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Solubility of Hydrogen Sulfide in [bmim][PF$_6$]

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New experimental data are presented for the solubility of hydrogen sulfide in the ionic liquid 1-*N*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$]) at five temperatures in the range (298–403) K at pressures up to 9.6 MPa. The ionic liquid [bmim][PF$_6$] is a good solvent for hydrogen sulfide. At 9 MPa the mole fraction H_2S in the liquid is about 0.7. The solubility is a strong function of temperature; at 2 MPa the solubility (mole fraction H_2S) decreases from about 0.84 at 298 K to about 0.2 at 403 K.
The Krichevsky–Kasarnovsky equation was used to correlate the experimental data, and Henry's constants were obtained. The solution thermodynamic properties at standard temperature and pressure were calculated.

KEY WORDS: Henry's constants; hydrogen sulfide; ionic liquid; solubility.

1. INTRODUCTION

Ionic liquids have been proposed for the separation of gas mixtures. In particular, ionic liquids have been suggested for the removal of the acid gases, hydrogen sulfide, and carbon dioxide, from natural gases and refinery gases. At present, the method most used is absorption in aqueous alkanolamine solutions with desorption by the reduction of pressure and heating of the solution. Although these aqueous alkanolamine solutions are in commercial use, there are some disadvantages in using them. There is the loss of the volatile alkanolamine and the transfer of water into the gas stream. As well, the energy required for regeneration is rather large (up to 80 kJ/mol solute). For these reasons the use of ionic liquids was considered [1,2]. The work was undertaken to determine if a typical

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ionic liquid was suitable for replacement of alkanolamines in gas treating for the removal of hydrogen sulfide.

2. EXPERIMENTAL SECTION

The experimental apparatus has been described previously [3], and only a short description will be provided here. The equilibrium cell was mounted in an air bath. The temperature of the contents of the cell was measured by a calibrated iron-constantan thermocouple (Type J) and the pressure in the cell was measured with digital Heise gauges (0–10, 0–35 MPa). The uncertainty in the temperature measurement is 0.1°C and the uncertainty of the pressure gauges is 0.1% of full scale.

The ionic liquid, 1-*N*-butyl-3-methylimidazolium hexafluorophosphate, hereafter called [bmim][PF_6], was obtained from Solvent Innovation GmbH, Cologne, Germany and had a purity of 98%. Hydrogen sulfide (c.p. grade) was obtained from Praxair.

Prior to the introduction of the fluids, the cell was evacuated at 80°C for 2 h and then about 80 cm^3 of ionic liquid was drawn into the cell. Since the ionic liquid has almost no vapor pressure at 80°C, impurities such as water and air were removed by purging with dry hydrogen sulfide. Then hydrogen sulfide was added to the cell by the cylinder pressure or by means of a spindle press, depending upon the pressure desired. The circulation pump was started and the vapor bubbled through the solvent for at least 8 h to ensure that equilibrium was reached.

The ionic liquid was analyzed from time to time by gas chromatography for water content. The water peak area was compared with that of a known quantity of water in ethylene glycol. The water content of the ionic liquid was found to be 0.05–0.1 mass%.

A sample of the ionic liquid was taken into a 40 mL bomb containing enough 1.0 N NaOH to convert the hydrogen sulfide to involatile sulfide ion. An aliquot of the aqueous portion was titrated by iodimetry. No trace of sulfide ion was found in the ionic liquid phase. Due to the limited solubility between the ionic liquid and the aqueous portion, the solubility of hydrogen sulfide in the ionic liquid was calculated by an iterative procedure similar to that used for carbon dioxide.

The uncertainty of the liquid phase analyses is estimated to be 2%.

3. RESULTS AND DISCUSSION

The solubility of hydrogen sulfide in [bmim][PF_6] was measured at temperatures of (298.15, 313.15, 343.15, 373.15, 403.15) K at pressures up to 9.6 MPa. The results are given in Table I and plotted in Fig. 1. The

Table I. Solubility of Hydrogen Sulfide in [bmim][PF_6]

