

Solubility of H₂S in Ionic Liquids [bmim][PF₆], [bmim][BF₄], and [bmim][Tf₂N]

Amir Hossein Jalili,^{*,†} Mahboubeh Rahmati-Rostami,[‡] Cyrus Ghotbi,[‡] Masih Hosseini-Jenab,[†] and Amir Naser Ahmadi[†]

Gas Science Department, Research Institute of Petroleum Industry (R.I.P.I.), National Iranian Oil Company (NIOC), P.O. Box 14665-1998, West Boulevard., Azadi Sports Complex, Tehran, Iran, and Department of Chemical and Petroleum Engineering, Sharif University of Technology, Tehran, Iran

The solubility of hydrogen sulfide in three ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf₂N]), at temperatures ranging from (303.15 to 343.15) K and pressures up to 1 MPa was determined. The solubility data were correlated using the Krichevsky–Kasarnovsky equation, and Henry's law constants at different temperatures were obtained. From the solubility data, the partial molar thermodynamic functions of solution such as Gibbs energy, enthalpy, and entropy were calculated. Comparison showed that the solubility of H₂S in these three ionic liquids was in sequence: [bmim][Tf₂N] > [bmim][BF₄] > [bmim][PF₆].

Introduction

Hydrogen sulfide (H₂S) is produced along with methane and hydrocarbons in many gas fields as well as hydrodesulfurization processes of crude oils containing sulfur compounds.¹ Alkanolamines, especially monoethanolamine, diethanolamine, and methyldiethanolamine, are the main constituents of aqueous solutions used in industrial natural gas treating and sweetening plants.¹ There are some disadvantages in the commercial use of these alkanolamine solutions, including loss of alkanolamine and transfer of water into the gas stream during the desorption stage and degradation of alkanolamines to form corrosive byproducts, which makes the process economically expensive.²

Room-temperature ionic liquids (RTILs) are molten salts that are liquid over a wide temperature range including ambient.³ Their most remarkable characteristic is that they have negligibly small vapor pressure, meaning that ionic liquids are essentially nonvolatile, nonflammable, and odorless. They also have high thermal and electrochemical stability. Nowadays, one of the active research areas is to explore task-specific ionic liquids⁴ to replace conventional alkanolamine solutions for acid gas (CO₂ and H₂S) removal in gas sweetening processes.

One of the properties that is important in the evaluation of ionic liquids (ILs) for potential use in industrial natural gas treating processes is the knowledge about the solubility of gases at various temperatures and pressures. In the past few years, a growing number of measurements reporting CO₂ solubility in various ILs have become available. (See, for example, refs 5 to 10.) However experimental data for the solubility of hydrogen sulfide in ILs is scarce. Jou and Mather¹¹ have reported the solubility of H₂S in [bmim][PF₆] at temperatures from (298.15 to 403.15) K and pressures up to 9.6 MPa. They have correlated the experimental data by the Krichevsky–Kasarnovsky equation¹² to obtain Henry's law constant. The solubility of H₂S in different 1-butyl-3-methylimidazolium-based ILs with different anions and in a series of bis(trifluoromethyl) sulfonylimide ILs

with different cations at 298.15 K and 1400 kPa is reported by Pomelli et al.¹³ In addition, they have investigated the interaction between H₂S and the employed ILs by quantum chemical calculations.

In this work, the results of the measurement of the solubilities of H₂S in the three ILs, [bmim][PF₆], [bmim][BF₄], and [bmim][Tf₂N], at five temperatures from (303.15 to 343.15) K and pressures up to 1 MPa are reported. The solubilities determined were used to estimate Henry's law constants and partial molar thermodynamic functions of solution of H₂S at different temperatures.

Experimental Section

Materials. 1-Butyl-3-methylimidazolium hexafluorophosphate (174501-64-5), [bmim][PF₆], and 1-butyl-3-methylimidazolium tetrafluoroborate (174501-65-6), [bmim][BF₄], were supplied by Merck with nominal purities > 99 % and water mass fractions < 10⁻⁴. 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, (174899-83-3), [bmim][Tf₂N], was provided by Merck with nominal purity > 98 % and water mass fraction < 10⁻², and hydrogen sulfide (c.p. grade 99.5 % min) was obtained from Roham gas company. All of the materials were used without further purification.

