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Study on absorption and spectral properties of H_2S in carboxylate protic ionic liquids with low viscosity

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ABSTRACT. The exorbitant price and high viscosity are two major disadvantages for ionic liquids (ILs), which influence their practical applications in gas separation. Here we synthesized ten carboxylate protic ionic liquids (PILs), containing *N*-ethylmorpholine acetate, *N*-ethylmorpholine propionate, *N*-ethylmorpholine butyrate, *N*-ethylmorpholine methoxylacetate, 4-(2-hydroxyethyl) morpholine acetate, and 4-(2-hydroxyethyl) morpholine methoxylacetate, triethylamine acetate, triethylamine propionate, triethylamine propionate, and triethylamine methoxylacetate, with low cost and viscosity for absorption of H₂S. The densities and viscosities of these carboxylate PILs were measured in the temperature range of (298.2 to 333.2) K at atmospheric pressure. The solubility of H₂S in these PILs was determined using an isochoric saturation technique at 298.2 ~ 318.2 K and 0 ~ 1.096 bar. It was found that the solubility of H₂S in these PILs increased with the increasing pressure and length of the alkyl chains on the carboxylic acid. The absorption processes obeyed Henry's law within the given experimental conditions and Henry's constants were calculated from solubility data. In addition, the FTIR and

NMR spectral properties in the absorption process of H_2S in *N*-ethylmorpholine butyrate [NEMH][Bu] also were investigated to present important information on absorption mechanism. The results indicated that [NEMH][Bu] demonstrated a highest absorption capacity among these PILs and absorption of H_2S is a physical behavior. Comparisons of PILs with the common ILs and organic solvents were also done to demonstrate the advantages of PILs.

KEYWORDS. H₂S capture, *N*-ethylmorpholine, Ionic liquids, Solubility, Absorption mechanism.

1. Introduction

Hydrogen sulfide (H_2S) is one of the notorious acid gases, thus controlling its concentration has been a world issue to be urgently solved in the field of air pollution control [1]. The presence of highly toxic H_2S in natural gas, syngas, and hydro desulfurization gas imposes significant threat to the safety and efficiency of energy utilization [2,3]. Consequently, the reduction, capture, or utilization of H_2S discharged from industrial processes have become the central focus of current scientific and technological studies. An important technology for natural gas sweetening is absorption in liquids, in which organic amines are widely used as the absorbents [4-8]. Typically, aqueous solutions of amines, such as monoethanolamine (MEA), diethanolamine (DEA), *N*-methyldiethanolamine (MDEA), and diisopropanolamine (DIPA), are widely used for removal of H_2S from gas streams with dilute H_2S content in natural gas sweetening. Some physical absorbents, including methanol, propylene carbonate, polyethylene glycol dimethyl ether, and *N*-methylpyrrolidone are also used to remove H_2S in some commercial processes [4-8]. However, inherent disadvantages, such as volatile loss of solvents, equipment corrosion, oxide deactivation of amines, high energy consumption of desorption

process, are still difficult to overcome. Furthermore, traditional processes for natural gas sweetening are not preferred from the viewpoint of green and sustainable chemistry.

The development of efficient absorbent for the capture of H_2S is of critical importance in the absorption process. Ionic liquids (ILs), a kind of typical green solvents, have attracted much attention in the field of H_2S separation due to their unique features such as high thermal stability, negligible vapor pressure, and adjustable chemical properties [2,9,10]. Compared to other gases (e.g. CO_2 and SO_2), the solubility of H_2S are available in only a few conventional ILs [11,12], such as [Bmim][PF₆], [Bmim][BF₄], [Bmim][Tf₂N], [Hmim][PF₆], [Hmim][BF₄], and [Hmim][Tf₂N]. Although significant progresses have been made in improving the absorption of H_2S by ILs, the cost and viscosity of the room temperature ionic liquids (RTILs) reported in literature are still relatively high [11,12], and the high viscosity is usually unfavorable for the diffusion of H_2S .

Protic ionic liquids (PILs) are a kind of ILs with low cost and low viscosity, which can be easily prepared from simple materials through the direct neutralization between corresponding acid and base. In this respect, our research group have paid great attention to PILs for H₂S removal based on their favorable properties and excellent selectivity to separate H₂S and CO₂ [13-15]. These important conclusions encourage us to develop high performance PILs for H₂S removal. Although designed PILs exhibit good H₂S absorption capacity, the problem of high viscosity of these PILs still needs improvement [13-15]. For instance, the viscosity of methyldiethanolammonium acetate ([MDEAH][Ac]) exceeded 270 mPa·s at 303.2 K [13]. Herein, we prepared ten kinds of PILs with the low viscosity and inexpensive price containing three cations [*N*-ethylmorpholine, 4-(2-hydroxyethyl) morpholine, and trimethylamine] and four

anions (acetate, propionate, butyrate, and methoxy acetate). The density and viscosity of these carboxylate PILs, and solubility of H_2S in these PILs were measured, respectively. These PILs showed both low viscosity and considerable loading capacity of H_2S . Particularly, *N*-ethylmorpholine butyrate ([NEMH][Bu]) demonstrated a highest absorption capacity among these PILs. The absorption of H_2S in [NEMH][Bu] is a physical behavior according to results of absorption and FTIR and NMR spectral. These results could be used to provide important information for the design and operation of the absorption and desorption processes of H_2S with potential industrial application for these PILs.

