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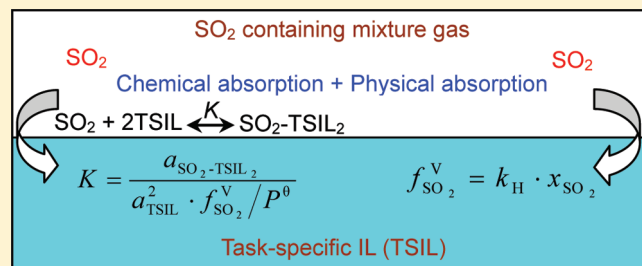
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Solubilities and Thermodynamic Properties of SO₂ in Ionic LiquidsMeijin Jin,[†] Yucui Hou,[‡] Weize Wu,^{*,†} Shuhang Ren,[†] Shidong Tian,[†] Li Xiao,[†] and Zhigang Lei[†][†]State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China;[‡]Department of Chemistry, Taiyuan Normal University, Taiyuan 030012, China

S Supporting Information

ABSTRACT: Task-specific ionic liquids (TSILs) have been experimentally demonstrated to absorb more sulfur dioxide (SO₂) than normal ILs from gas mixtures with low SO₂ concentrations; however, the differences of SO₂ solubilities in the two kinds of ILs at given temperatures and pressures have not been studied systematically. Moreover, the mechanism of the interaction between SO₂ and ILs still remains unclear. In this work, the solubilities of SO₂ in TSILs (1,1,3,3-tetramethylguanidinium lactate and monoethanolaminium lactate) and normal ILs (1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium hexafluorophosphate) were determined. The solubilities of SO₂ are correlated by a modified Redlich–Kwong equation of state (RK EoS). The chemical absorption and physical absorption are differentiated, and the absorption mechanism has been proposed with the aid of the modified RK EoS. SO₂ absorption capacity in TSILs is contributed from both chemical interaction and physical interaction. Two TSIL molecules chemically absorb one SO₂ molecule, and the chemical absorption amount follows the chemical equilibrium. Normal ILs only physically absorb SO₂ following Henry's law. The chemical equilibrium constant, reaction enthalpy, Gibbs energy of reaction, reaction entropy, and Henry's law constant of SO₂ absorbed in ILs have been calculated. The present model can predict SO₂ absorption capacity for capture and SO₂ equilibrium concentration in IL for recovery.



INTRODUCTION

Air pollution has been a serious problem for years and has attracted growing attention all over the world. SO₂, one of the main air pollutants, is emitted from burning of fossil fuels and results in acid rain and smog, which are harmful to the environment and the human health. Therefore, the removal and separation of SO₂ from flue gas before released are crucial subjects in terms of sustainable development and green chemistry. A variety of approaches for SO₂ control, called flue-gas desulfurizations (FGDs), including limestone-based FGD, activated carbon adsorption, pressure swing adsorption, and temperature swing adsorption, have been adopted to purify flue gas.^{1–3} Presently, flue-gas desulfurization is one of the most effective methods to control emissions of SO₂ from the combustion of fossil fuels.^{4–6} Unfortunately, there are some obvious defects in those methods: for example, low efficiency and a huge number of gypsum wastes.⁷ It is acceptable that one of the most attractive processes for the removal of a target compound from a gas mixture is selective absorption into a liquid.

In recent years, room-temperature ionic liquids (ILs) have been proposed for SO₂ separation and may provide a more cost-effective and environmentally friendly alternative.^{8–22} ILs are molten organic salts consisting of organic cations and organic or inorganic anions. They are potentially attractive components due to their unique properties, such as extremely low vapor pressure, high thermal and chemical stability, and excellent solvent power for a wide range of both organic and inorganic materials. More

interesting is that the properties of ILs could be tuned by appropriate selection of the structures of their cations and anions, which further increases the unique features and applicability of ILs in complex systems and challenging conditions compared to the traditional industrial solvents.

Recently, ILs were synthesized with functional groups and studied to absorb SO₂ from gas mixtures or simulated flue gas. Han et al.⁸ first used 1,1,3,3-tetramethylguanidinium lactate ([TMG]L) to absorb SO₂ from a gas mixture of SO₂ and N₂ with high absorption capacity and high selectivity. They proposed that this process had both physical and chemical absorption, and 1 mol of [TMG]L can chemically absorb 1 mol of SO₂. Since then, numerous ILs with SO₂ absorption ability have been the focus of many scientific investigations,^{9–22} and their absorption mechanisms have been studied.^{8,9,12,13,19–21} Riisager et al.^{9,23} synthesized several new TMG-based ILs, such as [TMG][BF₄] and [TMG][BTA], and reported that these ILs could absorb a large amount of SO₂ only through physical interaction. Zhang et al.¹² synthesized a series of hydroxyl ammonium ILs and measured the solubilities of SO₂ in those ILs. They deduced that SO₂ is chemically interacted with the cations of ILs, and one monoethanolaminium lactate ([MEA]L) molecule attracted one SO₂ molecule chemically. Recently, Wu et al.²⁰ analyzed the

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changes of viscosity, conductivity, and density of task-specific ILs and normal ILs during the absorption of SO₂. They suggested that task-specific ILs absorbed SO₂ chemically when the mole ratio of SO₂ to IL was below 0.5 and continued to physically absorb SO₂ when the mole ratio of SO₂ to IL was above 0.5, but normal ILs absorbed SO₂ only physically. Mark et al.¹⁹ neglected the physical contribution of task-specific ILs absorbing SO₂ and deduced the chemical complexes formatted in the binary task-specific IL + SO₂ mixtures.

