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Selectivities of Carbon Dioxide Over Ethane in Three Methylimidazolium- Based Ionic Liquids: Experimental Data and Modeling

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Abstract: This work focused on the solubility of ethane in three promising ionic liquids {1-Hexyl-3-methylimidazolium bis(trifluormethylsulfonyl) imide [HMIM][Tf2N], 1-Butyl-3-methyl-imidazolium dimethyl-phosphate [BMIM][DMP] and 1-Propyl-3- methylimidazolium bis(trifluoromethyl-sulfonyl)-imide [PMIM][Tf2N]}. The solubilities were measured at 303.15 K to 343.15 K and pressures up to 1.4 MPa using a gravimetric microbalance. The overall ranking of ethane solubility in the ionic liquids from highest to lowest is the following: [HMIM][Tf2N] > [PMIM][Tf2N] > [BMIM][DMP]. The Peng- Robinson equation of state was used to model the experimental data using three different mixing rules: van der Waals one, van der Waals two and Wong-Sandler mixing rules combined with the Non-Random Two-Liquid model. The average absolute deviations for the three mixing rules for the ionic liquids at the three temperatures were (4.39, 2.45 and 2.45) %, respectively. Henry's Law constants for ethane in [BMIM] [DMP] were the highest (lowest solubility) amongst other ionic liquids studied in this work. The selectivity of CO_2 over C_2H_6 was estimated at the three temperatures and the overall ranking of the selectivity was in the following order: [PMIM][Tf2N] > [BMIM][DMP] > [HMIM][Tf2N]> Selexol. Selexol, a widely used physical solvent in gas sweetening has better selectivity than the three ionic liquids studied. [PMIM][Tf2N], a promising solvent, has the highest selectivity among the three ILs studied, and would therefore be the best choice if in addition to carbon dioxide capture, ethane co-absorption was to be avoided. The enthalpy and entropy of solvation at infinite dilution were also estimated.

Keywords: ionic liquid; ethane; carbon dioxide; solubility; selectivity; equation of state

1. Introduction

As reported by the Energy Information Agency (EIA) in 2023, approximately 83% of the total energy produced in the United States came from fossil fuels i.e. oil, coal and natural gas. [1] Fossil fuels when burned, produce large quantities of CO_2 and other gases. These gases will result in greenhouse gas effects resulting in the absorption of the heat coming from the sun and causing the temperature of the earth's atmosphere to rise. Global Warming is consequently considered a detrimental and even catastrophic change in the climate. According to the Scripps Institution of Oceanography and the National Oceanic and Atmospheric Administration (NOAA), the CO_2 May monthly average in 2024 reached 426.7 ppm an increase of 2.92 ppm over that recorded in 2023. [2] NOAA also reports that 2023 is the warmest year on record by far. [3]

There are multiple methods of slowing down the rate of global warming. One of those methods is through emission reduction with carbon capture. The most up-to-date technology in carbon capture is the process of absorbing CO_2 generated by power generation plants. This latest technology is similar to   the removal of acid gases from natural gas sweetening except that a mixture of amines are used as solvents. Capturing CO_2 using non-aqueous solvents is an advanced, next-generation post-combustion capture technology that seeks to remove CO_2 emitted from power generation and industrial flue gas streams.

Natural gas is one of the types of energy from the diverse portfolio of fossil fuels. It is a naturally occurring hydrocarbon composed mainly of methane. In general, it also contains natural gas liquids such as ethane, propane, butane and pentane as well as non-hydrocarbon gases such as nitrogen, carbon dioxide and hydrogen sulphide. Natural gas is formed from the remains of plants and animals exposed to extreme heat and pressure under the earth's surface hundreds of millions of years ago. It constitutes the major source of energy consumed today; the demand for natural gas has not ceased to icrease year after year in the last decade. According to the International Energy Agency, the world's natural gas consumption reached 4,138 billion cubic meters (bcm) in 2022 and is expected to reach 4,299 bcm in 2050. [4]