2. Experimental section

2.1. Materials

All chemicals are analytically pure agents purchased from Chemical Co. Ltd. with a commercial purity and were used without further purification unless otherwise indicated. H_2S (99.9%) was obtained from Nanjing Messer Gas. (Nanjing, China). The deuterated solvents were purchased from CIL (Cambridge Isotope Laboratories). Completely specification of all chemicals is listed in Table 1.

Table 1.

2.2. Synthesis and characterization of carboxylate PILs

The investigated carboxylate PILs in this work, including *N*-ethylmorpholine acetate ([NEMH][Ac]), *N*-ethylmorpholine propionate ([NEMH][Pro]), *N*-ethylmorpholine butyrate ([NEMH][Bu]), *N*-ethylmorpholine methoxylacetate ([NEMH][MOAc]), 4-(2-hydroxyethyl)

morpholine acetate ([NHEMH][Ac]), and 4-(2-hydroxyethyl) morpholine methoxyacetate ([NHEMH][MOAc]), triethylamine acetate ([TEAH][Ac]),triethylamine propionate ([TEAH][Pro]), triethylamine propionate ([TEAH][Bu]), and triethylamine methoxylacetate ([TEAH][MOAc]), were prepared by direct neutralization between corresponding acid and base [13] without any solvents. Their chemical structures are shown in Figure 1. Typically, the 50 mmol of butyric acid was dropwise added to equimolar N-ethylmorpholine under ice bath. The reaction was stirred for 2 h, and then mixture was warmed to 50 °C and stirred for 24 h. The resulting crude product was washed for three times with diethyl ether to remove unreacted reactants (PILs are insoluble in diethyl ether). The obtained product was dried under vacuum for 24 h to remove trace of solvent, offering brown liquid of [NEMH][Bu]. Other PILs were synthesized referring to the same method. The chemical structure of the PILs prepared in this work was confirmed by NMR and FTIR spectra. The Bruker AV 400 spectrometer was used to conduct the NMR experiments. FTIR spectra were recorded on a Nicolet iS50 infrared spectrometer.

Figure 1.

[NEMH][Ac]: ¹H NMR (400 MHz, CDCl₃) δ = 13.35 (s, 1H), 3.84 – 3.76 (m, 4H), 2.82 – 2.57 (m, 6H), 2.01 (s, 3H), 1.16 (t, *J* = 7.3 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 175.55 (s), 65.68 (s), 52.13 (s), 22.09 (s), 10.23 (s) ppm. IR 2968.5, 2860.2, 2806.0, 1709.1, 1361.5, 1255.4, 1113.2, 1020.7, 860.4, 770.2, 612.2, 451.9 cm⁻³.

[NEMH][**Pro]:** ¹H NMR (400 MHz, CDCl₃) δ = 13.43 (s, 1H), 3.80 (d, *J* = 4.8 Hz, 4H), 2.69 – 2.55 (m, 6H), 2.29 (q, *J* = 7.6 Hz, 2H), 1.14 (dt, *J* = 10.4, 7.4 Hz, 6H) ppm. ¹³C NMR (101 MHz,

CDCl₃) $\delta = 178.58$ (s), 65.78 (s), 52.16 (s), 28.32 (s), 10.30 (s), 9.47 (s) ppm. IR 2982.1, 2864.7, 2810.5, 1713.6, 1456.3, 1210.3, 1120.0, 1020.7, 853.7, 767.9, 606.9 cm⁻³.

[NEMH][Bu]: ¹H NMR (400 MHz, CDCl₃) δ = 12.01 (s, 1H), 3.80 – 3.75 (m, 4H), 2.69 – 2.55 (m, 6H), 2.25 (t, *J* = 7.4 Hz, 2H), 1.73 – 1.57 (m, 2H), 1.15 (t, *J* = 7.3 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 177.79 (s), 65.76 (s), 52.15 (s), 37.18 (s), 18.71 (s), 13.78 (s), 10.27 (s) ppm. IR 2961.8, 2869.2, 1718.1, 1451.8, 1255.4, 1205.8, 1120, 1029.7, 903.3, 860.4, 774.7, 609.9, 454.2 cm⁻³.

[NEMH][**MOAc]:** ¹H NMR (400 MHz, CDCl₃) δ = 13.35 (s, 1H), 3.84 – 3.76 (m, 4H), 2.82 – 2.57 (m, 6H), 2.01 (s, 3H), 1.16 (t, *J* = 7.3 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 175.18 (s), 71.25 (s), 65.09 (s), 58.74 (s), 52.04 (s), 51.60 (s), 9.71 (s) ppm. IR 2873.7, 2815.0, 1596.2, 1447.3, 1260.0, 1196.7, 1111.0, 1025.2, 939.4, 695.7, 603.1, 445.1 cm⁻³.