In terms of recent reports, the mechanism that task-specific ILs can absorb SO₂ chemically has been accepted by most of researchers, but the chemical association between task-specific ILs and SO₂ and whether the physical contribution can be neglected in the system of task-specific IL + SO₂ have remained unclear. It is known that the solubilities of SO₂ in ILs enhance with the increase of pressure and decrease with the increase of temperature. For normal ILs, these phenomena can be explained by Henry's law. What is the reason for task-specific ILs' absorption behavior? Does the chemical absorption capacity of SO₂ in task-specific ILs also increase with increasing pressure and decrease with increasing temperature or remain constant at any temperature or any pressure? In addition, most researchers focused on absorbing pure SO₂ or high concentration of SO₂ by ILs, and few covered absorbing SO₂ by task-specific ILs and normal ILs at low partial pressure, which was nearly actual industrial conditions. Furthermore, binary *PTx* (pressure–temperature–composition) data for SO₂ have been measured using only a few ILs.^{15,19}

In this work, we studied the solubilities of SO₂ in the two kinds of ILs (task-specific ILs and normal ILs) at temperatures ranging from 293.15 to 333.15 K and SO₂ partial pressures ranging from 0.344 to 101.25 kPa. The solubility data, which were correlated by a modified Redlich–Kwong equation of state (RK EoS),^{15,19,21,24–30} provide useful information on the fundamental knowledge for physical and chemical interactions between IL and SO₂ on the molecular level. We try to explain the chemical absorption capacity of SO₂ in task-specific ILs at given temperatures and pressures and the chemical association between task-specific IL and SO₂ by binary *PTx* data of SO₂ in the task-specific IL. In addition, the chemical equilibrium constant, K^θ ; molar Gibbs energy of reaction, $\Delta_r G_m^\theta$; molar reaction enthalpy, $\Delta_r H_m^\theta$; molar reaction entropy, $\Delta_r S_m^\theta$; and Henry's law constant for our example ILs + SO₂ systems were obtained to clearly understand the difference in solubilities of SO₂ in task-specific ILs and normal ILs.

Recent reports^{8,9,11,12,23} have suggested that [TMG]L and [MEA]L were the most promising substitutes for conventional organic solvents in purification of SO₂-containing gas, such as flue gas desulfurization, because of their higher absorption capacities of SO₂ than other ILs. So we employed [TMG]L and [MEA]L as task-specific ILs in this work.

EXPERIMENTAL SECTION

Materials. SO₂ with a mole fraction of 99.95% and N₂ with a mole fraction of 99.95% were obtained from Beijing Haipu Gases. 1,1,3,3-Tetramethylguanidine, which was distilled before use, was supplied by Baigui Chemical Company (Shijiazhuang, China). Monoethanolamine was purchased from Tianjin Fuchen Chemical Company (Tianjin, China). Lactic acid was from Tianjin Bodi Chemical Co. (Tianjin, China). 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), with a

Table 1. Water Contents of ILs Used in This Work

ILs	[TMG]L	[MEA]L	[bmim][BF ₄]	[bmim][PF ₆]
mass fraction of water	0.0142	0.0181	0.00486	0.00294

purity of 99%, were obtained from Henan Lihua Pharmaceutical Co. Ltd. (Henan, China). All reactants and solvents were A.R. grade. [TMG]L and [MEA]L were synthesized and characterized following the procedures reported in the literature.^{8,10,12} All of the ILs were dried under vacuum at 353.15 K for at least 48 h to remove organic solvents and water before use. The mass fractions of water in the ILs were determined by Karl Fischer titration, and the results are shown in Table 1. Water concentrations after absorption were also measured, and there was no obvious change in the water contents before and after absorption.

Apparatus and Procedure. A series of gases with SO₂ volume fractions of 0.0034, 0.0070, 0.060, 0.300, 0.500, and 1.00 were prepared by mixing SO₂ and N₂. The absorption experiments were carried out under an ambient pressure at 298.15, 313.15, and 333.15 K. The gas stream was bubbled through a predetermined amount (~5 g) of IL loaded in a glass tube with an i.d. of 12 mm, and the flow rate was ~100 mL·min⁻¹, which was monitored by a rotameter and calibrated by a soap-film flow meter. The glass tube was partly immersed in a water bath, the temperature of which was controlled by a temperature controller with an accuracy of ±0.1 K. A small sample of IL was taken from the glass tube at regular intervals, and then the content of SO₂ absorbed in the IL was analyzed.

