

RESEARCH PROJECT No. 1510

**Acid Gas Removal Using Ionic Liquids**

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## ABSTRACT

The solubility of carbon dioxide in the ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]), has been determined at six temperatures in the range from 25 °C to 130 °C at pressures up to 16.0 MPa. The disagreement between previously published data in the literature has been resolved. The solubility of hydrogen sulfide in the same ionic liquid has been determined at five temperatures in the range from 25 °C to 130 °C at pressures up to 9.6 MPa. The use of this ionic liquid is suitable for bulk removal of acid gases, which are present in high concentrations. However, the current methods using alkanolamine solutions are more suitable for typical natural gases.

## KEYWORDS

Ionic liquid, acid gases, carbon dioxide, hydrogen sulfide, solubility

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## INTRODUCTION

Most natural gases in Alberta contain significant amounts of the acid gases, hydrogen sulfide and carbon dioxide. They must be removed in the process of making the gas useful for fuel, as the hydrogen sulfide is toxic and the carbon dioxide reduces the heating value of the gas stream. The method used for the removal of the acid gases from natural gas (and refinery gases) is absorption in an aqueous solution of a weak base, commonly an alkanolamine. The acid gases are recovered from the solution by heating and by reduction of the pressure. The major costs involved in this method of treating gases are the energy required for regeneration of the solution, the energy required to recirculate the solution, and the unavoidable loss of amine into the treated gas because of the vapour pressure of the solution.

Recently, a new class of solvents, ionic liquids, has been discovered. These ionic liquids have gained popularity as solvents for a variety of applications [1]. A typical ionic liquid consists of a relatively large ionic cation and an inorganic or organic anion. A typical example is 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]). Such compounds have negligible vapour pressure at room temperature and are stable over a wide range of temperatures. The purpose of this research is to determine if ionic liquids have advantages in the removal of acid gases from gas streams.

## EXPERIMENTAL SECTION

The experimental apparatus has been described previously [2] and only a short description will be provided. A schematic diagram of the apparatus is presented as Figure 1. 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 accuracy of the thermocouple is  $\pm 0.1$  °C and the accuracy of the pressure gauges is  $\pm 0.1$  % of full scale.

The ionic liquid, 1-*n*-butyl-3-methylimidazolium hexafluorophosphate, hereafter called [bmim] [PF<sub>6</sub>], was obtained from Solvent Innovation GmbH, Cologne, Germany and had a purity of 98%. Nitrogen and carbon dioxide (both with purities greater than 99.99%) were obtained from Praxair. Certified 0.1 N and 1.0 N HCl, as well as monoethanolamine (MEA) were obtained from Fisher Scientific. The water content of the MEA as purchased was determined by gas chromatography to be 0.3 wt. %. Deionized water was used in the preparation of MEA solutions.

Prior to the introduction of the fluids, the cell was evacuated at 80 °C for 2 h and then about 80 cm<sup>3</sup> of ionic liquid was drawn into the cell. Since the ionic liquid has almost no vapour pressure at 80 °C, impurities such as water and air were removed by purging with dry carbon dioxide. Then carbon dioxide or 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 vapour bubbled through the solvent for at least 8 h to ensure that equilibrium was reached.

The ionic liquid was analysed 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 to 0.1 mass per cent.

## Carbon Dioxide Analysis

A HP 5890 gas chromatograph with a thermal conductivity detector was used for the analysis. A column of 2 m x 3.175 mm OD stainless steel, packed with 80/100 mesh Chromosorb 104 was programmed at 160 °C for 1.5 min and then ramped at 64 °C/min to 250 °C. The helium flow rate was 40 mL/min. A glass-lined injection port and detector block were maintained at 260 °C.

The injection of the ionic liquid was attempted. The H<sub>2</sub>O and CO<sub>2</sub> peaks appeared at 160 °C and were well-separated, but the ionic liquid did not appear after one hour. It was found that the ionic liquid remained on the wall of the injection port and did not enter the chromatographic column. Hence this method of analysis was abandoned.