[NHEMH][Ac]: ¹H NMR (400 MHz, CDCl₃) δ = 8.66 (s, 2H), 3.85 – 3.74 (m, 6H), 2.90 – 2.73 (m, 6H), 2.02 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 176.62 (s), 65.49 (s), 59.97 (s), 57.05 (s), 52.99 (s), 22.13 (s) ppm. IR 2871.5, 1709.1, 1564.6, 1399.9, 1266.7, 1115.5, 1009.4, 912.4, 858.2, 646.0, 449.7 cm⁻³.

[NHEMH][MOAc]: ¹H NMR (400 MHz, CDCl₃) $\delta = 8.78$ (s, 2H), 3.95 (s, 2H), 3.93 – 3.82 (m, 6H), 3.43 (s, 3H), 3.07 – 2.84 (m, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃) $\delta = 176.15$ (s), 71.21 (s), 64.88 (s), 60.00 (s), 58.86 (s), 56.64 (s), 52.93 (s) ppm. IR 2871.5, 1594.0, 1399.9, 1205.8, 1115.5, 903.3, 700.2, 600.9, 435.6 cm⁻³.

[TEAH][**Ac]**: ¹H NMR (400 MHz, CDCl₃) δ = 13.69 (s, 1H), 2.99 (q, *J* = 7.3 Hz, 6H), 1.99 (s, 3H), 1.24 (t, *J* = 7.3 Hz, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 176.80 (s), 44.70 (s), 23.06

(s), 8.63 (s) ppm. IR 2975.3, 1711.3, 1564.6, 1361.5, 1248.7, 1004.9, 833.4, 650.5, 609.9, 442.9 cm⁻³.

[TEAH][Pro]: ¹H NMR (400 MHz, CDCl₃) δ = 14.21 (s, 1H), 2.91 (q, *J* = 7.3 Hz, 6H), 2.26 (q, *J* = 7.6 Hz, 2H), 1.15 (dt, *J* = 33.1, 7.4 Hz, 12H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 180.09 (s), 44.70 (s), 29.56 (s), 10.10 (s), 9.00 (s) ppm. IR 2979.8, 1715.9, 1562.4, 1348.0, 1246.4, 1007.1, 828.8, 657.3, 451.9 cm⁻³.

[TEAH][Bu]: ¹H NMR (400 MHz, CDCl₃) δ = 12.12 (s, 1H), 2.91 (q, *J* = 7.3 Hz, 6H), 2.21 (dd, *J* = 8.5, 6.4 Hz, 2H), 1.71 – 1.57 (m, 2H), 1.19 (t, *J* = 7.3 Hz, 9H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 179.33 (s), 44.72 (s), 38.63 (s), 19.24 (s), 13.95 (s), 9.05 (s) ppm. IR 2970.8, 1715.9, 1569.1, 1463.0, 1399.9, 1201.3, 1036.5, 842.4, 774.7, 465.5 cm⁻³.

[TEAH][MOAc]: ¹H NMR (400 MHz, CDCl₃) δ = 13.26 (s, 1H), 3.91 (s, 2H), 3.42 (s, 3H), 3.09 (q, *J* = 7.3 Hz, 6H), 1.29 (t, *J* = 7.3 Hz, 9H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 175.54 (s), 71.74 (s), 58.45 (s), 44.69 (s), 8.34 (s) ppm. IR 2975.3, 2889.5, 2815.0, 1596.2, 1381.8, 1201.3, 1113.2, 939.4, 828.8, 695.7, 549.0 cm⁻³.

2.3. Physical properties of carboxylate PILs

The density and viscosity of these PILs were measured in the temperature range of (298.2 to 333.2) K. The densities were determined using an DM40/DM45 DeltaRange/DM50 automatic densiometer with a precision of 0.00001 g·cm⁻³, which was calibrated using distilled water at desired temperature. The relative uncertainties of density measurements are estimated to be \pm 0.02%. Viscosities were measured on a HAAKE Rheostress 600 viscometer with an uncertainty of \pm 1% in relation to the full scale. The measurement temperatures were controlled by a bath

with an uncertainty of \pm 0.1 K. TG traces were recorded on a PerkinElmer Pyris 1 TGA from room temperature to 400 °C with a scanning rate of 10 °C·min⁻¹ under N₂ atmosphere to determine the decomposition temperatures of [NEMH][Bu] and NEM.

2.4. Absorption of H₂S

Experimental apparatus for the measurement of H_2S solubility is similar to our previous work [16]. The experimental facility is shown in Figure 2.

Figure 2.