Analysis of SO₂ Content in ILs. The content of SO₂ in the sampled ILs was measured by using the standard iodimetry (HJ/T 56-2000, a standard method of the State Environmental Protection Administration of China). The detailed procedure was reported in the literature.³¹ The experimental method was the same as that described in our group's previous work.¹⁷

RESULTS AND DISCUSSION

Absorption and Solubilities of SO₂ in ILs. The absorption of SO₂ of 0.0034 volume fraction in simulated flue gas by [TMG]L was tested versus time at different temperatures and under ambient pressure. The results are illustrated in Figure 1. Obviously, at the beginning of absorption (less than 500 min), the SO₂ absorption rate, which is determined by the slope of the curve at the beginning time, is enhanced with increasing temperature. This may result from the decrease in the viscosity of [TMG]L with the increase in the temperature.³² Under the relatively low partial pressure, the diffusion rate of SO₂ in viscous IL and at the gas–liquid interface plays a vital role in the absorption rate of SO₂. The low viscosity of IL favors diffusion. When the absorption reached equilibrium, the mole fractions of SO₂ in [TMG]L at 298.15, 313.15, and 333.15 K reached 0.354, 0.342, and 0.281 (0.171, 0.161, and 0.122 g SO₂/g IL), respectively. This indicated that [TMG]L was able to absorb SO₂ efficiently from the flue gas containing a low SO₂ content.

Figure 2 shows the absorption of SO₂ with a volume fraction of 0.0034 by [MEA]L as a function of time at different temperatures and under ambient pressure. The absorption behavior of [MEA]L is similar to that of [TMG]L. The solubilities of SO₂ in [MEA]L decrease with the increase in the temperature, but there were some differences. At the beginning of absorption, the rate of absorbing SO₂ at 313.15 K was the highest. The lower rate of absorbing SO₂ at 333.15 K may result from the low SO₂

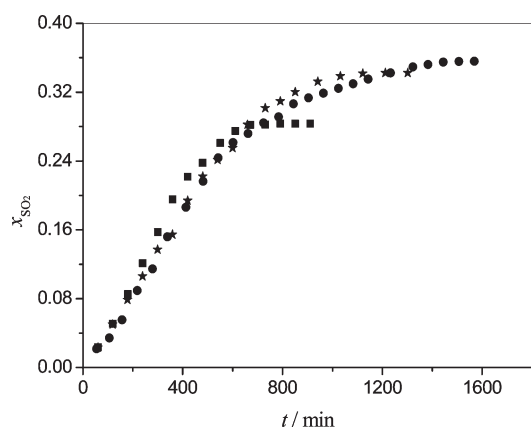


Figure 1. The mole fraction of SO₂ absorbed by [TMG]L with 0.0034 volume fraction of SO₂ as a function of time at different temperatures: ●, 293.15 K; ★, 313.15 K; ■, 333.15 K.

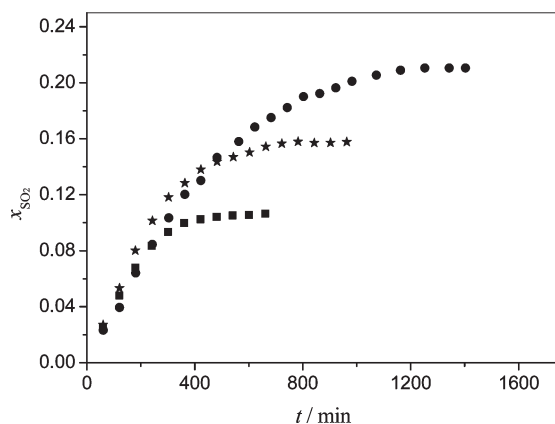


Figure 2. The mole fraction of SO₂ absorbed by [MEA]L with 0.0034 volume fraction of SO₂ as a function of time at different temperatures: ●, 293.15 K; ★, 313.15 K; ■, 333.15 K.

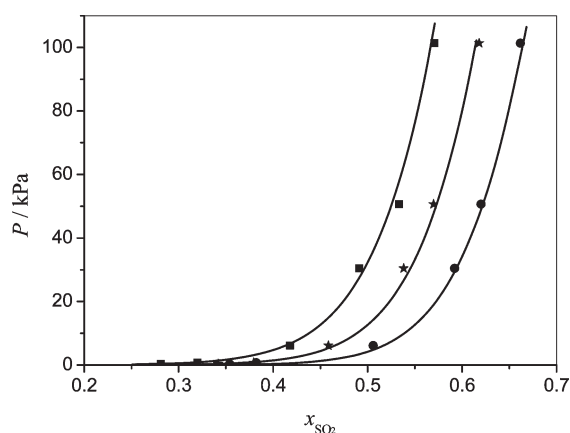


Figure 3. Isothermal P - x (pressure–liquid composition) phase diagram of a [TMG]L + SO₂ binary system at different temperatures: ●, 293.15 K; ★, 313.15 K; ■, 333.15 K. Lines, RK EoS calculation results; symbols, experimental data.

absorption capacity at 333.15 K. The absorption capacity for SO₂ in [MEA]L at 298.15, 313.15, and 333.15 K were 0.210, 0.157, and 0.106 (0.112, 0.079, and 0.050 g SO₂/g IL), respectively.

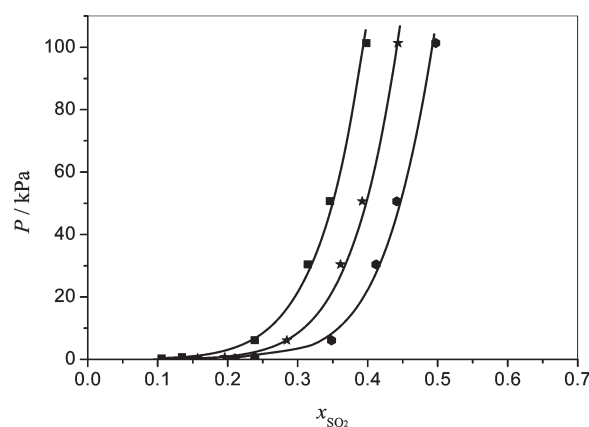


Figure 4. Isothermal P - x (pressure–liquid composition) phase diagram of [MEA]L + SO₂ binary system at different temperatures: ●, 293.15 K; ★, 313.15 K; ■, 333.15 K. Lines, RK EoS calculation results; symbols, experimental data.