To this day, carbon capture is done by capturing CO_2 from both high-pressure natural gas streams and low-pressure gas streams with amines-based chemical solvents. [5] However, this process is not very economical in the case of flue gases because of the large amount of energy required to regenerate the solvent, and the serious solvent degradation that occurs. In natural gas applications, it is more economical to use physical solvents rather than chemical solvents for carbon capture, when cleaning targets are not at the ppm level. There have been multiple different processes that have been used in the past for carbon capture depending on the partial pressure of CO_2 in the feed and the required degree of treatment. Aside from amines and their blends, organic physical solvents are one of these processes. One of the main advantages is the low energy needed for solvent regeneration. [5] Commonly, physical solvents have a low energy of regeneration and relatively low vapor pressure. They are non-corrosive, with high thermal stability. They could be used in the treating of natural gas as standalone or mixed with aqueous amines in the case of flue gases. Ionic liquids (ILs) represent a category of physical solvents that utilize intermolecular forces for CO_2 capture. ILs are normally defined as compounds composed of ions (a cation and an anion) with a melting point below 100 °C. The objective of this study is to examine three new and promising ionic liquids and analyze their capacities for ethane at three different temperatures (303.15 K, 323.15 K, 343.15 K) within a range that is important to the industry and pressures up to 1.4 MPa. The experiments were conducted using a gravimetric microbalance (IGA-003).

2. Results

### 2.1. Verification of the C_2H_6 Solubility Measurement

A verification test was performed to ensure the IGA-003 is functioning as it should be. In this verification test, [BMIM][PF6] was used and the results were compared with Anthony et al. (2005) at 298.15 K [6]. As found in Figure 1, the results between the measured data and those published by Anthony et al. are in excellent agreement. As you can see our slopes are almost the same and the error bars indicate that the difference between my data and that of the literature is very little.
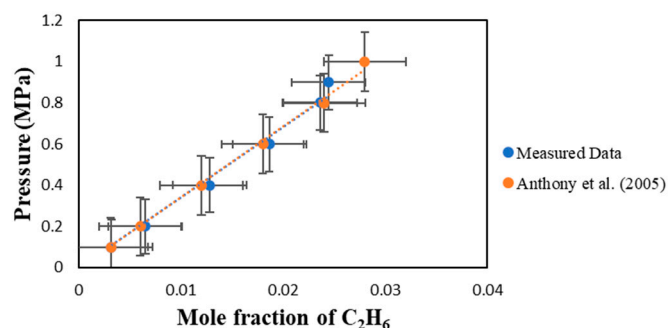

Figure 1. Comparison between the measured data for the solubility of C_2H_6 in [BMIM][PF6] and those reported by Anthony et al. (2005) [6] at 298.15 K.