The whole device consists of two 316 L stain less steel chambers whose volume are 120.802 cm³ (V_1) and 47.368 cm³ (V_2), respectively. The bigger chamber, used as gas reservoir, isolates the gas before it contacts with the absorbent in the smaller chamber. The smaller chamber, named as equilibrium cell, is equipped with a magnetic stirrer. The temperature (T) of both chambers are controlled using a water bath with an uncertainty of \pm 0.1 K. The pressures in the two chambers are monitored using two pressures 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. Typically, a known mass (W) of absorbent was placed into the equilibrium cell, and the air in the two chamber was evacuated to be p_0 (< 0.1 kPa). H₂S from cylinder was then fed into the gas reservoir to 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 pressure of the two chambers remained constant for at least 2 h. The equilibrium pressures were denoted as p_2 for the equilibrium cell as p'_1 for the gas reservoir. The

gas partial pressure in the equilibrium cell was $p_g = p_2 - p_0$. The H₂S uptake, $n(p_g)$, could thus be calculated using Eq. (1):

$$n(p_{g}) = \rho_{g}(p_{1}, T)V_{1} - \rho_{g}(p_{1}, T)V_{1} - \rho_{g}(p_{g}, T)(V_{2} - W/\rho_{a})$$
(1)

where $\rho_{g}(p_{i}, T)$ represents the density of the gas in mol·cm⁻³ at p_{i} (i = 1, 2, s) and T, and is obtained according to the NIST standard reference data. The ρ_a is the density of absorbent in $g \cdot cm^{-3}$ at T. The volume increase of the ILs in the equilibrium cell as the result of gas solubility is very small and neglected. V_1 and V_2 represent the volumes in cm³ of the two chambers, respectively. Continual determinations of solubility data at elevated pressure performed by introducing more H₂S into the equilibrium. The solubility of H₂S was defined in terms of mole fraction (xH_2S) in this work. After determinations, the gas remaining in the chambers were introduced into an off-gas absorber containing aqueous solution of NaOH to prevent gas leakage into atmosphere. Solubility of H₂S in ten PILs was measured under desired temperature and pressure. The average reproducibility of the solubility data in this work is well within ± 2.0 %. The H₂S release was done after the absorption, in which the H₂S saturated [NEMH][Bu] was heated to 80 °C in a pre-heated oil bath, refluxed for one hour in a 25 mL single necked roundbottom flask and then cooled down for another absorption cycle. The regenerative process was determined according to H₂S loading capacity and system weight change. (Attention: Due to the high toxicity of H_2S gas, experiments must be performed under good ventilation conditions).

3. Results and discussion

3.1. Physical properties

The density and viscosity of absorbents are requisite fundamental data for the process design of gas separation. These physical properties can also influence the absorption of gas in liquid. The detailed density and viscosity data of these PILs are still unknown. Therefore, we measured the density and viscosity of these PILs in the temperature range of (298.2 to 333.2) K at atmospheric pressure. The results are listed in Table 2 and plotted in Figure 3. It was found that the densities decrease linearly with the increasing temperature and alkyl chain on anion, whereas the viscosities decrease in an exponential manner for all PILs. As is known, viscosity is an important parameter that determines the diffusion of gas in liquid. Particularly, the NEM and TEA-based PILs exhibit much lower viscosity (< 40 mPa·s), which is regard to be helpful to the mass transfer of H₂S during the absorption. Compared with normal imidazolium-based ILs [11,12] and MDEA-based PILs in our previous work [14], the PILs have lower viscosities under same experimental conditions. However, the extremely high viscosity was observed due to the strong hydrogen bond network in [NHEMH][Ac] and [NHEMH][MOAc]. Therefore, the NEM and TEA-based PILs with lower viscosities are more applicable in the real case of H₂S capture.

The dependence of densities and viscosities on temperatures are presented by the first-order equation (2) and Arrhenius-like equation (3) [17], respectively. The correlations of temperatures dependence for densities and viscosities could be used to predict densities or viscosities for PILs especially when the temperatures are different from experimental extent, this method is useful for theoretical study and industrial application.

$$\rho = a_0 + a_1 T \tag{2}$$

$$\eta = \eta_0 e^{\frac{E_a}{RT}} \tag{3}$$

where a_0 , a_1 , and η_0 , are the undetermined parameters, E_a is activation energy, ρ and η are the densities and viscosities of PILs, respectively. These parameters could be obtained by fitting the experimental values to aforesaid equations.

Table 2.

Figure 3.

The thermal stability of absorbent is another important factor that identifies their practical application in industry, and a higher thermal decomposition temperature is necessary for the recycling circle. For organic acid-based PILs, the thermal decomposition temperatures (T_d) are usually low, and the substances of acid or amine with low boiling point might also evaporate in the TGA instrument under the same temperatures. Figure 4 shows the TG curve of the *N*-ethylmorpholine (NEM) and IL of [NEMH][Bu], the T_d of NEM appears to be below 50 °C although its boiling point is 115 °C under normal pressure. It is exciting to find that [NEMH][Bu] has higher T_d values (above 85 °C). The results showed that the volatility of amines could be effectively reduced by the formation of ionic liquids, which also helped to improve the reusability of the absorbent.