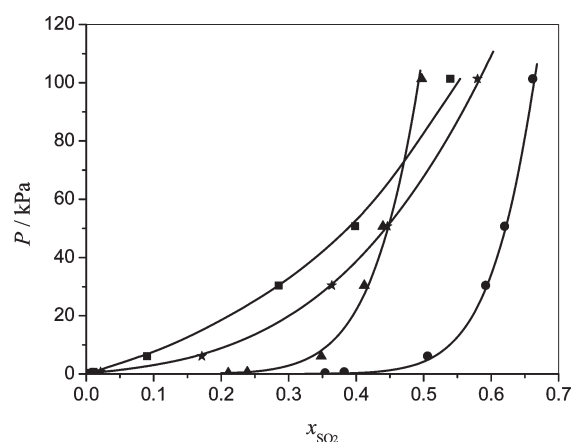


Figure 5. The solubilities of SO₂ in the investigated ILs at 293.15 K. ILs are labeled as follows: ★, [bmim][BF₄]; ■, [bmim][PF₆]; ▲, [MEA]L; ●, [TMG]L. Lines, RK EoS calculation results; symbols, experimental data.

This suggests that [MEA]L was also able to absorb SO₂ excellently from gas containing a low content of SO₂.

The SO₂ solubilities in [bmim][BF₄] and [bmim][PF₆] were also determined at 293.15 K. They were 0.010 and 0.005 in mole fraction, respectively, suggesting that these normal ILs almost cannot absorb SO₂ from the flue gas containing SO₂ with as low as 0.0034 volume fraction.

The solubilities of SO₂ in [TMG]L, [MEA]L, [bmim][BF₄], and [bmim][PF₆] for other simulated flue gases with different SO₂ contents were also measured in our work; the solubility data are presented in Figures 3, 4 and 5. Since nitrogen was almost not absorbed by ILs,³³ we neglected the effect of nitrogen in the systems of IL + SO₂ and reckoned the partial pressure of SO₂ as the system pressure for SO₂ absorption.

Modeling. Our experimental data are correlated by a modified RK EoS, which was successfully employed by a group at DuPont in their series of reports^{15,19,21,24–30} and Kumelan.³⁰ The detail description can be found in the Supporting Information.

The EoS constants for pure SO₂, [bmim][BF₄] and [bmim][PF₆] were taken from the literature,^{19,29} and T_c and

P_c for [TMG]L and [MEA]L were estimated using the method reported by Joback et al.³⁴

The isothermal P - x plots by the modified RK EoS for [TMG]L + SO₂, [MEA]L + SO₂, [bmim][BF₄] + SO₂ and [bmim][PF₆] + SO₂ are provided in Figures 3, 4, and 5, respectively. The figures indicate that all the solubilities of SO₂ over the entire range of experimentally investigated temperatures and pressures were correlated successfully by the modified RK EoS. The relative absolute deviation between the experimental results and the correlation results for the solubilities of SO₂ at our investigated pressures and temperatures were not more than 4.4%. Therefore, the modified RK EoS can be allowed for the direct calculation of solubility at a given temperature and pressure. The relative deviation between 1.7 mol SO₂/mol [TMG]L at 313 K and under 1.2 bar reported by Han et al.⁸ and the predicted data for this work under the same conditions is 0.5%.

Mechanism of the Absorption of SO₂ by ILs. Separating SO₂ by ILs has drawn growing attention, and the mechanism has been studied in recent years. In this work, the solubilities of SO₂ in task-specific ILs and normal ILs at 293.15 K are shown in the Figure 5. It can be found that the absorption behavior of [TMG]L was similar to that of [MEA]L. The solubilities of SO₂ in [TMG]L and [MEA]L decreased slowly with a decrease in pressure at high pressures (such as >6 kPa) and decreased remarkably with a decrease in pressure under low pressures (such as <6 kPa), but the solubilities were still much higher than zero, even at the relatively low pressures. For example, the solubilities of SO₂ in [TMG]L were 0.382 and 0.354 mol fraction at pressures as low as 0.709 and 0.344 kPa, respectively.

The SO₂ absorption behaviors of [bmim][BF₄] and [bmim][PF₆] were also similar to each other. Their absorption capacities of SO₂ increased with an increase in pressure. At the same low partial pressure of SO₂ as 0.344 kPa, both [bmim][BF₄] and [bmim][PF₆] can absorb SO₂ from a gas mixture with solubilities of 0.010 and 0.005 mol fraction at 293.15 K. But at high partial pressures of SO₂, they can absorb SO₂ effectively. For example, at 101.325 kPa, [bmim][BF₄] and [bmim][PF₆] can absorb SO₂ with solubilities of 0.586 and 0.540 in mole fraction, respectively.