P (kPa)	Mole fraction H_2S	P (kPa)	Mole fraction H_2S	P (kPa)	Mole fraction H_2S
$T = 298.15$ K		$T = 313.15$ K		$T = 343.15$ K	
2120[a]	0.875	2890[b]	0.853	5400[b]	0.792
2100[b]	0.873	1850	0.616	3650	0.631
2000	0.840	1020	0.401	2380	0.482
1700	0.739	620	0.267	1590	0.364
1100	0.540	335	0.153	800	0.210
559	0.317	115	0.056	800(repeat)	0.213
276	0.175			310	0.090
128	0.086			120	0.035
115	0.077				
69.0	0.046				
$T = 373.15$ K		$T = 403.15$ K			
9200	0.767	9630	0.643		
7500	0.709	7020	0.545		
4700	0.555	4210	0.401		
2490	0.357	2530	0.269		
960	0.161	1150	0.135		
332	0.059	630	0.076		
135	0.025	262	0.032		
		132	0.016		

[a] Three-phase point (vapor, [bmim][PF_6]-rich liquid, H_2S-rich liquid).
[b] Dew point.

experimental data were modeled by the Krichevsky–Kasarnovsky [4] equation:

$$\ln\left(\hat{f}_2/x_2\right) = \ln H_{21} + \frac{\bar{v}_2^{\infty}(P - P_1^{s})}{RT} \tag{1}$$

Here $\hat{f}_2$ is the fugacity of hydrogen sulfide, x_2 is the mole fraction hydrogen sulfide in the liquid phase, H_{21} is Henry's constant, $\bar{v}_2^{\infty}$ is the partial molar volume of hydrogen sulfide at infinite dilution, P is the total pressure, P_1^{s} is the vapor pressure of the solvent, R is the universal gas constant, and T is the absolute temperature. The fugacity of the hydrogen sulfide was calculated by the Peng–Robinson [5] equation of state. The Krichevsky–Kasarnovsky plots are shown in Fig. 2. The curves at lower temperatures were fit by quadratic functions, while the curve at 403.15 K was fit by a linear function of pressure. The intercepts at the ordinate are

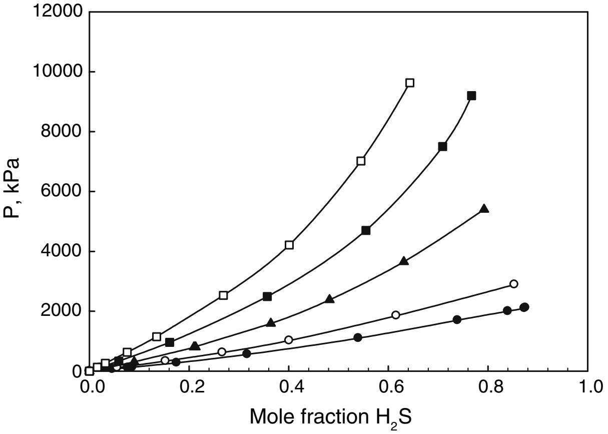

Fig. 1. Solubility of hydrogen sulfide in [bmim][PF$_6$]: ● 298.15 K; ○ 313.15 K; ▲ 343.15 K; ■ 373.15 K; □ 403.15 K.

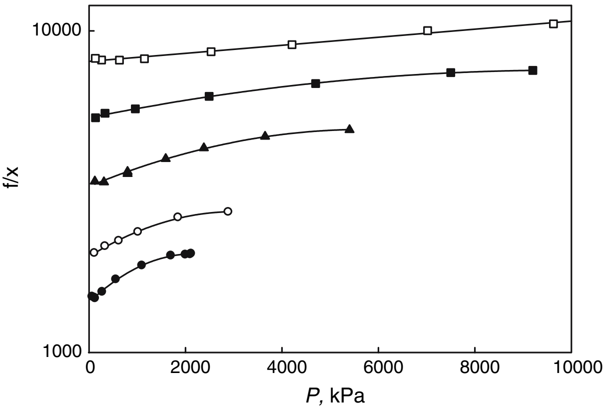

Fig. 2. Krichevsky–Kasarnovsky plot: ● 298.15 K; ○ 313.15 K; ▲ 343.15 K; ■ 373.15 K; □ 403.15 K.

the values of the Henry's constants. They are given in Table II, with their standard deviations.

The values were fit by the equation,

$$\ln H_{21} = 13.85 - \frac{1963.8}{T} \tag{2}$$

where H_{21} is in MPa.