Figure 4.

3.2. Solubility of H₂S in carboxylate PILs

The solubility of H_2S in ten carboxylate PILs was measured at temperature of 298.2 K as a function of H_2S partial pressure. These solubility data are listed in Table 3 and plotted in Figure 5. It can be seen that the solubility of H_2S shows linear correlation with H_2S partial pressure,

which agreed well with characteristic of physical absorption. Particularly, the solubility of H₂S is highest in [NEMH][Bu] (Figure 5A), achieving 0.156 mole fraction at 1.056 bar and 298.2 K. In comparison with those normal ILs [11,12,18], the PILs exhibit a much better absorption capacity. For example, $[C_4Py][BF_4]$ and $[C_4Py][SCN]$ have the solubility of 0.07 and 0.10 molar fraction at 1.0 bar and 313.15 K, respectively [18]. However, the high viscosity was observed due to the strong hydrogen bond network in [NHEMH][Ac], leading to a long time of absorption equilibration. The [NHEMH][Ac] showed a lowest absorption capacity of H₂S under same absorption conditions (Figure 5B). For the same cation (Figure 5C), the solubility of H₂S increases with the increasing alkyl chain on anion. The solubility of H₂S decreases in the order [TEAH][Bu] > [TEAH][Pro] > [TEAH][Ac], which is consistent with the order of the alkalinity of the three anions. It is worth mentioning that the introduction of methoxy group shows positive effect on the H₂S solubility ([TEAH][Ac] vs [TEAH][MOAc]). These results indicated that both the alkalinity of anions and the ether oxygen atoms on the anions are beneficial to favoring the absorption of H₂S. The effect of different cations on the solubility of H₂S was also discussed (Figure 6). The solubility of H_2S with the same anion follows the sequence [NEMH][Ac] > [TEAH][Ac] > [NHEMH][Ac]. The champion solubility of H₂S in MEM-based PILs may be due to active sites of ether oxygen atom.

Table 3.

Figure 5.

Figure 6.

3.3. Henry's law constant

Gas solubility in the liquid is based on purely physical absorption and can be described generally in terms of Henry's law [19]. According to the result of the above H₂S absorption in carboxylate PILs, it can be described by Henry's law. The solubility of H₂S in these PILs can be expressed with Henry's constant based on mole fraction H_x as follows,

$$H_{x}(p,T) \equiv \lim_{x \to 0} \frac{f^{\mathrm{H}_{2}\mathrm{S}}(p,T,x)}{x} \cong \frac{p\varphi(p,T)}{x}$$
(4)

where H_x is the Henry's law constant based on the mole fraction, x is mole fraction of H₂S dissolved in PILs, f^{H_2S} is the fugacity of H₂S, p is the pressure of H₂S at equilibrium, and fugacity coefficient (φ) at relatively low pressure can be calculated using two-term Virial equation. Thus, H_x were obtained by calculating the linear slope of fugacity vs mole fraction of H₂S and are summarized in Table 4. It can be seen that the H_x of H₂S in these PILs at 298.2 K scatter from 6.9 to 11.0 bar with the lowest for [NEMH][Bu] and the largest for [NHEMH][Ac]. Comparison with some RTILs or solvents reported in the literatures [11-13,18,20-22], the present carboxylate PILs demonstrate competitive or superior absorption capacity of H₂S (Table 4) based on their Henry's law constant and molality concentrations. Therefore, owing to the low cost, low viscosity, and the considerable performance in H₂S absorption, carboxylate PILs are believed to be potential absorbents in the sweetening of natural gas, even though more work should be done before practical application.

Table 4.

3.4. Thermodynamic parameters

To investigate the effects of temperature on the H₂S absorption, [NEMH][Bu] was selected due to its excellent absorption property of H₂S. As shown in Figure 7, the solubility of H₂S decreases with the increasing temperature. The above results indicated that the absorbed H₂S can be stripped out from [NEMH][Bu] by heating or reducing of pressure. The thermodynamic parameters, such as dissolution enthalpy changes (ΔH), dissolution entropy changes (ΔS), and dissolution Gibbs free energy changes (ΔG), are important to understand and develop the H₂S capturing process. These data can reflect the dissolution behavior of H₂S in ionic liquids from the molecular level. Furthermore, these data are also crucial and essential for the design of process in gas separation technology. Based on the solubility data of H₂S at (298.2 to 318.2) K, three thermodynamic parameters, including ΔH , ΔS , and ΔG , can be deduced according to the following relationships [23,24]:

$$\Delta G = -\mathbf{R}T\ln(H_x/p_0) \tag{5}$$

$$\Delta G = \Delta H - T \Delta S \tag{6}$$

where R is the ideal gas constant (8.314 Pa·m³·mol⁻¹·K⁻¹), *T* is the absolute temperature, and the standard pressure $p_0 = 1$ bar. Here ΔH can reflect the intermolecular interaction between the absorbents and H₂S in the liquid phase, and ΔS is represents the change of solution order degree. The thermodynamic parameters of ΔH and ΔS , and ΔG are given in Table 6. As for the H₂S dissolving in [NEMH][Bu] under specific conditions, the negative ΔH indicates the absorption process is exothermic and that dissolution of H₂S in [NEMH][Bu] is also favorable from the enthalpy view, meanwhile, the low ΔH means easy desorption of the absorbents. The negative ΔS indicates that the solution became a higher ordering degree after the dissolution of H₂S from

molecular level. It was found that ΔG are always less than zero, which reveals the absorption processes of H₂S in [NEMH][Bu] is spontaneous and enthalpy driving behavior under the given conditions [23,24].

Figure 7.

Table 6.

Table 5.

The excellent absorption capacity of H_2S in [NEMH][Bu] enables the PILs an attractive substitute for the removal of H_2S . However, for practical application, the reusability of [NEMH][Bu] is very necessary. As expected, the absorbed H_2S can be released completely by bubbling N_2 at 80 °C in five absorption-desorption cycles, illustrating that the solvent can be recycled and reused (Figure 8). The regenerated [NEMH][Bu] was then reused for the measurement of gas solubility for the next cycle of H_2S absorption-desorption experiment. After five cycles of absorption and desorption processes, the absorption capacities of H_2S decline slightly within five cycles, which exhibit a relatively stable recyclability for H_2S absorption.

Figure 8.

3.5. Spectral properties

All above these results are much valuable for [NEMH][Bu] as best candidate among investigative PILs used for absorbing H_2S from a gaseous stream. In this case, FTIR and NMR were carried out to get the absorption mechanism of H_2S in [NEMH][Bu]. Compared the FTIR spectra before and after H_2S absorption in [NEMH][Bu] (Figure 9), no new peaks or a significant

shift of peaks can be observed, which means that the absorption process is physical absorptions [25]. In addition, the chemical shifts of all hydrogen atoms of [NEMH][Bu] moved downfield (Figure 10A), which is attribute to the solvent-induced shift based on the intermolecular interactions between H₂S and solvent molecule [26]. Notably, the chemical shift of protons (a + a') shifted from 3.72 to 3.58 ppm after H₂S absorption, indicating that strong hydrogen bond interactions have occurred between H₂S and ether oxygen atom on *N*-ethylmorpholine. Meanwhile, no obvious changes are found in ¹³C NMR (Figure 10B), suggesting that H₂S interacts physically with [NEMH][Bu]. From these results, it is evident that the H₂S gas must be physically absorbed in the [NEMH][Bu], providing no chemical bond between the IL and H₂S.

Figure 9.

Figure 10.

4. Conclusion

In summary, ten kinds of carboxylate PILs were synthesized for absorption of H_2S . Their densities and viscosities were measured over the range of (298.2 to 333.2) K, and the density and viscosity are found to decrease with the increasing temperature. The solubility of H_2S in these PILs increased with the increasing pressure and length of the alkyl chains on the carboxylic acid. Based on the results of spectra and absorption experiments, the absorption processes obeyed Henry's law within the given experimental conditions and Henry's constants were calculated from solubility data. The [NEMH][Bu] demonstrated a highest absorption capacity among these PILs and absorption of H_2S is a physical behavior. The results illustrated that carboxylate PILs are a kind of promising absorbents for separation of H_2S .

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Figure 1. Chemical structure of the PILs prepared in this work.

SCEPTION NAME



Figure 2. Apparatus for the determination of H_2S solubility. 1 H_2S gas cylinder; 2 storage tank of H_2S ; 3 equilibrium cell; 4 constant temperature bath; 5 pressure sensor; 6 real-time data acquisition instrument; 7 PC; 8 microthermometer; 9 vacuum pump.



Figure 3. The density (A) and viscosity (B) of carboxylate PILs from 298.2 to 338.2 K.

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Figure 4. The TG curves of the NEM and [NEMH][Bu], the decomposition temperatures T_d is defined as the temperature at which the IL loses 5% of its initial mass.

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Figure 5. Solubility of H_2S in PILs at 298.2 K as a function of H_2S partial pressure. (A):

NEM-based PILs; (B) NHEM-based PILs, (C): TEA-based PILs. lines: linear fit.

A CCC



Figure 6. The effect of different cations on the solubility of H_2S . lines: linear fit.

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Figure 7. The effect of temperature on the solubility of H₂S in [NEMH][Bu]. lines: linear

fit.



Figure 8. Absorption/desorption cycles of H₂S in [NEMH][Bu].

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Figure 9. FTIR spectra for [NEMH][Bu] before and after capture of H₂S.

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Figure 10. NMR spectra for [NEMH][Bu] before and after capture of H₂S, A: ¹H

NMR; B: ¹³C NMR..