2.2. Solubility of C_2H_6 in Ionic Liquids

C_2H_6 solubility data were studied by many researchers who found the ionic liquids to have lower solubility than CO_2. This work used three ionic liquids with different cations and anions to understand the factors affecting the solubility of C2H6 in ILs. C_2H_6 solubility in [HMIM][Tf2N], [BMIM][DMP] and [PMIM][Tf2N] were measured at 303.15 K, 323.15 K and 343.15 K and pressures up to 1.4 MPa. The results were plotted in P-*x* form in Figures 2–4 for the 3 solvents. The values of the experimental data can be found in Tables 1–3.
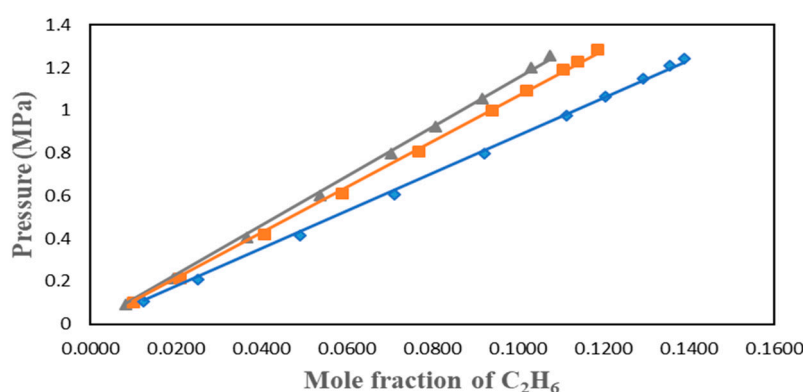
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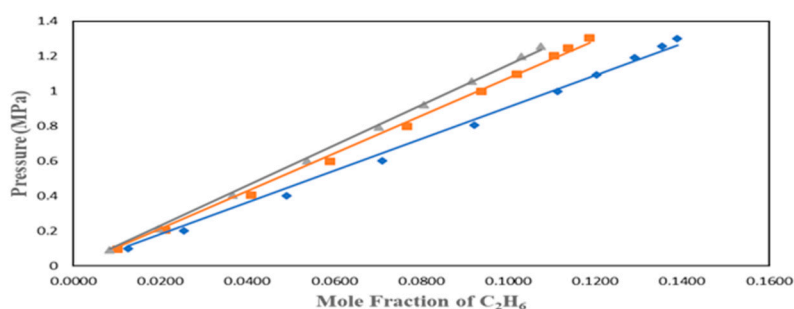
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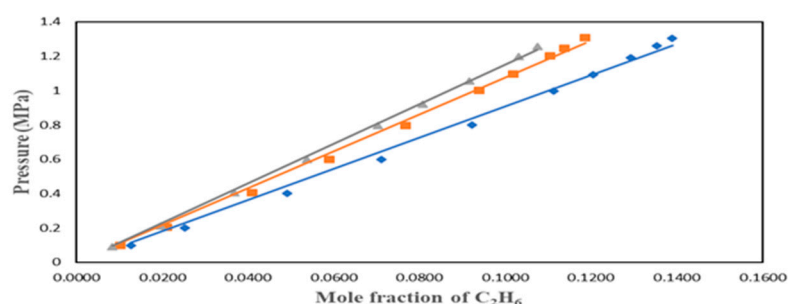
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Figure 2. Solubility data for C_2H_6 in [HMIM][Tf2N] at different temperatures and pressures up to 1.4 MPa: ♦ 303.15 K; ■ 323.15 K; ▲: 343.15 K. Experimental VLE data were correlated with: i) PR+vdW1, ii) PR+vdW2 and iii) PR+WS+NRTL.
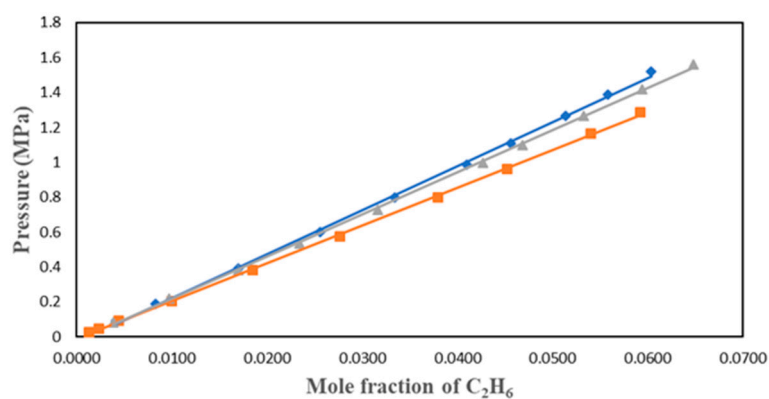
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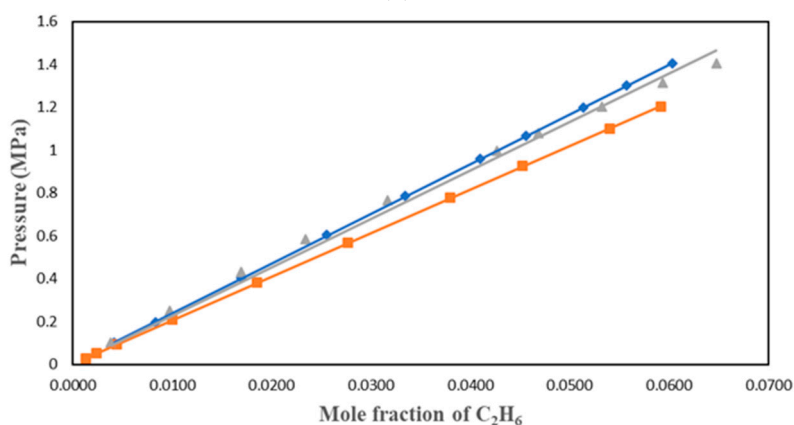
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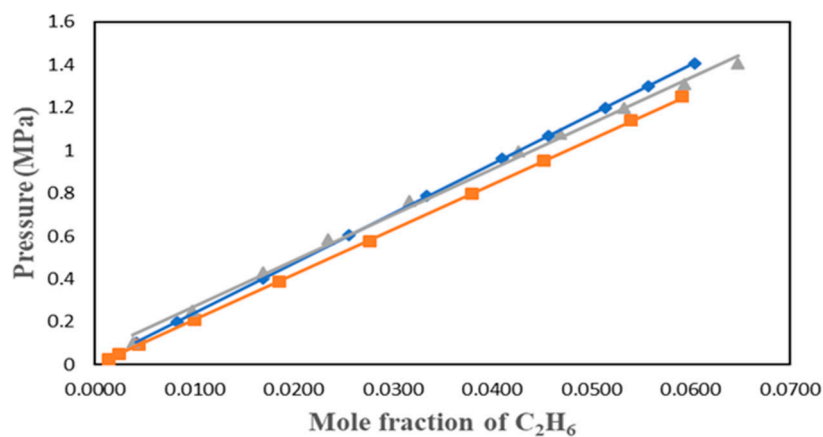
(**c**)