Table II. Henry's Constant of Hydrogen Sulfide in [bmim][PF_6]

T (K)	H_{21} (MPa)	ΔH_{21} (MPa)
298.15	1.43	0.01
313.15	1.98	0.02
343.15	3.26	0.04
373.15	5.35	0.03
403.15	8.01	0.06

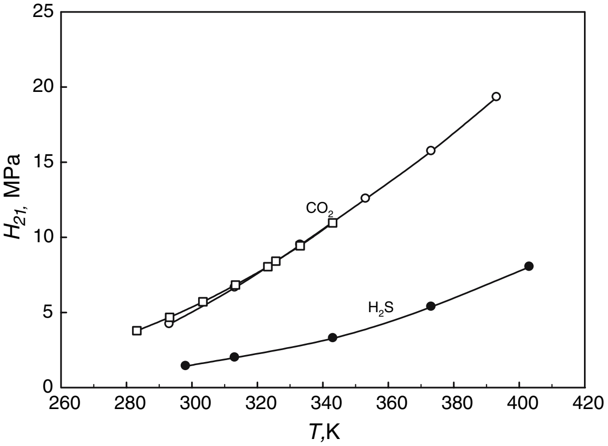

Fig. 3. Henry's constants for H_2S and CO_2 in [bmim][PF_6]; • This work; ○ Ref. [6]; □ Ref. [7].

Figure 3 shows a comparison with the values of the Henry's constant for CO_2 in [bmim][PF_6]. The values of Pérez-Salado Kamps et al. [6] were first converted to a mole fraction scale. There is good agreement between the two sets of data for CO_2 where they overlap. Hydrogen sulfide is about three times as soluble as carbon dioxide in this ionic liquid.

A knowledge of the temperature dependence of the Henry's constant allows calculation of the thermodynamic properties of solvation as shown by Jacquemin et al. [7]. The values for hydrogen sulfide are given in Table III for comparison with those for carbon dioxide. Again the values of Pérez-Salado Kamps et al. [6] were converted to a mole fraction scale.

The Gibbs energy of solvation for hydrogen sulfide is smaller than that for carbon dioxide, which in turn was the smallest value of the eight gases studied by Jacquemin et al. [7]. The enthalpy of solvation of carbon

Table III. Thermodynamic Properties of Solvation at $T = 298.15$ K and $p = 0.1$ MPa

	H_2S	CO_2 [7]	CO_2 [6]
$\Delta_{sol}G^{\infty}$ (kJ·mol^{-1})	6.59	9.78	9.59
$\Delta_{sol}H^{\infty}$ (kJ·mol^{-1})	−16.3	−14.4	−17.1
$\Delta_{sol}S^{\infty}$ (J·mol^{-1}·K^{-1})	−76.9	−81.1	−89.5

dioxide was the most negative, and again the value for hydrogen sulfide is similar, indicating an exothermic solvation. The entropy of solvation is similar to the values found for the eight gases studied by Jacquemin et al. [7].

4. CONCLUSIONS

The dependence of the solubility of hydrogen sulfide in [bmim][PF$_6$] on pressure is typical of that of “physical” solvents. This is also the case of carbon dioxide as shown by Pérez-Salado Kamps et al. [6]. Hence, it is unlikely that ionic liquids can supplant alkanolamines for the removal of hydrogen sulfide and carbon dioxide from gas streams. They would be useful only for bulk removal of the acid gases, when the partial pressure of the acid gases is high. They are unable to reduce the concentration of the acid gases to the low levels required in gas processing.

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REFERENCES

1. J. L. Anthony, E. J. Maginn, and J. F. Brennecke, *ACS Symp. Ser.* **818**:260 (2002).
2. E. D. Bates, R. D. Mayton, I. Ntai, and J. H. Davis, Jr., *J. Am. Chem. Soc.* **124**:926 (2002).
3. F.-Y. Jou, A. E. Mather, and F. D. Otto, *Can. J. Chem. Eng.* **73**:140 (1995).
4. I. R. Krichevsky and J. S. Kasarnovsky, *J. Am. Chem. Soc.* **56**:2168 (1935).
5. D.-Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fund.* **15**:59 (1976).
6. Á. Pérez-Salado Kamps, D. Tuma, J. Xia, and G. Maurer, *J. Chem. Eng. Data* **48**:746 (2003).
7. J. Jacquemin, P. Husson, V. Majer, and M. F. Costa Gomes, *Fluid Phase Equilib.* **240**:87 (2006).