Chemicals	Source	Purity (wt.%)	Purification method
N-ethylmorpholine	Energy Chemical,	\geq 99 %	Desiccation with 4A
	Shanghai, China		molecular sieve
4-(2-hydroxyethyl)	Energy Chemical,	\geq 99 %	Desiccation with 4A
morpholine	Shanghai, China		molecular sieve
Triethylamine	Aladdin Chemical, Beijing,	\geq 99 %	Desiccation with 4A
	China		molecular sieve
Acetic acid	Sinopharm Chemical,	\geq 99.5 %	None
	Shanghai, China		
Propanoic acid	Sinopharm Chemical,	≥99.5 %	None
	Shanghai, China		
Butyric acid	Sinopharm Chemical,	\geq 99 %	None
	Shanghai, China		
Methoxy acetic acid	Adamas Chemical, Adamas Adam		None
	Shanghai, China	6	
CDCl ₃	CIL (Cambridge	≥99 %	None
	Isotope Laboratories)		

Table 1. Specification of chemicals.

. (China Chemical, shai, China . (Cambridge pe Laboratories)

Table	2.	The	density	and	viscosity	data	of	carboxylate	PILs	from	(298.2	to	338.2)	Κ	at
atmosp	oher	ric pro	essure. ^a												

Carboyylata DIL a	Density (g·cm⁻³)				Viscos	ity (mPa	·s)		
Carboxylate Fills	298.2	308.2	318.2	328.2	338.2	298.2	308.2	318.2	328.2	338.2
[NEMH][Ac]	1.07289	1.06791	1.05789	1.04779	1.03758	9.4	5.8	3.8	3.5	3.0
[NEMH][Pro]	1.05636	1.05141	1.04144	1.03135	1.02112	4.3	3.6	3.2	3.0	2.8
[NEMH][Bu]	1.01312	1.00826	0.9985	0.98862	0.97862	6.7	5.0	3.6	3.3	2.9
[NEMH][MOAc]	1.14401	1.13924	1.12966	1.12002	1.11033	31.4	19.3	13.3	11.0	9.2
[NHEMH][Ac]	1.17027	1.16552	1.15589	1.1461	1.13611	105.2	59.3	33.0	19.6	14.4
[NHEMH][MOAc]	1.22612	1.22157	1.21235	1.20324	1.19394	552.5	252.1	126.3	68.1	54.6
[TEAH][Ac]	1.02572	1.02177	1.01384	1.00582	0.99771	14.2	10.1	7.6	5.9	5.1
[TEAH][Pro]	1.00117	0.99707	0.98882	0.98047	0.97200	11.4	8.9	6.7	5.2	4.8
[TEAH][Bu]	0.97824	0.97416	0.96591	0.95756	0.94907	15.3	10.7	8.1	6.4	5.4
[TEAH][MOAc]	1.09500	1.09110	1.08328	1.07547	1.06764	36.6	23.6	16.2	11.8	9.8

^{*a*} Standard uncertainties *u* are u(T) = 0.1 K, u(Density) = 0.00001 g/cm³ and u(Viscosity) = 1%.

$pH_2S(bar)$	xH_2S (mole fraction)	<i>p</i> H ₂ S(bar)	<i>x</i> H ₂ S(mole fraction)
	[NEMH][Ac]		[NEMH][Pro]
0.000	0.000	0.000	0.000
0.042	0.009	0.037	0.011
0.088	0.016	0.078	0.018
0.125	0.020	0.113	0.023
0.168	0.024	0.173	0.032
0.242	0.034	0.235	0.040
0.319	0.043	0.362	0.058
0.449	0.058	0.485	0.074
0.574	0.072	0.588	0.088
0.707	0.087	0.715	0.102
0.838	0.102	0.862	0.128
1.060	0.127	1.057	0.151
	[NEMH][Bu]	[]	NEMH][MOAc]
0.000	0.000	0.000	0.000
0.035	0.012	0.043	0.010
0.067	0.018	0.084	0.016
0.102	0.024	0.123	0.023
0.139	0.030	0.175	0.030
0.188	0.037	0.259	0.041
0.322	0.058	0.357	0.054
0.480	0.079	0.484	0.069
0.586	0.094	0.596	0.085
0.718	0.110	0.737	0.104
0.856	0.125	0.828	0.117
1.056	0.156	1.059	0.142
	$[NEMH][Bu]^b$		[NEMH][Bu] ^c
0.000	0.000	0.000	0.000
0.053	0.008	0.030	0.007
0.113	0.018	0.076	0.012
0.158	0.022	0.138	0.018
0.224	0.029	0.202	0.023
0.363	0.043	0.306	0.031
0.500	0.056	0.437	0.043
0.619	0.073	0.551	0.052
0.734	0.085	0.641	0.061
0.812	0.092	0.741	0.069
0.942	0.103	0.833	0.079
1.070	0.114	1.050	0.098