A sample of the liquid phase was withdrawn from the cell into a weighed 40 cm<sup>3</sup> sample bomb, which contained a 50 wt% aqueous solution of monoethanolamine (MEA). The pressure in the bomb was about 10 kPa to make the sampling easier. The sample bomb was reweighed to determine the mass of the sample. After complete mixing, the contents of the bomb were transferred to a 250 mL Erlenmeyer flask. When the two phases were well-separated, a 2 µL sample of the aqueous liquid was taken with a 10 µL syringe for injection into the chromatograph and a sample with a 0.5 mL syringe for the determination of the density and subsequent titration of the MEA. The retention times (min) are: H<sub>2</sub>O: 0.39, CO<sub>2</sub>: 0.74, MEA: 4.56. The standards used for the analysis were an aqueous solution of 50 wt% MEA (actual value: 49.842 % MEA) and 5-50 µL of carbon dioxide. Since the aqueous liquid contains a small amount of ionic liquid, which accumulates after each injection, the glass liner and the initial few cm of the chromatographic column must be replaced after about 50 injections. The ionic liquid phase was found to contain no carbon dioxide, confirming that the MEA solution had extracted it completely.

Another method of analysis, precipitation of carbon dioxide as BaCO<sub>3</sub>, was also used to confirm the chromatographic analysis. A sample of the ionic liquid from the cell was taken in a weighed 40 cm<sup>3</sup> sample bomb containing enough NaOH solution to convert all the CO<sub>2</sub> to involatile ionic species. The contents of the bomb were transferred to a 250 mL Erlenmeyer flask containing excess BaCl<sub>2</sub> solution. The bomb was washed

three times with deionized water and the water poured into the flask. The precipitation took 5-7 days to reach completion due to the very small particles of  $\text{BaCO}_3$  that form. Filter paper #5 was used for the filtration. It is important that the ionic liquid not come into contact with the filter paper. The filter paper and the precipitate were transferred to another flask and 100 mL of deionized water was added. The filter paper was shredded by the magnetic stirring bar and the titration was carried out with either 0.1 N or 1.0 N HCl. Air was used to purge any  $\text{CO}_2$ . The end point was determined by a pH meter, at a pH of  $5.4 \pm 0.1$ .

#### Hydrogen Sulfide Analysis

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. The aqueous portion was titrated by iodimetry. No trace of sulfide ion was found in the ionic liquid phase. Because of the limited solubility between the ionic liquid and the aqueous portion, the solubility of hydrogen sulphide in the ionic liquid was calculated by an iterative procedure similar to that used for carbon dioxide.

The accuracy of the liquid phase analyses is estimated to be  $\pm 2$  per cent.



## RESULTS AND DISCUSSION

Measurements with carbon dioxide were made at (25, 40, 60, 80, 100, 130) °C at pressures up to 16.0 MPa. The data are presented in Table 1. The first observation that should be noted is that the analyses by the two different methods are in good agreement. However, the fact that the BaCO<sub>3</sub> precipitation technique is very time-consuming has resulted in most of the data being obtained using gas chromatography.

When this work was started there was a large discrepancy between the values of Blanchard et al. [3] and those of Kamps et al. [4]. Although the analytical techniques were different, it was not possible to decide which data were reliable. The present results confirm the work of Kamps et al. A typical example is shown in Figure 2 for data at 40 °C. The present work is within the accuracy claimed by Kamps et al. (the smooth curve is drawn through their data), and differs greatly from the data of Blanchard et al. Similar results are obtained at other temperatures where comparisons can be made.

Measurements with hydrogen sulfide were made at (25, 40, 70, 100, 130) °C at pressures up to 9.6 MPa. The data are presented in Table 2. No other data are available for comparison, as these are the first results to be obtained for the solubility of hydrogen sulfide in this ionic liquid.