Apparatus and Procedure. The experimental setup used in this work for solubility measurements is shown schematically in Figure 1. It consists of a high-pressure equilibrium cell and a H₂S gas container. All wetted compartments of the apparatus are constructed from stainless steel 316. The equilibrium cell was equipped with a graduated side glass to measure the volume of the liquid and gas phase inside the cell and a magnetically driven mechanical stirrer on the top (not shown in Figure 1) to facilitate heat and mass transfer inside the cell. The equilibrium cell was placed inside a water recirculation bath (Haake, model D8), the temperature of which was controlled to within 0.1 K. The equilibrium temperature was measured with a Lutron model TM-917 digital thermometer with a 0.01 K resolution using a Pt-100 sensor inserted into the cell. The pressure of the equilibrium cell was measured using a BD model D95199 pressure transmitter sensor in the range of (0 to 1) MPa, and

* Corresponding author. E-mail: jaliliah@ripi.ir. Tel/Fax: 98-21-44739591.

[†] National Iranian Oil Company (NIOC).

[‡] Sharif University of Technology.

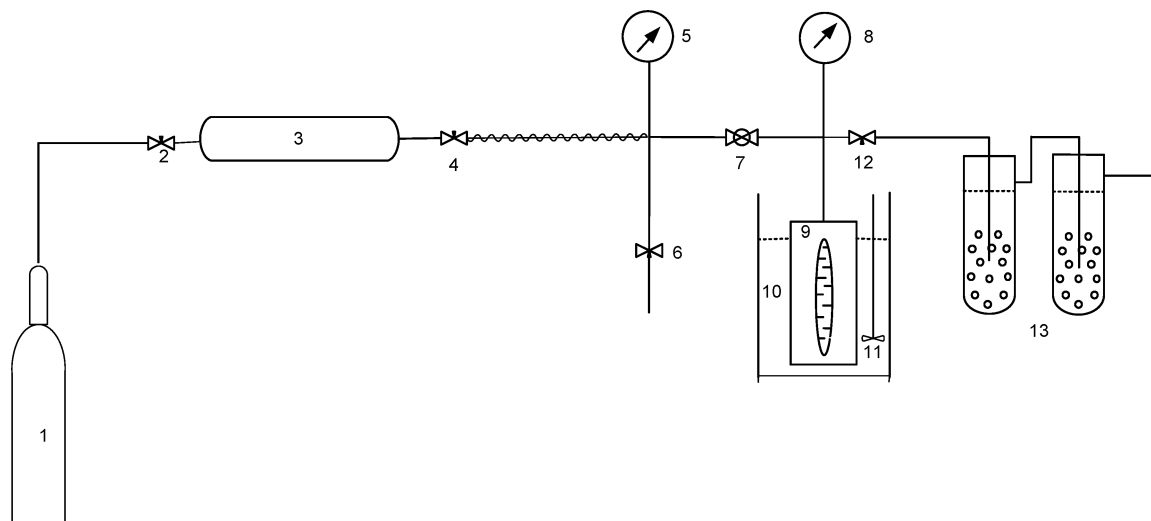


Figure 1. Apparatus for the measurement of the solubility of hydrogen sulfide in liquids: 1, H₂S gas cylinder; 2, needle valve; 3, H₂S gas container; 4, needle valve; 5, pressure sensor (transmitter); 6, ball valve; 7, needle valve; 8, pressure sensor (transmitter); 9, equilibrium cell; 10, water bath; 11, mixer; 12, needle valve; 13, H₂S gas scrubber.

Table 1. Mole Fraction Solubility of Hydrogen Sulfide Gas, x , in [bmim][PF₆]^a

p/kPa	x	p/kPa	x	p/kPa	x
$T = 303.15 \text{ K}$		$T = 313.15 \text{ K}$		$T = 323.15 \text{ K}$	
165	0.075	171	0.075	123	0.047
217	0.113	237	0.110	257	0.096
277	0.148	313	0.142	380	0.139
333	0.177	385	0.169	527	0.189
393	0.206	453	0.197	650	0.229
444	0.229	514	0.220	749	0.261
515	0.260	580	0.242	893	0.299
625	0.312	674	0.290	993	0.333
737	0.358	793	0.334		
826	0.405	905	0.369		
$T = 333.15 \text{ K}$		$T = 343.15 \text{ K}$			
137	0.044	229	0.065		
289	0.090	338	0.093		
424	0.130	447	0.121		
588	0.176	545	0.146		
726	0.213	642	0.171		
839	0.242	727	0.192		
1011	0.285	823	0.212		

^a Estimated uncertainty of the measured mole fractions is ± 0.002 .

that of the H₂S gas container was measured with a Druck model PTX 1400 pressure transmitter sensor in the range of (0 to 4) MPa. The pressure sensors were calibrated against a dead-weight gauge and were uncertain to within 0.1 % of full scale. The volumes of different compartments of the apparatus were measured using a calibrated bulb of known volume. This way, the calibrated bulb was connected to the apparatus via valve 12 (Figure 1). The whole system was evacuated, and then valve 12 was closed. We pressurized the apparatus to atmospheric pressure by opening valve 6 and allowing the temperature to equilibrate. The volume of the system, using the ideal gas law, was calculated from the pressure drop when valve 12 was again opened. We measured the volume of the calibrated bulb to within a tenth of a milliliter by filling the bulb with distilled water and then measuring the mass of the water by an analytical balance. The measured volume of the various parts of the apparatus was uncertain to within $\pm 0.2 \text{ mL}$.