The phenomena indicate that both task-specific ILs and normal ILs can absorb pure SO₂ or feed gas streams with high contents of SO₂, whereas task-specific ILs can excellently absorb SO₂ even from flue gas containing very low contents of SO₂. The absorption of SO₂ by task-specific ILs at a relatively low pressure can be contributed to chemical interaction between a task-specific IL and SO₂.^{8,12} Chemical interaction, which is much stronger than physical interaction, is not influenced significantly by pressure. Physical interaction is greatly dependent on pressure, which normally obeys the Henry's law, $P = k_H \cdot x$, at low pressures. Therefore, when the partial pressure of SO₂ decreases, the solubility of SO₂ also decreases linearly, as predicted by Henry's law. From the above analysis, we can conclude that there is predominantly chemical interaction formed in the binary task-specific IL + SO₂ mixtures at low SO₂ pressures, and there are both chemical interaction and physical interactions at high SO₂ pressure, which may be beyond the chemical absorption capacity. There is only simple physical interaction between normal ILs and SO₂. This is the reason why task-specific ILs can absorb SO₂ even under the relatively low partial pressure, but normal ILs cannot.

The absorption of SO₂ in task-specific IL is the sum of the chemical and physical contributions. Therefore, in this work,

the moles of SO₂ absorbed per mole of the task-specific IL were divided into two parts, which is expressed as follows,

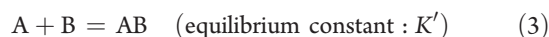
$$n_{\text{SO}_2} = n'_{\text{SO}_2} + n''_{\text{SO}_2} \quad (1)$$

where n_{SO_2} is the total moles of SO₂ absorbed by 1 mol of task-specific IL; n'_{SO_2} is the moles of SO₂ by physical absorption; n''_{SO_2} is the moles of SO₂ by chemical absorption.

Until now, there have been two kinds of chemical associations or complex formations of SO₂ with a task-specific IL. Han et al.⁸ and Zhang et al.¹² reported that one molecule of SO₂ was in equilibrium with one molecule of task-specific IL. Our previous work²⁰ indicated that one molecule of SO₂ was in equilibrium with two molecules of task-specific IL. In this work, we try to find which one can be fit for the equilibrium of SO₂ with a task-specific IL from a thermodynamic point of view. SO₂ is simplified as A, and the task-specific IL as B; therefore, the two kinds chemical equilibrium of SO₂ with task-specific IL can be expressed by the following eqs, 2 and 3,



or



Then the equilibrium constant, K^θ , is calculated by the following equations, respectively,

$$K^\theta = \frac{a_{AB_2}}{a_B^2 \cdot f_A^V / P^\theta} = \frac{\gamma_{AB_2} \cdot C_{AB_2}}{\gamma_B^2 \cdot C_B^2 \cdot f_A^V / P^\theta} \quad (4)$$

Or

$$K^{\theta'} = \frac{a_{AB}}{a_B \cdot f_A^V / P^\theta} = \frac{\gamma_{AB} \cdot C_{AB}}{\gamma_B \cdot C_B \cdot f_A^V / P^\theta} \quad (5)$$

where a_{AB_2} , a_{AB} , and a_B are activities of AB₂ complex, AB complex, and B, respectively; f_A^V is the fugacity of A in the vapor phase; P^θ is the standard pressure; γ_{AB_2} , γ_{AB} , and γ_B stand for activity coefficients of AB₂ complex, AB complex, and B, respectively; C_{AB_2} , C_{AB} , and C_B are molar concentrations of AB₂ complex, AB complex, and B, respectively. The activity coefficients of ILs were calculated via the quantum chemical conductor-like screening model for real solvents (COSMO-RS) method. The calculation results (see the Supporting Information) indicate that the activity coefficients of the ILs are almost equal to 1, so it can be reasonably assumed that $\gamma_{AB_2} = 1$, $\gamma_{AB} = 1$, and $\gamma_B = 1$. Then eqs 4 and 5 lead to

$$K^\theta = \frac{C_{AB_2}}{C_B^2 \cdot f_A^V / P^\theta} = \frac{C_0 - C_t}{2 \cdot C_t^2 \cdot f_A^V / P^\theta} \quad (6)$$

or

$$K^{\theta'} = \frac{C_{AB}}{C_B \cdot f_A^V / P^\theta} = \frac{C_0 - C_t}{C_t \cdot f_A^V / P^\theta} \quad (7)$$

where C_0 is the initial molar concentration of task-specific IL and C_t is the equilibrium molar concentration of the task-specific IL, which can be obtained by eqs 8, 9, and 10.

$$C_0 = \frac{1}{1 \times M / \rho_0} \times 10^{-3} \quad (8)$$

Table 2. The Physical Solubility and Chemical Solubility of SO₂ in per Mole Task-Specific ILs at 293.15 K

[TMG]L + SO ₂				[MEA]L + SO ₂			
P^a /kPa	$n_{\text{SO}_2}^b$	$n_{\text{SO}_2}^{c'}$	$n_{\text{SO}_2}^{c''}$	P^a /kPa	$n_{\text{SO}_2}^b$	$n_{\text{SO}_2}^{c'}$	$n_{\text{SO}_2}^{c''}$
0.344	0.548	0.074	0.474	0.344	0.266	0.006	0.260
0.709	0.619	0.139	0.480	0.709	0.326	0.010	0.316
6.08	1.025	0.533	0.492	6.08	0.534	0.107	0.427
30.398	1.452	0.955	0.497	30.398	0.701	0.235	0.466
50.663	1.632	1.135	0.497	50.663	0.791	0.318	0.474
101.325	1.956	1.459	0.497	101.325	0.989	0.508	0.481