One facet of this work is a comparison with solvents now used for the removal of the acid gases from gas streams. A commonly used solvent is an aqueous mixture of monoethanolamine (MEA). It reacts with the acid gases at the absorption temperature (typically 30-40 °C) and is regenerated by heating to a higher temperature (typically 100-120 °C), and by reduction of the pressure. The present results for carbon dioxide in the ionic liquid are compared with data for a 30 wt.% solution of MEA in Figure 3. The smoothed results for a 30 wt.% solution of MEA were taken from the book of Kohl and Nielsen [5]. Here the abscissa is the loading of carbon dioxide in the liquid phase,  $\alpha$ , moles of CO<sub>2</sub>/mole of MEA (or ionic liquid). This quantity is obtained from the data by use of the equation:

$$\alpha = \frac{x}{1-x}$$

where  $x$  is the mole fraction of the acid gas in the liquid phase. This variable is normally used for absorption and stripping calculations. The first thing to note is that the ionic liquid acts like a typical “physical” solvent, in that the partial pressure of the acid gas is proportional to the partial pressure of the acid gas. In this respect it differs from the MEA solution, which is a “chemical” solvent. Chemical solvents are able to reduce the acid gas content of the vapor phase to a low level, while physical solvents are useful for bulk removal of acid gases, but are unable to achieve the same low concentrations of the acid gas. Figure 3 indicates that the ionic liquid is not as good as the MEA solution at pressures up to about 5 MPa. Since this pressure is higher than that encountered in most natural gases, it can be concluded that this ionic liquid has no advantage over aqueous MEA solutions for most applications.

A similar comparison for hydrogen sulfide is presented in Figure 4. Again, the MEA solution is superior at pressures of the acid gas up to about 1 MPa, a value reached in only a few natural gases.

## CONCLUSIONS

1. A reliable method of analysis of the carbon dioxide content of ionic liquids has been developed. Agreement between the two methods is within about 2 per cent. However, the time-consuming precipitation method is unsuitable for obtaining reasonable amounts of experimental data.
2. The disagreement in the solubility of carbon dioxide in [bmim][PF<sub>6</sub>] found by previous workers has been resolved. It is clear that the data of Kamps et al. [4] are reliable.
3. Data have been obtained for the solubility of hydrogen sulfide in [bmim][PF<sub>6</sub>] have been obtained over a range of temperatures and pressures for the first time.

## PROGRESS IN TRAINING HQP

Unfortunately, I was unsuccessful in obtaining an M.Sc. student for this research. Dr. Jou, who was to be involved in the development of the analytical procedures, continued to perform the solubility measurements.

## OVERALL CONCLUSIONS

1. Analytical techniques suitable for the determination of the concentration of acid gases in ionic liquids have been developed. By comparison with wet chemical analyses ( $\text{BaCO}_3$  precipitation) the gas chromatographic method has been shown to give reliable results.
2. The disagreement between the two published papers on the solubility of carbon dioxide in the ionic liquid [bmim][PF<sub>6</sub>] has been resolved.
3. Data have been obtained for the solubility of hydrogen sulfide in [bmim][PF<sub>6</sub>] have been obtained over a range of temperatures and pressures for the first time.
4. The use of this ionic liquid for the removal of acid gases is suitable only for bulk removal, when the partial pressures of the acid gases are large. It does not appear to have a role in treatment of natural gases typically found in Alberta.

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Table 1 Solubility of Carbon Dioxide in [bmim][PF<sub>6</sub>]

t = 25 °C		t = 40 °C		t = 60 °C	
P/MPa	Mole Fraction CO <sub>2</sub>	P/MPa	Mole Fraction CO <sub>2</sub>	P/MPa	Mole Fraction CO <sub>2</sub>
6.438	0.5535 <sup>b</sup>	10.340	0.5686	16.000	0.5328 <sup>a</sup>
5.700	0.5414	8.080	0.5169	12.750	0.5250
4.540	0.4887	8.080	0.5138 <sup>a</sup>	10.340	0.4898 <sup>a</sup>
4.540	0.4938 <sup>a</sup>	5.517	0.4382	8.450	0.4400
2.750	0.3782	3.240	0.3270 <sup>a</sup>	6.500	0.3946 <sup>a</sup>
1.120	0.1840	2.920	0.2911	5.800	0.3643
0.130	0.0247	1.110	0.1411	3.600	0.2743
		0.360	0.0527	3.050	0.2399 <sup>a</sup>
		0.133	0.0191	1.622	0.1495
				0.950	0.0923 <sup>a</sup>
				0.402	0.0422
				0.140	0.0143 <sup>a</sup>
				0.128	0.0137