The operation of the apparatus was carried out in such a way that at first, a known mass (about 10 g) of an IL was introduced to the equilibrium cell, and then the whole equipment (except gas container) was evacuated to pressures below 1.0 kPa by a

vacuum pump, and the temperature was raised to 343 K. The IL inside the cell was kept at this temperature under vacuum for at least 48 h to remove trace amounts of water and volatile impurities. The water content of ILs was carefully determined before the solubility measurements by a Karl Fischer volumetric titrator from Mettler model DL-37. In all cases, their water mass fraction was found to be below $(1 \pm 0.1) \cdot 10^{-4}$. (Several tests were done to check the time and the conditions for drying and degassing the IL sample. It was found that the IL was appropriately degassed and dried after it was pumped under a pressure of 1 Pa for about 24 h at a fixed temperature of 343 K.) The temperature was then adjusted to the desired value through the water bath, and a known amount of H₂S was introduced to the equilibrium cell from the gas container of a known volume. One can calculate the total number of moles of H₂S injected into the equilibrium cell from

$$n_{\text{H}_2\text{S}} = \frac{V_{\text{gc}}}{RT_{\text{gc}}} \left(\frac{P_i}{Z_i} - \frac{P_f}{Z_f} \right) \quad (1)$$

where V_{gc} denotes the volume of the gas container, Z_i and Z_f are the compressibility factors corresponding to the initial and final pressures, P_i and P_f , respectively in the gas container before and after transferring the H₂S, and T_{gc} is the temperature of the gas container. Compressibility factors were calculated using the Peng–Robinson (PR) equation of state.¹⁴ Mixing and equilibration between liquid and vapor phases inside the cell was normally achieved within about 2 h by the operation of the mechanical stirrer, and given an additional hour, the pressure of the equilibrium cell, $P_{\text{H}_2\text{S}}$, was read. The moles of remaining H₂S in the gas phase, $n_{\text{H}_2\text{S}}^g$, was determined from

$$n_{\text{H}_2\text{S}}^g = \frac{V_g P_{\text{H}_2\text{S}}}{Z_{\text{H}_2\text{S}} RT} \quad (2)$$

where V_g is the gas-phase volume, T is the equilibrium temperature of the cell, and $Z_{\text{H}_2\text{S}}$ is the compressibility factor of hydrogen sulfide at $P_{\text{H}_2\text{S}}$ and T . The moles of H₂S in the liquid phase was then determined from

$$n_{\text{H}_2\text{S}}^1 = n_{\text{H}_2\text{S}} - n_{\text{H}_2\text{S}}^g \quad (3)$$

Results and Discussion

The results of the measurement of the solubility of hydrogen sulfide in the three ILs considered in this work at temperatures of (303.15, 313.15, 323.15, 333.15, and 343.15) K and pressures up to 1 MPa are summarized in Tables 1, 2, and 3. To validate the reliability and accuracy of the data, we compared the solubility of hydrogen sulfide in [bmim][PF₆] obtained in this work with that of Jou and Mather¹¹ at temperatures of (313.15 and 343.15) K. The results are summarized in Figure 2 as percent fractional deviation of partial pressure of H₂S-[bmim][PF₆] obtained by quadratic interpolation of the data of Jou and Mather¹¹ from experimental values of this work. It can be observed that both of them are quite consistent with each other in the sense that the relative percent deviations (except one point at 313.15 K) are generally less than 4 %. The Krichevsky–Kasarnovsky equation¹² was used to model the experimental data obtained in this work

$$\ln\left(\frac{f_2}{x_2}\right) = \ln K_h + \frac{V_2^\infty(P - P_1^s)}{RT} \quad (4)$$

where f_2 is the fugacity of hydrogen sulfide in the gas phase, x_2 is the mole fraction of hydrogen sulfide in the solvent 1, P_1^s is the saturated vapor pressure of solvent 1, K_h is Henry's law constant of gas solute 2 in solvent 1 at the pressure, P , V_2^∞ is the partial molar volume of gas solute 2 at infinite dilution, R is the universal gas constant, and T is the absolute temperature. In this case, the vapor pressure of the solvent, the IL, is negligible; the saturated vapor pressure P_1^s is zero, and f_2 can be substituted by the fugacity of pure hydrogen sulfide gas, f_2^o . Equation 4 then can be turned to eq 5