Figure 3. Solubility data of C_2H_6 in [BMIM][DMP] at different temperatures: ♦ 303.15 K; ■ 323.15 K ; ▲ 343.15 K. Experimental VLE data were correlated with: i) PR+vdW1, ii) PR+vdW2 and iii) PR+WS+NRTL.

(a)

(b)

(c)

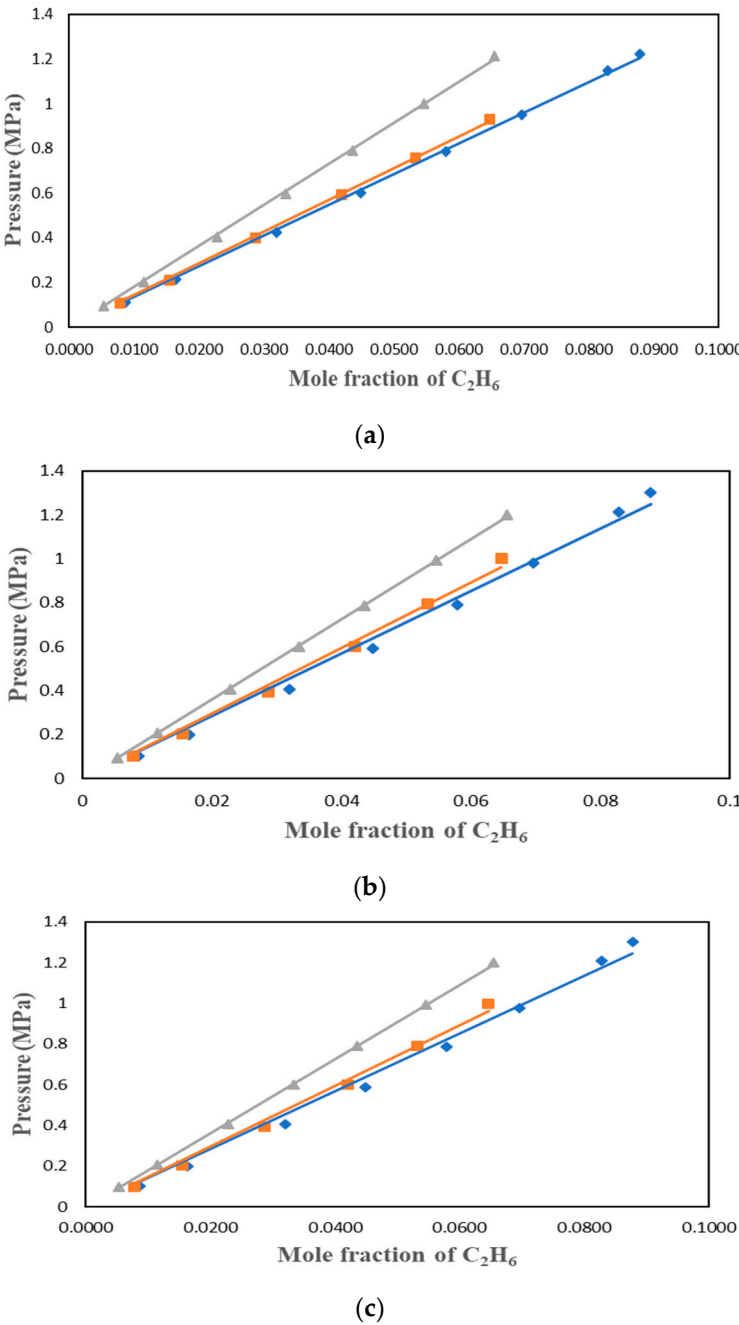**Figure 4.** Solubility data of C_2H_6 in [PMIM][Tf2N] at different temperatures: ♦ 303.15 K; ■ 323.15 K; ▲ 343.15 K and model correlation: lines with i) PR+vdW1, ii) PR+vdW2 and iii) PR+WS+NRTL.