t = 80 °C		t = 100 °C		t = 130 °C	
P/MPa	Mole Fraction CO <sub>2</sub>	P/MPa	Mole Fraction CO <sub>2</sub>	P/MPa	Mole Fraction CO <sub>2</sub>
14.300	0.4781	15.500	0.4576	14.200	0.3839 <sup>a</sup>
14.300	0.4702 <sup>a</sup>	11.600	0.3898	11.000	0.3237
11.500	0.4441	8.600	0.3337	7.720	0.2588
8.520	0.3815	7.960	0.3245 <sup>a</sup>	6.490	0.2267 <sup>a</sup>
7.000	0.3471 <sup>a</sup>	6.040	0.2628 <sup>a</sup>	5.170	0.1964
5.050	0.2750	5.500	0.2486	3.080	0.1284 <sup>a</sup>
3.600	0.2132 <sup>a</sup>	2.020	0.1198	2.160	0.0946
1.770	0.1250	0.552	0.0352	1.000	0.0466 <sup>a</sup>
1.050	0.0776 <sup>a</sup>	0.172	0.0116	0.750	0.0361
0.480	0.0386			0.205	0.0103
0.168	0.0140				

<sup>a</sup>Analysed by BaCO<sub>3</sub> precipitation; all other points analysed by gas chromatography.

<sup>b</sup>Three phase point: ionic liquid, CO<sub>2</sub>-rich liquid, CO<sub>2</sub>-rich vapour.

Table 2 Solubility of Hydrogen Sulfide in [bmim][PF<sub>6</sub>]

t = 25 °C		t = 40 °C		t = 70 °C	
P/kPa	Mole Fraction H <sub>2</sub> S	P/kPa	Mole Fraction H <sub>2</sub> S	P/kPa	Mole Fraction H <sub>2</sub> S
2120(3ph)	0.875	2890(dew pt)	0.853	5400(dew pt)	0.792
2100(dew pt)	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 = 100 °C		t = 130 °C	
P/kPa	Mole Fraction H <sub>2</sub> S	P/kPa	Mole Fraction H <sub>2</sub> S
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