^a P , SO₂ partial pressure in the gas mixture. ^b n_{SO_2} , moles of SO₂ per mole task-specific IL. ^{c'} $n_{\text{SO}_2}^{c'}$, moles of SO₂ per mole task-specific IL with physical absorption. ^{c''} $n_{\text{SO}_2}^{c''}$, moles of SO₂ per mole task-specific IL with chemical absorption.

$$C_t = \frac{1 - 2n_{\text{SO}_2}^{c''}}{1 \times M/\rho_t} \times 10^{-3} \quad (9)$$

or

$$C_t = \frac{1 - n_{\text{SO}_2}^{c''}}{1 \times M/\rho_t} \times 10^{-3} \quad (10)$$

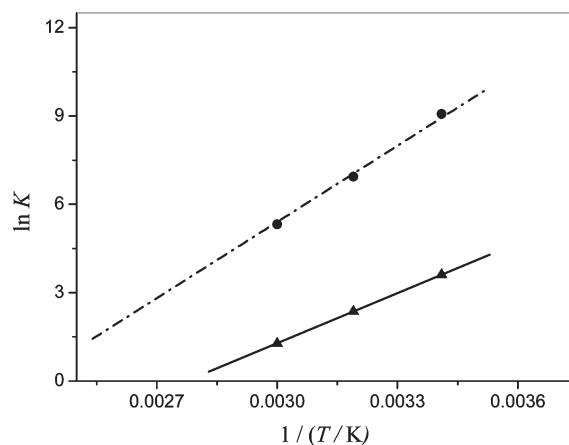
where M is the molar mass of the task-specific IL, ρ_0 is the initial density of the task-specific IL, and ρ_t is the equilibrium density of the task-specific IL. The density data of the task-specific ILs are taken from our group's previous publication.²⁰

Chemical interaction between the task-specific IL and SO₂ is much stronger than physical interaction, and at low SO₂ pressure, chemical interaction dominantly contributes to the solubilities of SO₂ in the task-specific IL, evidenced as compared with the behaviors of SO₂ solubilities in the task-specific ILs and normal ILs in Figure 5. Therefore, it can reasonably omit the physical contribution to the SO₂ solubility in task-specific ILs at low mole fractions of SO₂ and low SO₂ partial pressures. In this work, we assume that task-specific ILs absorb SO₂ only chemically at mole fractions of SO₂ lower than 0.25. The chemical solubilities of SO₂ can be calculated by the modified RK EoS with the binary interaction parameters, and then the equilibrium constants K^θ at different temperatures can be obtained through eqs 6–10.

Using the equilibrium constants K^θ obtained at low mole fractions of SO₂ and low SO₂ partial pressures, we can calculate the equilibrium molar concentration of task-specific IL, C_t , at given pressures and temperatures, then the moles of SO₂ by the task-specific IL with chemical absorption, $n_{\text{SO}_2}^{c''}$, can be gained by eq 9 or 10. The moles of SO₂ by physical absorption, $n_{\text{SO}_2}^{c'}$, can be obtained using eq 1, i.e. $n_{\text{SO}_2} - n_{\text{SO}_2}^{c''}$.

The values of $n_{\text{SO}_2}^{c'}$ calculated by eqs 1, 7, and 10 at 0.344 and 0.709 kPa are negative, and the values of $n_{\text{SO}_2}^{c'}$ calculated by eqs 1, 6, and 9 at 0.344 and 0.709 kPa are positive. This result indicates that eq 2 is in accord with the experimental results; that is, there is a chemical complex AB₂, not AB, formed in the system of the task-specific IL and SO₂ that is in agreement with our previous results by determining the viscosity, conductivity, and density of task-specific ILs during absorbing SO₂.²⁰

The moles of SO₂ by per mole of task-specific IL physical absorption, $n_{\text{SO}_2}^{c'}$, and the moles of SO₂ by per mole task-specific IL chemical absorption, $n_{\text{SO}_2}^{c''}$, at our investigated pressures and

**Figure 6.** Effect of temperature on the equilibrium constants, K^θ , for SO₂ in task-specific ILs [TMG]L (●) and [MEA]L (▲).

at 293.15 K are listed in Table 2, calculated by eqs 1, 6, and 9, and the modified RK EoS. The values of both $n_{\text{SO}_2}^{c'}$ and $n_{\text{SO}_2}^{c''}$ increase with increasing pressure. For physical absorption, the absorption capability, $n_{\text{SO}_2}^{c'}$, increases with the increase in SO₂ partial pressure by obeying Henry's law; for chemical absorption, the absorption capability, $n_{\text{SO}_2}^{c''}$, reaches equilibrium with SO₂ partial pressure, complying by chemical equilibrium (as shown in eq 2) with the equilibrium constant, K^θ ; and the absorption capability, $n_{\text{SO}_2}^{c''}$, also increases with an increase in the SO₂ partial pressure. Because chemical interaction between task-specific IL molecules and SO₂ molecules is stronger than physical interaction, therefore, at low SO₂ partial pressures (such as P lower than 0.709 kPa), chemical absorption shows a high SO₂ absorption capability, whereas physical absorption shows a low SO₂ absorption capability. For instance, at $T = 293.15$ K and $P = 0.344$ kPa, 1 mol of [TMG]L can absorb 0.474 mol of SO₂ by chemical absorption, and 0.074 mol of SO₂ by physical absorption. The chemical absorption capability is limited by the chemical equilibrium, as shown in eq 2 because chemical reaction follows a stoichiometric ratio. Although physical absorption follows Henry's law, the physical absorption capability is not limited and increases with raising SO₂ pressure. Therefore, at high SO₂ partial pressure, the chemical absorption capacity increases to a very small extent with the increase in the SO₂ partial pressure, but the physical absorption capacity increases greatly with increasing SO₂ partial pressure, even larger than the chemical absorption capacity.