Table 1. Solubility of C_2H_6 in [HMIM][Tf2N] at 303.15 K, 323.15 K and 343.15 K.

[HMIM][Tf2N]					
303.15 K		323.15 K		343.15 K	
x_{C2H6}	Pressure (MPa)	x_{C2H6}	Pressure (MPa)	x_{C2H6}	Pressure (MPa)
0.003	0.01991	0.003	0.0199	0.003	0.0199
0.006	0.0499	0.005	0.0499	0.005	0.0499
0.013	0.09989	0.010	0.1000	0.008	0.0999
0.025	0.20004	0.021	0.1998	0.020	0.2002
0.049	0.3998	0.041	0.3997	0.037	0.3998
0.071	0.59988	0.059	0.5998	0.054	0.5998
0.092	0.7999	0.077	0.7998	0.070	0.7995

0.111	0.9994	0.094	0.9996	0.081	0.9999
0.120	1.0998	0.102	1.0998	0.091	1.1000
0.129	1.1988	0.110	1.2011	0.103	1.1994
0.135	1.2495	0.114	1.2503	0.107	1.2513
0.139	1.3007	0.119	1.3009	-	-

Standard uncertainty u(x) = 0.006; Standard uncertainty u(T) = 0.1 K; Standard uncertainty u(P) = 0.0008 MPa.

Table 2. Solubility of C_2H_6 in [BMIM][DEP] at 303.15 K, 323.15 K and 343.15 K.

[BMIM][DMP]					
303.15 K		323.15 K		343.15 K	
x_{C2H6}	Pressure (MPa)	x_{C2H6}	Pressure (MPa)	x_{C2H6}	Pressure (MPa)
0.001	0.01978	0.001	0.0198	0.002	0.0196
0.002	0.0499	0.002	0.0499	0.002	0.0499
0.004	0.09989	0.004	0.0999	0.004	0.1001
0.008	0.19985	0.010	0.1999	0.010	0.1999
0.017	0.39991	0.018	0.4002	0.017	0.3996
0.026	0.59976	0.028	0.6006	0.023	0.5999
0.034	0.79991	0.038	0.7998	0.032	0.7999
0.0422	0.9998	0.045	0.9998	0.043	1.0006
0.050	1.2003	0.054	1.0997	0.047	1.0998
0.056	1.2996	0.059	1.2005	0.053	1.2012
0.059	1.3486	-	-	0.059	1.3011
0.063	1.4006	-	-	0.065	1.4006

Standard uncertainty u(x) = 0.006; Standard uncertainty u(T) = 0.1 K; Standard uncertainty u(P) = 0.0008 MPa.

Table 3. Solubility of C_2H_6 in [PMIM][Tf2N] at 303.15K, 323.15K and 343.15K.

[PMIM][Tf2N]					
303.15 K		323.15 K		343.15 K	
x_{C2H6}	Pressure (MPa)	x_{C2H6}	Pressure (MPa)	x_{C2H6}	Pressure (MPa)
0.002	0.0198	0.003	0.0199	0.002	0.0198
0.005	0.0499	0.005	0.0499	0.002	0.0500
0.009	0.0999	0.008	0.0999	0.005	0.0999
0.016	0.1999	0.015	0.1999	0.011	0.1999
0.032	0.4001	0.029	0.3999	0.023	0.4002
0.045	0.5999	0.042	0.5997	0.033	0.6011
0.058	0.7999	0.053	0.7998	0.044	0.8000
0.070	0.9999	0.065	0.9998	0.054	0.9999
0.083	1.1991	-	-	0.065	1.2012
0.088	1.30132	-	-	0.070	1.2998
-	-	-	-	0.079	1.4000

Standard uncertainty u(x) = 0.006; Standard uncertainty u(T) = 0.1 K; Standard uncertainty u(P) = 0.0008 MPa.