$$\ln \frac{f_2^o}{x_2} = \ln K_h + \frac{V_2^\infty P}{RT} \quad (5)$$

The fugacity of hydrogen sulfide was calculated using the Peng–Robinson equation of state.¹⁴ The intercept of Krichevsky–Kasarnovsky plots (i.e., plots of $\ln(f_2^o/x_2)$ vs P) at each temperature, T , yields $\ln K_h$ at the specified temperature. The Henry's law constants are given in Table 4 for each of the ILs studied in this work together with their standard deviations. The Henry's law constants were fit by the equation

$$\ln(K_h/\text{MPa}) = \sum_{i=0}^2 A_i(T/\text{K})^{-i} \quad (6)$$

The parameters A_i of eq 6 obtained for each IL are summarized in Table 5. The Henry's law constants as a function of temperature are compared with each other in Figure 3 for the three ILs studied in this work. It can be observed that the solubility of hydrogen sulfide in the ILs decreases with increasing temperature, and it has the highest solubility in [bmim][Tf₂N] and the lowest solubility in [bmim][PF₆] among the ILs studied in this work. Also, the difference between the solubility of H₂S in [bmim][BF₄] and [bmim][Tf₂N] is low at the lower temperature limit and increases with increasing temperature. In their report, Pomeli et al.¹³ discuss that the

Table 2. Mole Fraction Solubility of Hydrogen Sulfide Gas, x , in [bmim][BF₄]^a

p/kPa	x	p/kPa	x	p/kPa	x
$T = 303.15 \text{ K}$		$T = 313.15 \text{ K}$		$T = 323.15 \text{ K}$	
60.8	0.039	71.8	0.038	83.8	0.035
124	0.081	146	0.076	170	0.074
188	0.120	221	0.111	257	0.110
293	0.163	346	0.166	401	0.168
328	0.183	387	0.180	450	0.187
411	0.228	485	0.220	562	0.225
524	0.270	568	0.250	613	0.240
624	0.310	644	0.280	757	0.280
736	0.354	757	0.320	813	0.303
$T = 333.15 \text{ K}$		$T = 343.15 \text{ K}$			
96.8	0.033	112	0.030		
195	0.070	222	0.066		
294	0.105	332	0.097		
459	0.150	518	0.149		
514	0.169	579	0.161		
639	0.201	718	0.203		
755	0.235	813	0.227		
836	0.269				

^a Estimated uncertainty of the measured mole fractions is ± 0.002 .

Table 3. Mole Fraction Solubility of Hydrogen Sulfide Gas, x , in [bmim][Tf₂N]^a

p/kPa	x	p/kPa	x	p/kPa	x
$T = 303.15 \text{ K}$		$T = 313.15 \text{ K}$		$T = 323.15 \text{ K}$	
94.4	0.070	107	0.065	120	0.060
177	0.128	200	0.120	224	0.114
246	0.174	279	0.163	313	0.157
297	0.209	338	0.196	379	0.188
350	0.241	399	0.227	447	0.219
406	0.273	464	0.258	521	0.252
478	0.307	547	0.291	615	0.293
583	0.364	667	0.347	751	0.340
715	0.444	825	0.434	888	0.403
826	0.510				
$T = 333.15 \text{ K}$		$T = 343.15 \text{ K}$			
133	0.055	146	0.051		
243	0.107	270	0.098		
345	0.148	378	0.134		
419	0.177	460	0.163		
494	0.206	542	0.190		
583	0.238	640	0.215		
682	0.272	748	0.246		
835	0.322	916	0.299		

^a Estimated uncertainty of the measured mole fractions is ± 0.002 .

solubility of hydrogen sulfide in [bmim][BF₄] is greater than that in [bmim][Tf₂N], whereas according to Table 2 of their article, there is no meaningful difference between the mole fraction solubility of H₂S in these two ILs within their mutual uncertainties. This may be due to the inherently low accuracy of the measurement method used in their work (i.e., quantitative NMR spectroscopy), the results of which cannot hence be used for this conclusion.