To further understand clearly the chemical solubility behaviors in the systems of a task-specific IL and SO₂, thermodynamic functions (equilibrium constant, K^θ ; molar Gibbs energy of reaction, $\Delta_r G_m^\theta$; molar reaction enthalpy, $\Delta_r H_m^\theta$; and molar reaction entropy, $\Delta_r S_m^\theta$) were investigated.

The logarithms of the equilibrium constants, K^θ , versus the inverse of temperature are shown in Figure 6. The molar reaction enthalpy, $\Delta_r H_m^\theta$, can be obtained by using the van't Hoff equation,

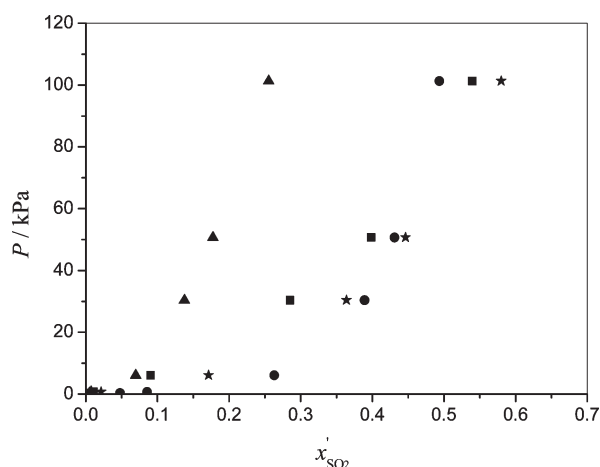
$$\frac{\partial \ln K^\theta}{\partial T} = \frac{\Delta_r H_m^\theta}{RT^2} \quad (11)$$

The molar Gibbs energy of reaction, $\Delta_r G_m^\theta$, and molar reaction entropy, $\Delta_r S_m^\theta$, can be calculated by the following equations:

$$\Delta_r G_m^\theta = -RT \ln K^\theta \quad (12)$$

Table 3. Molar Reaction Enthalpy, Molar Gibbs Energy of Reaction, and Molar Reaction Entropy of SO₂ in Task-Specific ILs at 293.15 K

ILs	$\Delta_r H_m^\theta$, kJ·mol ⁻¹	$\Delta_r G_m^\theta$, kJ·mol ⁻¹	$\Delta_r S_m^\theta$, J·mol ⁻¹ ·K ⁻¹
[TMG]L	-71.78	-21.78	-170.6
[MEA]L	-47.32	-8.79	-131.4

**Figure 7.** Isothermal P - x_{SO_2}' phase diagram for SO₂ and IL systems at 293.15 K. ILs are labeled as follows: ★, [bmmim][BF₄]; ■, [bmmim][PF₆]; ▲, [MEA]L; ●, [TMG]L.

$$\Delta_r S_m^\theta = (\Delta_r H_m^\theta - \Delta_r G_m^\theta) / T \quad (13)$$

The results of $\Delta_r H_m^\theta$, $\Delta_r G_m^\theta$, and $\Delta_r S_m^\theta$ are presented in Table 3. The negative molar reaction enthalpy values, $\Delta_r H_m^\theta$ for [TMG]L + SO₂ and [MEA]L + SO₂, correspond to various intermolecular interactions, such as the hydrogen bond⁸ and the N–S bond.¹² The $\Delta_r H_m^\theta$ values of -47.32 kJ·mol⁻¹ for ([MEA]L + SO₂) and -71.78 kJ·mol⁻¹ for ([TMG]L + SO₂) correspond to the weak chemical interaction between task-specific ILs and SO₂. The lower value of $\Delta_r H_m^\theta$ for ([MEA]L + SO₂) suggests molecular interaction between [MEA]L and SO₂ is weaker than that between [TMG]L and SO₂.

Infinite dilution properties, such as Henry's law constant, k_H , are often useful for assessing quickly the degree of gas solubility in a solvent. It is known that normal ILs absorbed SO₂ only by physical interaction, and task-specific ILs absorbed SO₂ by chemical and physical interactions. According to the values of n_{SO_2}' (the moles of SO₂ by per mole of a task-specific IL's physical absorption, shown in Table 2), the mole fraction of SO₂ by physical absorption, x_{SO_2}' , can be attained. Figure 7 provides P - x_{SO_2}' plots for ([bmmim][BF₄] + SO₂), ([bmmim][PF₆] + SO₂), ([TMG]L + SO₂), and ([MEA]L + SO₂) at 293.15 K. Obviously, there are similar absorption behaviors in these investigated systems, which further suggested that the part of SO₂ absorbed by task-specific ILs is attributed to the physical interaction.