3. Discussion

3.1. Factors that Affect the Solubility of C_2H_6

3.1.1. Pressure and Temperature

Figures 2–4 show that temperature and pressure affect the solubility of C_2H_6 in ionic liquids. As expected, it is observed that as the temperature rises, C_2H_6 solubility in the ionic liquid decreases. As pressure rises C_2H_6 solubility increases. As presented in Figure 5, a comparison between the solubility

of ethane in the 3 ionic liquids at 303.15 K shows that the solvent that absorbs ethane the least is [BMIM][DMP].
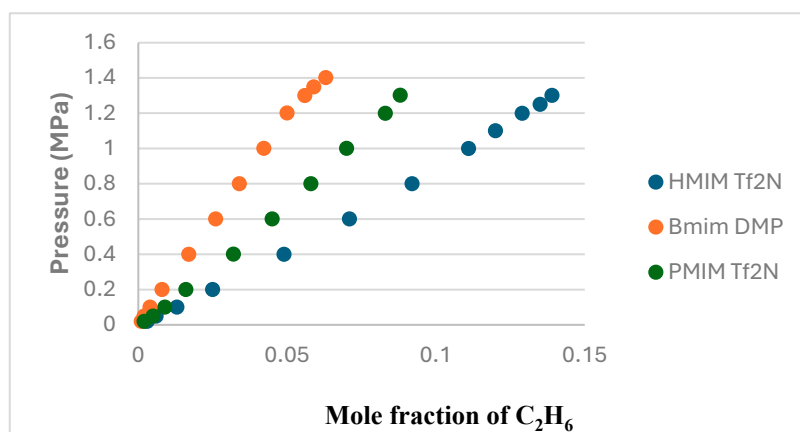
Figure 5. Comparison between the solubility of C_2H_6 in the 3 ILs at 303.15 K.

3.2. Optimization of Binary Interaction Parameters

3.1.2. Anion Effect

A significant amount of research has been done to understand the mechanism of how different ionic liquids have different solubility when it comes to capturing gases such as C_2H_6 and other gases. Anthony et al. [6] studied the anion effect on CO_2 solubility in [BMIM]-based ionic liquids with three different anions. Experiments were performed between 283.15K to 323.15 K and up to 1.4 MPa for three ionic liquids with three different anions, namely [BMIM][Tf2N], [BMIM][BF4] and [BMIM][PF6]. They reported that ethane along with other gases such as Ethylene, Oxygen and Argon have the lowest solubilities in ILs as compared to other common solvents.

3.1.3. Alkyl Chain Length with [Tf2N]-Anion

As presented in Figure 6, the alkyl chain effect will affect the solubility of C_2H_6 in ionic liquids. [HMIM] and [PMIM] are attached to an imidazolium-based cation with an n-methyl chain. The difference between their molecular structures is the hexyl and propyl alkyl chains. Hexyl has six methyl groups and propyl has three, in their carbon chains. The longer the chain the more gas the ionic liquid will absorb C_2H_6. This observation was made also by Zoubeik (2014) [7] and Tagiuri et al (2014) [8] based on several studies published in the literature.
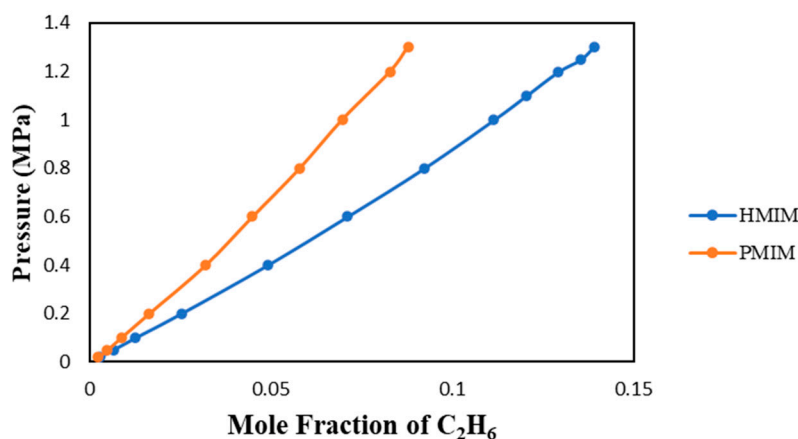
Figure 6. Solubility of C_2H_6 in the two ILs with [Tf2N]-anion at 303.15 K.

3.1.4. Cation with the Same [Tf2N] Anion

The effect of different cations with the same [Tf2N] anion is observed in Figure 6. The [PMIM] cation allowed for less C_2H_6 solubility than the [HMIM] cation. The solubility in ILs with the same anions will depend mostly on the cation. Based on studies published in the literature, methyl imidazolium cation-based ionic liquid tends to usually have a higher C_2H_6 solubility than other cation-based ionic liquids. The solubility of C_2H_6 in [HMIM] is higher than that in [PMIM] most probably because of its longer carbon (alkyl) chain as discussed earlier in the section entitled "Alkyl Chain Lengths" As reported by Taguiri (2019) [9] and others, this study confirms the fact that the anion of an ionic liquid has more of an impact on gas solubility than its cation.