Table 3. Solubility data of H_2S in carboxylate PILs at 298.2 K.^{*a*}

<i>p</i> H ₂ S(bar)	xH_2S (mole fraction)	pH ₂ S(bar)	xH_2S (mole fraction)
	[NHEMH][Ac]	[NH	EMH][MOAc]
0.000	0.000	0.000	0.000
0.035	0.005	0.029	0.006
0.081	0.009	0.068	0.012
0.121	0.012	0.099	0.015
0.162	0.017	0.137	0.020
0.223	0.022	0.178	0.025
0.287	0.028	0.242	0.032
0.386	0.037	0.348	0.043
0.517	0.049	0.477	0.056
0.612	0.057	0.604	0.069
0.778	0.072	0.805	0.091
1.067	0.098	1.032	0.114
	[TEAH][Ac]		FEAH][Pro]
0.000	0.000	0.000	0.000
0.008	0.001	0.018	0.005
0.020	0.003	0.035	0.007
0.032	0.004	0.065	0.011
0.060	0.008	0.093	0.014
0.107	0.012	0.147	0.020
0.183	0.020	0.213	0.028
0.309	0.033	0.264	0.034
0.418	0.042	0.384	0.047
0.603	0.061	0.562	0.067
0.802	0.081	0.708	0.084
1.046	0.105	1.035	0.121
	[TEAH][Bu]	[TI	EAH][MOAc]
0.000	0.000	0.000	0.000
0.040	0.009	0.056	0.010
0.075	0.014	0.109	0.019
0.120	0.018	0.158	0.025
0.168	0.026	0.260	0.039
0.219	0.031	0.323	0.047
0.313	0.041	0.462	0.065
0.450	0.053	0.546	0.076
0.557	0.067	0.651	0.091
0.741	0.093	0.762	0.105
0.910	0.112	0.872	0.118
1.096	0.135	1.015	0.138

^aStandard uncertainties: u(T) = 0.1 K, u(p) = 0.001 bar, and u(x) = 0.002. ^bSolubility data of H₂S in [NEMH][Bu] at 308.2 K. ^cSolubility data of H₂S in [NEMH][Bu] at 318.2 K.

Solvents	<i>T</i> (K)	H_x (bar)	Solubility (mol H ₂ S/kg solvent)	Ref.
[NEMH][Ac]	298.2	8.7	0.79	This work
[NEMH][Pro]	298.2	7.2	0.90	
[NEMH][Bu]	298.2	6.9	0.88	
[NEMH][MOAc]	298.2	7.5	0.82	
[NHEMH][Ac]	298.2	11.0	0.53	
[NHEMH][MOAc]	298.2	9.3	0.57	
[TEAH][Ac]	298.2	10.0	0.69	
[TEAH][Pro]	298.2	8.7	0.76	
[TEAH][Bu]	298.2	8.4	0.74	
[TEAH][MOAc]	298.2	7.5	0.83	
[MDEAH][Ac]	303.2	5.5	1.35	[13]
[MDEAH][For]	303.2	11.5	0.84	[13]
[DMEAH][Ac]	303.2	3.5	1.12	[13]
[DMEAH][For]	303.2	5.9	0.61	[13]
[Bmim][BF ₄]	303.2	15.5	0.31	[12]
$[Bmim][PF_6]$	303.2	18.6	0.21	[12]
[Bmim][NTf ₂]	303.2	13.7	0.20	[12]
$[Hmim][PF_6]$	303.2	17.9	0.19	[11]
[Hmim][BF ₄]	303.2	12.5	0.35	[11]
[Hmim][NTf ₂]	303.2	17.4	0.15	[11]
[HOemim][PF ₆]	303.2	27.7	0.38	[20]
[HOemim][Tf ₂ N]	303.2	18.9	0.60	[20]
[HOemim][OTf]	303.2	19.3	0.76	[20]
Sulfolane	298.2	17.4	0.60	[21]
Dimethylsulfoxide	298.2	10.9	1.57	[22]
1-methyl-2-pyrrolidine	298.2	6.4	1.66	[22]
	X			
C				
	7			
X				

Table 5. Comparison of H_x (bar) and solubility (mol H₂S/kg solvent) in present carboxylate PILs with some ILs and solvents.

T/K	H_x	$\Delta G/\mathrm{kJ}\cdot\mathrm{mol}^{-1}$	$\Delta H/kJ \cdot mol^{-1}$	$\Delta S/J \cdot mol^{-1} \cdot K^{-1}$
298.2	6.9	-43.1		
308.2	9.4	-44.0	-19.2	80.5
318.2	11.2	-44.8		
				\sim
				\sim
			*	
)		

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Table 6. The calculated thermodynamic parameters of H₂S in [NEMH][Bu].

Research Highlinghts

- 1. Carboxylate protic ionic liquids (PILs) with low cost and viscosity for absorption of H₂S.
- 2. Solubilities of H_2S in ten carboxylate protic ionic liquids (PILs) were measured.
- 3. Thermodynamic parameters were obtained from solubility data.
- 4. Spectral properties were studied to insight into the absorption mechanism of H_2S .

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