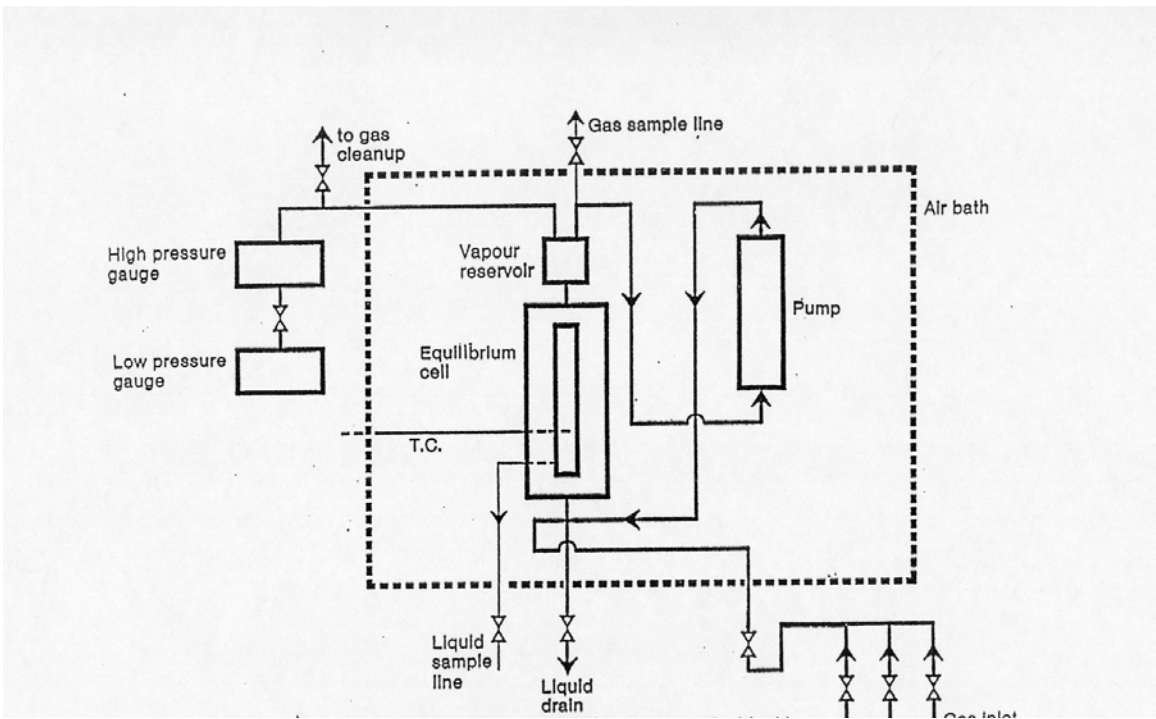


Figure 1. Schematic Diagram of the Experimental Apparatus



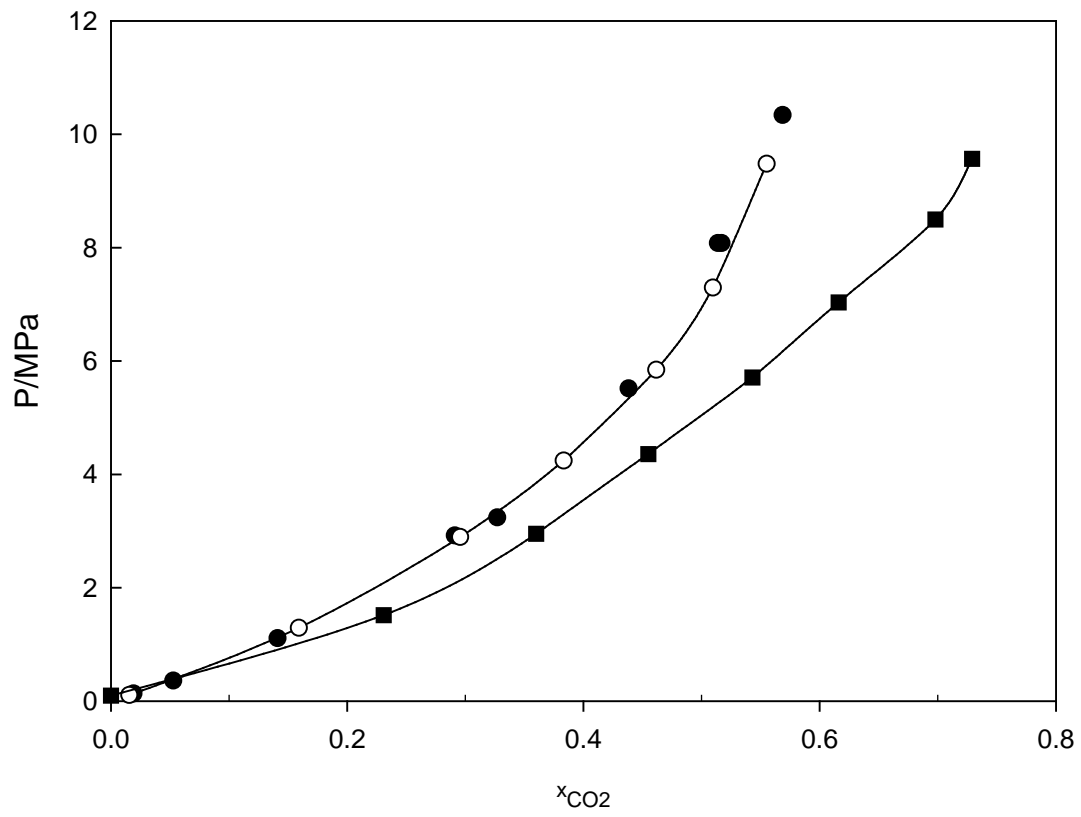


Fig. 2. Comparison of the data with published results at 40 °C.

