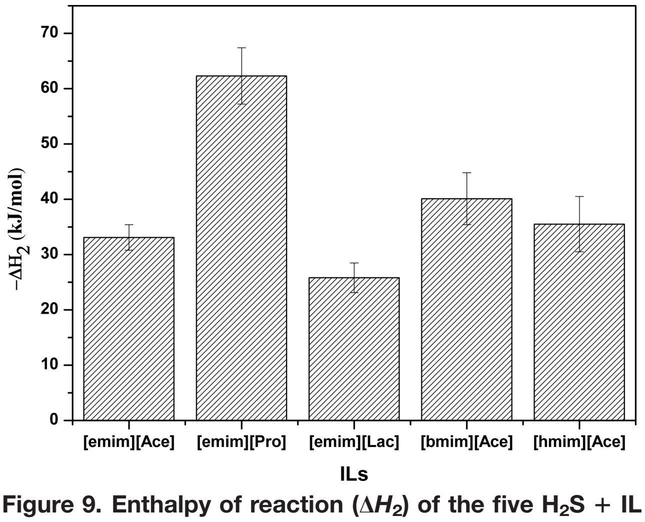

Figure 9. Enthalpy of reaction (ΔH_2) of the five H_2S + IL systems calculated using the RETM model.

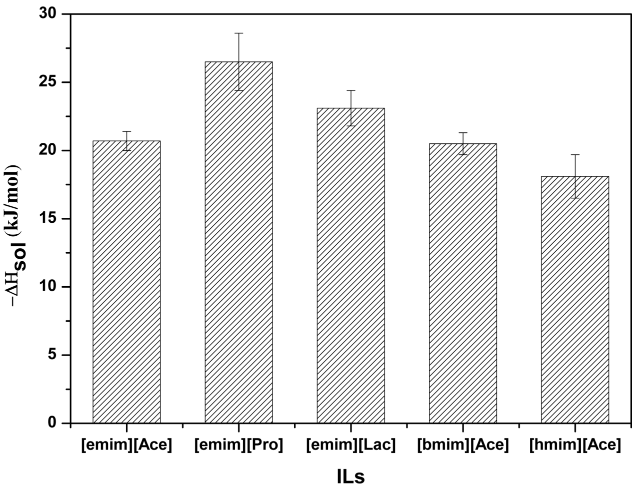

Figure 10. Enthalpy of solution (ΔH_{sol}) of the five H_2S + IL systems calculated using the RETM model.

$$\frac{\partial \ln H}{\partial T} = \frac{\Delta H_{\mathrm{sol}}}{RT^2} \tag{11}$$

The calculated results are shown and compared in Figure 10. ΔH_{sol} is found to range from -17 to -26 kJ/mol for all the five systems, being about twice as that of H_2S absorption in the normal ILs (from -10 to -15 kJ/mol[36,37,39–41,47]). This implies that the carboxylate-based ILs can act as both good physical and chemical absorbents of H_2S. Compared with the normal ILs in the literature, the carboxylate-based ILs are validated thermodynamically to be task-specific for H_2S absorption in this work.

The AB_2 complexation deduced from the model can only give elementary information about molecular structure. It is conceived that one H_2S molecule may be sandwiched by two ILs via hydrogen bonding or charge transfer. It is of great interest to know the actual molecular configuration and the nature of chemical bonding. There is no doubt that spectroscopic studies and/or *ab initio* calculations can provide more insights into this matter. We will focus on this in the following work.

Conclusions

The solubilities of H_2S in five 1-alkyl-3-methylimidazolium carboxylate ILs have been measured at temperatures from 293.15 to 333.15 K and pressures up to 350 kPa. The absorption profiles of H_2S in these ILs of weak alkalinity are found to be strongly nonideal, and the absorption capacities are dramatically larger than that of normal ILs in the literature, especially at low pressures. Chemical absorption is thought to occur accompanying with the physical one in the systems. A RETM is, thus, proposed in this work to correlate successfully the solubility data by assuming the formation of complexes. The fitting results favor a reaction mechanism of AB_2 complex formation that one H_2S molecule binds with two ILs in the systems. Thermodynamic parameters, such as H, K_2, and ΔH_2, were also obtained from the model to evaluate the absorption of H_2S into the five carboxylate-based ILs. It is demonstrated that both the anion and the cation have an influence on the absorption of H_2S and, thus, on the thermodynamic parameters. In particular, the anion of weak alkalinity plays the primary role in making the ILs to be task-specific for H_2S absorption. It is believed from the results of this work that the carboxylate-based ILs may also have potential use in the desulfurization of natural gas or syngas streams.

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