3.2. Optimization of Binary Interaction Parameters

MATLAB was used for the thermodynamic model and was based on a bubble point technique for the three mixing rules [5]. As shown in Eq. (20) [9,13–15], the binary interaction parameters were optimized by minimizing the objective function (Err). Because experimental data at lower pressures are more likely to be erroneous, the binary interaction parameters were optimized using a pressure range of 0.1 to 1.4 MPa.

$$\text{Err} = \frac{100}{n}\sum_{i=1}^{n}\left[\frac{P_{\text{Exp,i}}-P_{\text{Cal,i}}}{P_{\text{Exp,i}}}\right] \tag{20}$$

The average absolute deviation for the vdW1, vdW2 and WS-NRTL mixing rules when used in the ionic liquids for C_2H_6 were: 4.39%, 2.45% and 2.45%, respectively. The results for C_2H_6 were best when using either the vdW2 or WS-NRTL mixing rule as shown in Table 4.

Table 4. Optimized binary interaction parameters for different models and calculated AAD%.

Compound	Temperature (K) & Pressure (MPa)	Mixing rule	$k_{12}a$	$l_{12}b$	τ_{12}	τ_{21}	AAD%
C_2H_6(1) + [HMIM][Tf2N](2)	303.15 & 0.1-1.4	vdW1	0.0797	-	-	-	3.19
		vdW2	0.1566	0.0163	-	-	0.47
		WS + NRTL	1.305	-	0.2151	-0.1848	0.44
	323.15 & 0.1-1.4	vdW1	0.0694	-	-	-	2.11
		vdW2	0.1116	0.0104	-	-	0.83
		WS + NRTL	1.2293	-	0.7031	-0.5823	0.84
	343.15 & 0.1-1.4	vdW1	0.0452	-	-	-	3.37
		vdW2	0.0557	0.0026	-	-	3.30
		WS + NRTL	1.0256		0.0396	0.0123	3.30
C_2H_6(1) + [BMIM][DMP](2)	303.15 & 0.1-1.4	vdW1	0.1931	-	-	-	4.77
		vdW2	0.052	-0.0377		-	2.35
		WS + NRTL	0.9997	-	1.1024	0.6362	2.34
	323.15 & 0.1-1.4	vdW1	0.1564	-	-	-	7.13
		vdW2	0.0294	-0.0346	-	-	6.65
		WS + NRTL	1.1384	-	0.6327	0.2915	6.66
	343.15 & 0.1-1.4	vdW1	0.1494	-	-	-	7.40
		vdW2	-0.2053	-0.101	-	-	4.44
		WS + NRTL	-0.1133	-	0.4517	1.8268	4.39

C$_2$H$_6$(1) + [PMIM][Tf2N](2)	303.15 & 0.1-1.4	vdW1	0.1240	-	-	-	5.23
		vdW2	0.236	0.0308	-	-	1.47
		WS + NRTL	1.6977	-	-0.0402	-0.0385	1.53
	323.15 & 0.1-1.4	vdW1	0.0987	-	-	-	4.41
		vdW2	0.2757	0.0467	-	-	0.66
		WS + NRTL	1.7468	-	-0.5135	0.1939	0.66
	343.15 & 0.1-1.4	vdW1	0.1028	-	-	-	1.93
		vdW2	0.0678	-0.0093	-	-	1.86
		WS + NRTL	1.1086	-	0.0247	0.3612	1.87

a: $k_{12} = k_{21}$.; b: $l_{12} = l_{21}$

3.3. Henry's Law Constants, Enthalpies and Entropies

Using the solubility data, Henry's Law constants were derived for the three ionic liquids. For each temperature, the fugacities of C$_2$H$_6$ were plotted against mole fractions. The limiting slope of the data's second-order polynomial was used to determine Henry's Law constants for each temperature. Henry's law constants, H$_i$, of the solute (i) in the solvent (j) is the ratio of the fugacity of the solute (i) to the mole fraction of the solute (i) in solvent (j) at infinite dilution at temperature T and pressure P; f_i^L and f_i^V are the fugacity of solute (i) in the liquid phase and vapor phase, respectively, x_i and y_i are the mole fraction of solute (i) in the liquid phase and vapor phase, respectively; at temperature T and pressure P [5]. It is expressed as the following:

$$H_i = \lim_{x_i \to 0} \frac{f_i^L(T,P,x_i)}{x_i} = \lim_{x_i \to 0} \frac{f_i^V(T,P,y_i)}{x_i} \qquad (21)$$