● This work; ○ Kamps et al. [3]; ■ Blanchard et al. [2]

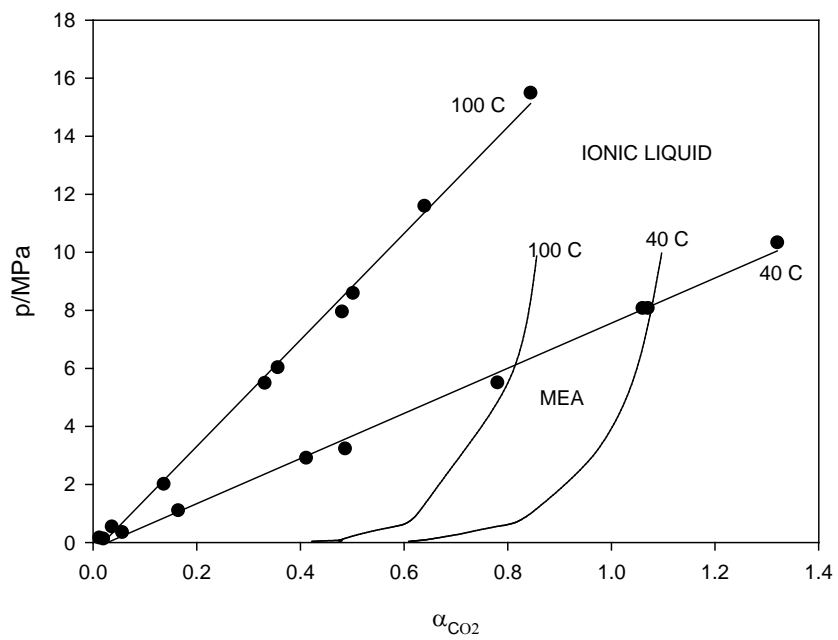


Figure 3. Comparison of the data for CO<sub>2</sub> in ionic liquid with that for MEA

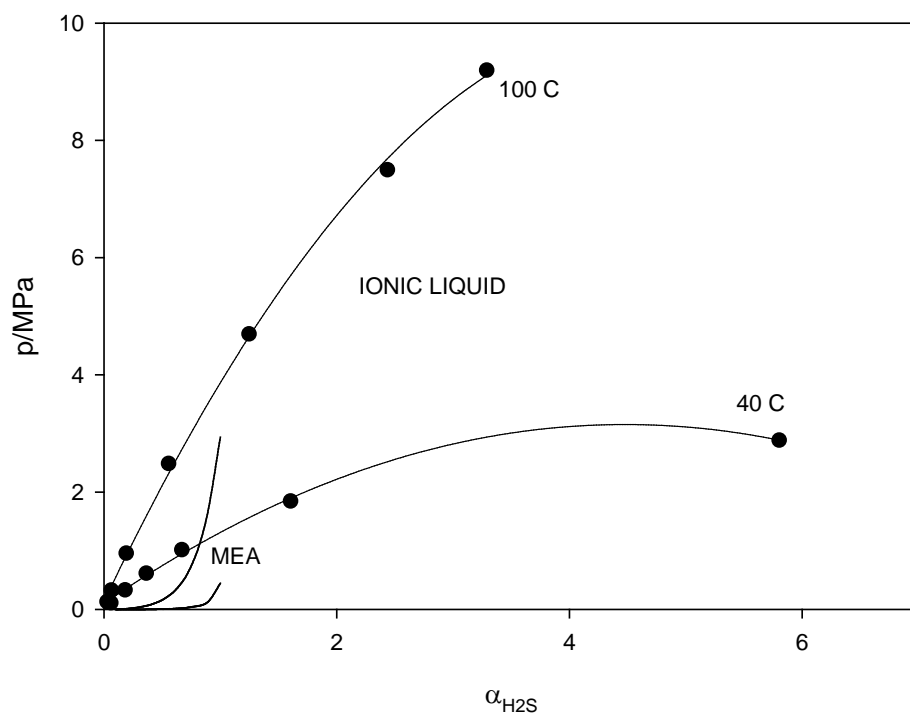


Figure 4. Comparison of the data for H<sub>2</sub>S in ionic liquid with that for MEA