By means of eq 6 for the Henry's law constants and the parameters of Table 5 and also by quadratic extrapolation of the experimental P - x data of Tables 1, 2, and 3, the solubility of hydrogen sulfide in the ILs was estimated and compared with the values of Pomelli et al.¹³ at 298.15 K and 1.40 MPa. The results are summarized in Table 6. The estimated values obtained by quadratic extrapolation are in good agreement with those of Pomeli et al.¹³ and Jou and Mather¹¹ in all cases. In the case of [bmim][BF₄] and [bmim][Tf₂N], the mole fraction solubilities estimated from Henry's law constants of this work are about 12 % and 20 % higher than those of Pomeli et al.,¹³ respectively. This overestimation may be ascribed to the extrapolation of the

Table 4. Thermodynamic Properties of H₂S in the ILs

T	K_h	$\Delta_{\text{sol}}G^\infty$	$\Delta_{\text{sol}}H^\infty$	$\Delta_{\text{sol}}S^\infty$
K	MPa	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
[bmim][PF ₆]				
303.15	1.86 ± 0.02	7.37	-14.5	-72.2
313.15	2.16 ± 0.04	8.00	-13.8	-69.7
323.15	2.57 ± 0.02	8.72	-13.2	-67.8
333.15	3.09 ± 0.10	9.50	-12.6	-66.3
343.15	3.38 ± 0.05	10.0	-12.0	-64.2
[bmim][BF ₄]				
303.15	1.55 ± 0.01	6.91	-12.9	-65.5
313.15	1.91 ± 0.01	7.67	-13.0	-66.0
323.15	2.34 ± 0.01	8.47	-13.1	-66.6
333.15	2.85 ± 0.04	9.28	-13.1	-67.3
343.15	3.34 ± 0.02	10.0	-13.2	-67.6
[bmim][Tf ₂ N]				
303.15	1.37 ± 0.01	6.51	-13.0	-64.3
313.15	1.65 ± 0.04	7.24	-13.9	-67.4
323.15	1.89 ± 0.01	7.90	-14.8	-70.1
333.15	2.17 ± 0.05	8.48	-15.7	-72.6
343.15	2.66 ± 0.03	9.31	-16.6	-75.6

Table 5. Numerical Values of the Parameters A_0 to A_2 of Equation 6

	A_0	A_1	A_2
[bmim][PF ₆]	2.1073	839.94	-392.153
[bmim][BF ₄]	6.7632	-1797.5	-36474
[bmim][Tf ₂ N]	12.979	-6299	746.848

correlations for the Henry's law constants to a temperature beyond the temperature range studied in this work. This is also the case when one uses the K_h value of Jou and Mather¹¹ for estimation of the mole fraction solubility of H₂S in [bmim][PF₆] at 298.15 K. (See Table 6.) Also shown in Figure 3, are the Henry's law constants for the solubility of CO₂ in the ILs as a function of temperature, which indicates that hydrogen sulfide is more than three times as soluble as carbon dioxide in these ILs. Pomelli et al.¹³ have investigated the high solubility of hydrogen sulfide in ILs by means of quantum chemical calculations at the B3LYP and MP2 levels of theory using the CEP-121G(d,p) basis sets. Results of their calculations show that the acidic solute, H₂S, has the most energetic interaction [(7 to 14) kcal/mol] via its hydrogen

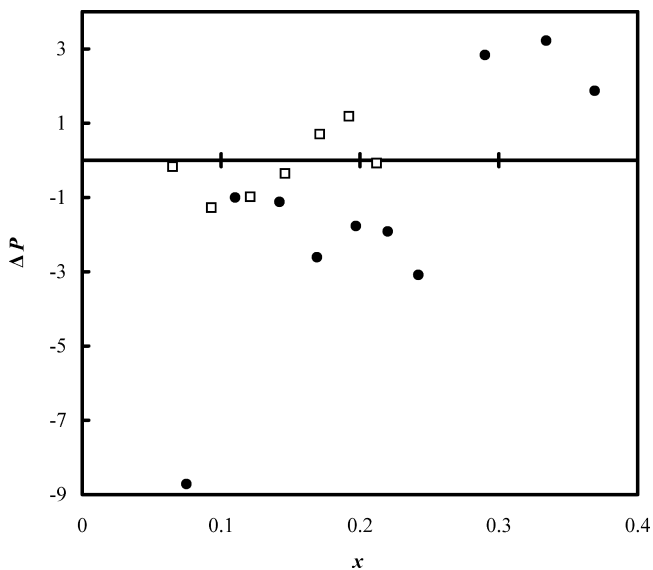


Figure 2. Fractional deviations, $\Delta P = [(P_{\text{Jou,Mather}} - P_{\text{This Work}}) \cdot 100] / P_{\text{This Work}}$, of the experimental partial pressures of H₂S + [bmim][PF₆] solutions obtained by Jou and Mather¹¹ from the values obtained in this work: ■, 313.15 K; □, 343.15 K.