The Henry's law constant, $k_H(T, P_T)$, can be defined as

$$f_1^V = P_T \phi_1^V y_1 = k_H(T, P_T) x_1 (x_1 \rightarrow 0) \quad (14)$$

where $k_H(T, P_T)$ is Henry's law constant of SO₂ at temperature

Table 4. Henry's Law Constants for SO₂ in Normal ILs and Task-Specific ILs at 293.15 K

IL	[bmmim][BF ₄]	[bmmim][PF ₆]	[MEA]L	[TMG]L
$k_H(T, P_T)/\text{kPa}$	50.0	100	254	9.60

T and total pressure P_T , f_1^V is the fugacity of SO₂ in the vapor phase, y_1 is the mole fraction of SO₂ in the vapor phase, x_1 is the mole fraction of SO₂ in the liquid phase, and ϕ_1^V is the fugacity coefficient of SO₂ in the vapor phase. Since the pressures of SO₂ are very low, the fugacity coefficient of SO₂ in the vapor phase can be set as 1. $P_T y_1$ is the partial pressure of SO₂, P , in the vapor phase (as shown in Table 2). Then eq 14 leads to

$$P = k_H(T, P_T) x_1 (x_1 \rightarrow 0) \quad (15)$$

For the systems of SO₂ + [TMG]L and SO₂ + [MEA]L, $x_1 = x_{\text{SO}_2}'$. Using SO₂ solubility data by experiments and by calculation with the modified RK EoS, the Henry's law constants of SO₂ in ILs, $k_H(T, P_T)$, can be obtained, which are shown in Table 4.

Henry's law constants, $k_H(T, P_T)$, of SO₂ dissolved in ILs at 293.15 K decrease following the order [MEA]L > [bmmim][PF₆] > [bmmim][BF₄] > [TMG]L. Henry's law constant $k_H(T, P_T)$ of SO₂ in [TMG]L was lowest, suggesting that the physical interaction between [TMG]L and SO₂ is stronger than other ILs and SO₂, which can also be clearly explained in Figure 7. Henry's law constants $k_H(T, P_T)$ of SO₂, 50.0 and 100 kPa in [bmmim][BF₄] and [bmmim][PF₆] at 293.15 K by this work, are lower than the values 104 and 112 kPa, respectively, at 298 K, reported by Jiang.¹¹ The deviation is mainly a result of the different temperatures we investigated.

It has been demonstrated that task-specific ILs can absorb SO₂ from gas mixtures with very low SO₂ concentrations and can be regenerated with heating and vacuum treatment to yield high-concentration SO₂, and they can be reused with high SO₂ absorption capacity, almost as high as the original ones.^{9,12} Can absorbed SO₂ be recovered thoroughly, and why does the recovery process need heating and vacuum treatment? As we discussed above, task-specific ILs absorb SO₂ at very low SO₂ concentrations, mainly by chemical interaction, which is limited by the thermodynamic equilibrium. At the recovery conditions, the equilibrium SO₂ concentration can be calculated through eqs 6, 8, 9, and 11 on the base of thermodynamic properties shown in Table 3. Taking [TMG]L absorption of SO₂ as an example, at recovery condition of 0.006 kPa, the equilibrium SO₂ concentrations are 0.035, 0.022, 0.011, and 0.0060 in molar ratios of SO₂ to IL at temperatures of 363, 373, 383, and 393 K, corresponding to 0.011, 0.0067, 0.0035, and 0.0019 for mass ratios of SO₂ to IL, respectively. The results are in agreement with our previous result,¹⁷ 0.011 for the mass ratio of SO₂ to IL at temperatures from 363 to 373 K and in vacuum. Furthermore, increasing the recovery temperature can decrease the equilibrium SO₂ concentration in the IL, which is favorable for recovery of SO₂.

CONCLUSION

Solubilities of SO₂ in two kinds of ionic liquids (task-specific ILs and normal ILs) have been studied at temperatures ranging from 293.15 to 333.15 K and partial pressures ranging from 0.344 to 101.25 kPa. Both task-specific ILs and normal ILs can absorb SO₂ effectively at high partial pressures of SO₂, but only task-specific ILs can absorb SO₂ when partial pressures of SO₂ are

relatively low. All the solubility data have been successfully correlated with the modified RK EoS. Some thermodynamic functions (such as the chemical equilibrium constant, K^θ , and Henry's law constant, $k_H(T, P_T)$) are calculated at 293.15 K.

Comparing the solubility isothermals of SO₂ in [TMG]L and [MEA]L with those in [bmim][BF₄] and [bmim][PF₆], the chemical absorption and physical absorption are differentiated, and the absorption mechanism is proposed. Task-specific ILs absorb SO₂ by chemical and physical contributions, whereas normal ILs only physically absorb SO₂. For the systems of task-specific IL and SO₂, two IL molecules absorb one SO₂ molecule by chemical interaction, and the chemical absorption amount follows the chemical equilibrium. Heating and vacuum treatment can regenerate SO₂-absorbed IL, but the residue amount of SO₂ in the IL is limited by the chemical equilibrium.

■ ASSOCIATED CONTENT

S Supporting Information. Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone/Fax: +86 10 64427603. E-mail: wzwu@mail.buct.edu.cn.

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