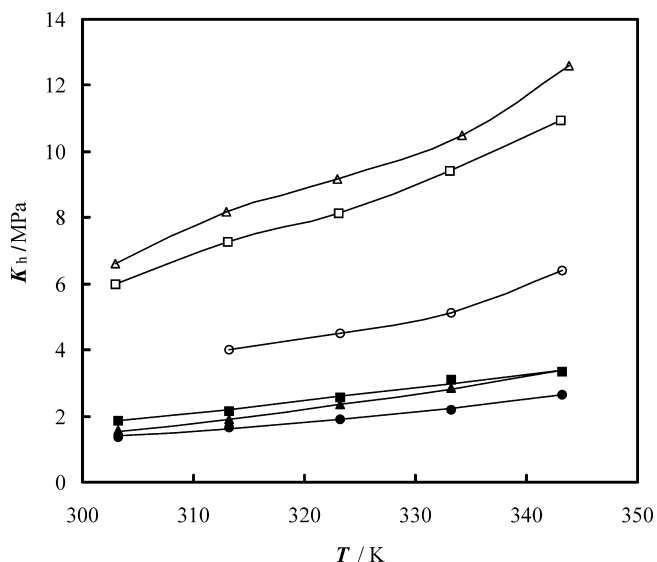


Figure 3. Comparison between Henry's law constants as a function of temperature for the solubility of H₂S and CO₂ in the ILs studied in this work: ■, H₂S in [bmim][PF₆]; ▲, H₂S in [bmim][BF₄]; ●, H₂S in [bmim][Tf₂N]; □, CO₂ in [bmim][PF₆] (ref 15); △, CO₂ in [bmim][BF₄] (ref 16); ○, CO₂ in [bmim][Tf₂N] (ref 17).

Table 6. Comparison between the Estimated Solubilities of H₂S, x , in the ILs of this Work with the Corresponding Data from Other Sources at 298.15 K and 1.40 MPa

	x (ref 13)	x (ref 11)	x (this work)
[bmim][PF ₆]	0.72 ± 0.02	0.87 ^a 0.66 ^b	0.75 ^a 0.71 ^b
[bmim][BF ₄]	0.79 ± 0.02		0.90 ^a 0.77 ^b
[bmim][Tf ₂ N]	0.77 ± 0.03		0.96 ^a 0.79 ^b

^a Estimated using Henry's law constant at 298.15 K. ^b Estimated from P - x data at 298.15 K.

atoms with fluorine atoms of the anions, which indicates that these interactions are as strong as the traditional hydrogen bond. In the case of nonpolar carbon dioxide, because of the absence of the hydrogen bonds and multipolar interactions with the anions, the solubilities are presumably lower than that of hydrogen sulfide. In Figure 4, the solubility of hydrogen sulfide in the ILs is compared with that of an aqueous 8.001 *m* solution of *N*-methyldiethanolamine (MDEA)¹⁸ at 313.15 K. MDEA is an example of chemical solvents that are currently employed in industrial natural gas treating plants. The pressure–molality absorption curve of these solvents in the presence of an acid gas is composed of two parts with different slopes. The low-pressure part with a low slope represents the absorption due to stoichiometric reaction between alkanolamine and the acid gas. When the overall molality of the sour gas surmounts the overall molality of MDEA, the total pressure increases steeply, and additional acid gas can no longer be absorbed chemically but rather must be dissolved physically. It can be observed that the solubility curve for the ILs resembles the high-pressure region of MDEA, and the molality of H₂S has not reached that of ILs, even at the high pressure of 0.9 MPa. This indicates that the solubility of H₂S in the ILs studied in this work is typical of that of physical solvents, therefore obeying the Henry's law.

The variation with temperature of the solubility of H₂S studied, expressed in Henry's law constant, is directly related to the thermodynamic properties of solution, which, in the

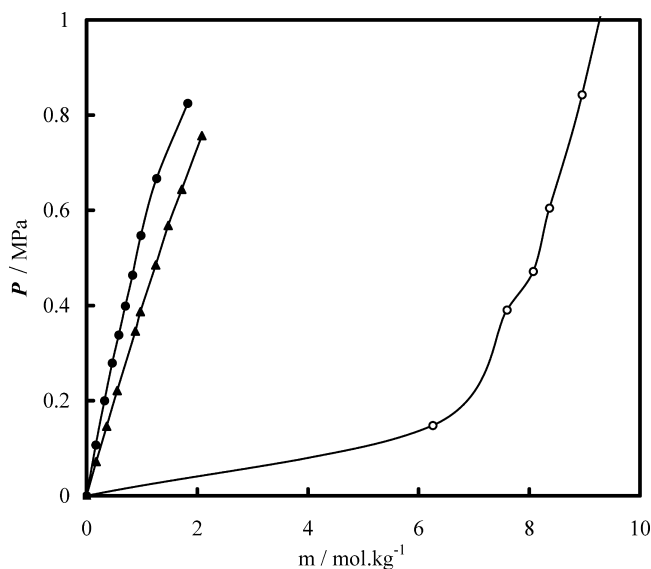


Figure 4. Comparison between the solubility of hydrogen sulfide as molality, m , in the ILs and an aqueous solution of *N*-methyldiethanolamine (MDEA) at $T = 313.15$ K: ●, H_2S in [bmim][Tf₂N]; ▲, H_2S in [bmim][BF₄]; ○, H_2S in aqueous MDEA solution ($m_{\text{MDEA}} = 8.001 \text{ mol}\cdot\text{kg}^{-1}$) (ref 18).

case of gaseous solutes at low pressures, are practically identical to the thermodynamic properties of solution.¹⁵ The Gibbs energy of solution, corresponding to the change in Gibbs energy when the solute is transferred at constant temperature from the pure perfect gas at the standard pressure to the standard state of infinite dilution of the solute in the solvent, is given by¹⁵

$$\Delta_{\text{sol}}G^{\infty} = RT \ln\left(\frac{K_{\text{h}}}{P^0}\right) \quad (7)$$

where P^0 is the standard-state pressure. The partial molar differences in enthalpy and entropy between the two states can be obtained by calculating the corresponding partial derivatives of the Gibbs energy with respect to temperature

$$\Delta_{\text{sol}}H^{\infty} = -T^2 \frac{\partial}{\partial T} \left(\frac{\Delta_{\text{sol}}G^{\infty}}{T} \right) = -RT^2 \frac{\partial}{\partial T} \left[\ln\left(\frac{K_{\text{h}}}{P^0}\right) \right] \quad (8)$$

$$\Delta_{\text{sol}}S^{\infty} = \frac{(\Delta_{\text{sol}}H^{\infty} - \Delta_{\text{sol}}G^{\infty})}{T} \quad (9)$$

The pressure range considered in this work is not too high to cause the Henry's law constant to be a strong function of pressure, and it is weakly dependent on pressure under the specified conditions. Therefore, it does not give rise to large errors if we ignore this pressure dependency. By means of this approximation, and by using eqs 7, 8, and 9, we estimated the thermodynamic functions of solution at infinite dilution for H_2S in the ILs. The values for the Gibbs energy, enthalpy, and entropy of solution are given in Table 4 for H_2S in [bmim][PF₆], [bmim][BF₄], and [bmim][Tf₂N] at five discrete temperatures between (303.15 and 343.15) K. As can be observed, the $\Delta_{\text{sol}}G^{\infty}$ values are positive and are lowest for [bmim][Tf₂N] and highest for [bmim][PF₆] and increase with temperature in a similar manner for all of the ILs. The $\Delta_{\text{sol}}H^{\infty}$

values and $\Delta_{\text{sol}}S^{\infty}$ values are negative. The variation with temperature of the $\Delta_{\text{sol}}H^{\infty}$ values and $\Delta_{\text{sol}}S^{\infty}$ values in [bmim][PF₆] is different from the other two ILs because they increase with temperature, whereas in the case of [bmim][BF₄] and [bmim][Tf₂N], they decrease by increasing temperature being more negative at the high temperature relative to the low-temperature limit. This effect is more enhanced in the case of [bmim][Tf₂N]. From a molecular point of view, this effect may be ascribed to the stronger solute–solvent interaction and the more free-volume contribution in the case of [bmim][Tf₂N] as compared with the other two ILs.

Conclusions

New experimental data for the solubility of hydrogen sulfide in the ILs [bmim][PF₆], [bmim][BF₄], and [bmim][Tf₂N] not previously reported in the literature have been measured and presented in this work. The data for [bmim][PF₆] of this work are quite consistent with the solubility data at (313.15 and 343.15) K of Jou and Mather and the solubility data of Pomelli and his coworkers at 298.15 K and 1.40 MPa. The solubility of hydrogen sulfide in the studied ILs is in the order [bmim][Tf₂N] > [bmim][BF₄] > [bmim][PF₆]. The solubility of hydrogen sulfide in the ILs studied in this work is of a physical nature and is much higher than that of carbon dioxide, indicating that these solvents can be used for the separation of these two gases from each other.

Literature Cited

- (1) Kohl, A. L.; Nielsen, R. B. *Gas Purification*, 5th ed.; Gulf Publishing Company: Houston, TX, 1997.
- (2) Galán Sánchez, L. M.; Meindersma, G. W.; de Haan, A. B. Solvent Properties of Functionalized Ionic Liquids for CO₂ Absorption. *Trans. Inst. Chem. Eng., Part A* **2007**, *85*, 31–39.
- (3) Wilkes, J. S. In *Ionic Liquids in Synthesis*; Wassercheid, P., Welton, T., Eds.; Wiley VCH: Weinheim, Germany, 2002.
- (4) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. CO₂ Capture by a Task-Specific Ionic Liquid. *J. Am. Chem. Soc.* **2002**, *124*, 926–927.
- (5) Shariati, A.; Peters, C. J. High Pressure Phase Equilibria of Systems with Ionic Liquids. *J. Supercrit. Fluids* **2005**, *34*, 171–176.
- (6) Kim, Y. S.; Choi, W. Y.; Jang, J. H.; Yoo, K.-P.; Lee, C. S. Solubility Measurement and Prediction of Carbon Dioxide in Ionic Liquids. *Fluid Phase Equilib.* **2005**, *228–229*, 439–445.
- (7) Kroon, M. C.; Shariati, A.; Constantini, M.; van Spronsen, J.; Witkamp, G.-J.; Sheldon, R. A.; Peters, C. J. High-Pressure Phase Behavior of Systems with Ionic Liquids: Part V. The Binary System Carbon Dioxide + 1-Butyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2005**, *50*, 173–176.
- (8) Constantini, M.; Toussaint, V. A.; Shariati, A.; Peters, C. J.; Kikic, I. High-Pressure Phase Behavior of Systems with Ionic Liquids. Part IV. Binary System Carbon Dioxide + 1-Hexyl-3-methylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2005**, *50*, 52–55.
- (9) Blanchard, L. A.; Gu, Z.; Brennecke, J. F. High-Pressure Phase Behavior of Ionic Liquid/CO₂ Systems. *J. Phys. Chem. B* **2001**, *105*, 2437–2444.
- (10) Aki, S. N. V. K.; Mellein, B. R.; Saurer, E. M.; Brennecke, J. F. High-Pressure Phase Behavior of Carbon Dioxide with Imidazolium-Based Ionic Liquids. *J. Phys. Chem. B* **2004**, *108*, 20355–20365.
- (11) Jou, F.-Y.; Mather, A. E. Solubility of Hydrogen Sulfide in [bmim][PF₆]. *Int. J. Thermophys.* **2007**, *28*, 490–495.
- (12) Krichevsky, I. R.; Kasarnovsky, J. S. Thermodynamical Calculations of Solubilities of Nitrogen and Hydrogen in Water at High Pressures. *J. Am. Chem. Soc.* **1935**, *57*, 2168–2171.
- (13) Pomelli, C. S.; Chiappe, C.; Vidis, A.; Laurenczy, G.; Dyson, P. J. Influence of the Interaction Between Hydrogen Sulfide and Ionic Liquids on Solubility: Experimental and Theoretical Investigation. *J. Phys. Chem. B* **2007**, *111*, 13014–13019.
- (14) Peng, D.-Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fund.* **1976**, *15*, 59–64.
- (15) Jacquemin, J.; Husson, P.; Majer, V.; Costa Gomes, M. F. Low-Pressure Solubilities and Thermodynamics of Solvation of Eight Gases in 1-Butyl-3-methylimidazolium Hexafluorophosphate. *Fluid Phase Equilib.* **2006**, *240*, 87–95.

- (16) Jacquemin, J.; Costa Gomes, M. F.; Husson, P.; Majer, V. Solubility of Carbon Dioxide, Ethane, Methane, Oxygen, Nitrogen, Hydrogen, Argon, and Carbon Monoxide in 1-Butyl-3-methylimidazolium Tetrafluoroborate between Temperatures 283 and 343 K and at Pressures Close to Atmospheric. *J. Chem. Thermodyn.* **2006**, *38*, 490–502.
- (17) Unpublished results from our laboratory.
- (18) Kamps, A. P.-S.; Balaban, A.; Jödecke, M.; Kuranov, G.; Smirnova, N. A.; Maurer, G. Solubility of Single Gases Carbon Dioxide and Hydrogen Sulfide in Aqueous Solutions of *N*-methyldiethanolamine at Temperatures from 313 to 393 K and Pressures up to 7.6 MPa:

New Experimental Data and Model Extension. *Ind. Eng. Chem. Res.* **2001**, *40*, 696–706.

Received for review December 8, 2008. Accepted March 5, 2009. We thank the research council of the Research Institute of Petroleum Industry and also the Research and Development of the National Iranian Oil Company for their support of this work.

JE8009495