Once Henry's Law has been estimated from the solubility data, estimating the enthalpy of solvation (ΔH∞) at infinite dilution and the entropy of solvation (ΔS∞) at infinite dilution can also be done using the following equations:

$$\Delta H^\infty = R \left(\frac{\partial (\ln H)}{\partial (1/T)} \right)_P \qquad (22)$$

$$\Delta S^\infty = -R \left(\frac{\partial (\ln H)}{\partial (\ln T)} \right)_P \qquad (23)$$

where ΔH∞ is the enthalpy of solvation at infinite dilution, (ΔS∞) is the entropy of solvation at infinite dilution, R is the universal gas constant, H is Henry's Law constant and T is temperature.
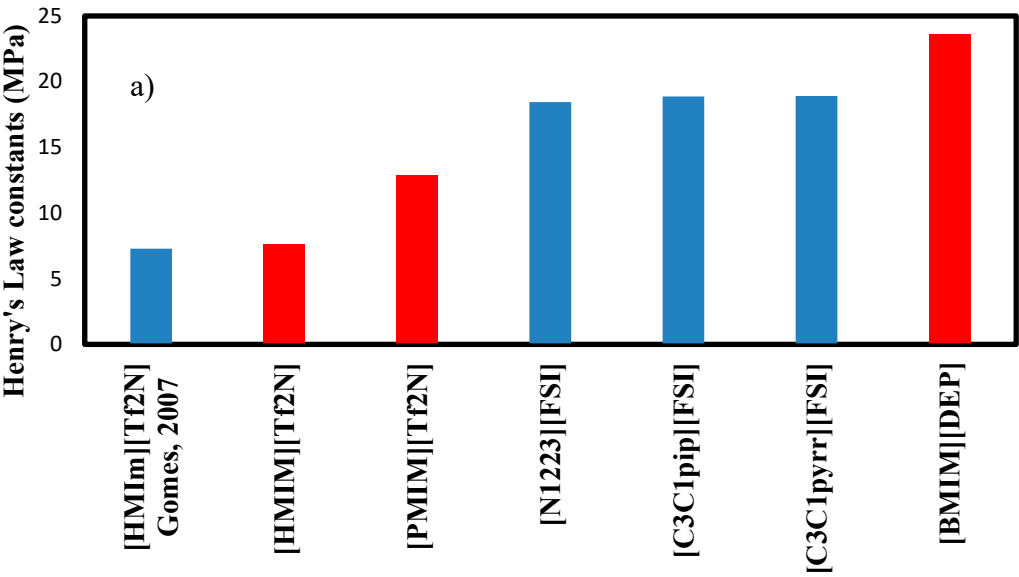
The comparison between the three ionic liquids is presented in Figure 7 for the three temperatures studied. Henry's Law constants for C$_2$H$_6$ in [HMIM][Tf2N] were published by Gomes et al. (2007) [10] and are reported here for comparison. The values are very close confirming the accuracy of the experimental data. The calculated values are presented in Table 5. Henry's Law constants of the three ionic liquids studied are compared to those found in the literature and presented in Figure 7 for the three temperatures studied.

Overall, the ranking of the Henry's Law constants for C$_2$H$_6$ is the following: [BMIM][DMP] >[PMIM][Tf2N] > [HMIM][Tf2N] at all temperatures. As the highest value is the best, [BMIM][DMP] is therefore the IL that absorbs ethane the least. Compared to other ionic liquids, the 3 ionic liquids are not the best but [BMIM][DMP] seems to be the best option.

Table 5. Henry's law constants, enthalpies and entropies for the solvation of C_2H_6 in ionic liquids at infinite dilution.

Ionic liquid	Henry's Law Constant (MPa)			ΔH^∞	ΔS^∞
	T = 303.15 K	T = 323.15 K	T = 343.15 K	(KJ/kmol)	(KJ/mol·K)
[HMIM][Tf2N]	7.63	9.43	10.69	-1.16	-3.61
[BMIM][DMP]	23.60	22.07	25.93	-0.81	-2.63
[PMIM][Tf2N]	12.85	13.61	17.35	-6.40	-20.02

Solubility of ethane in three ILs [[C3C1pip][FSI], [C3C1pyrr][FSI] and [N1223][FSI]] reported in Figure 7 was published by Nath et al (2017). [11].
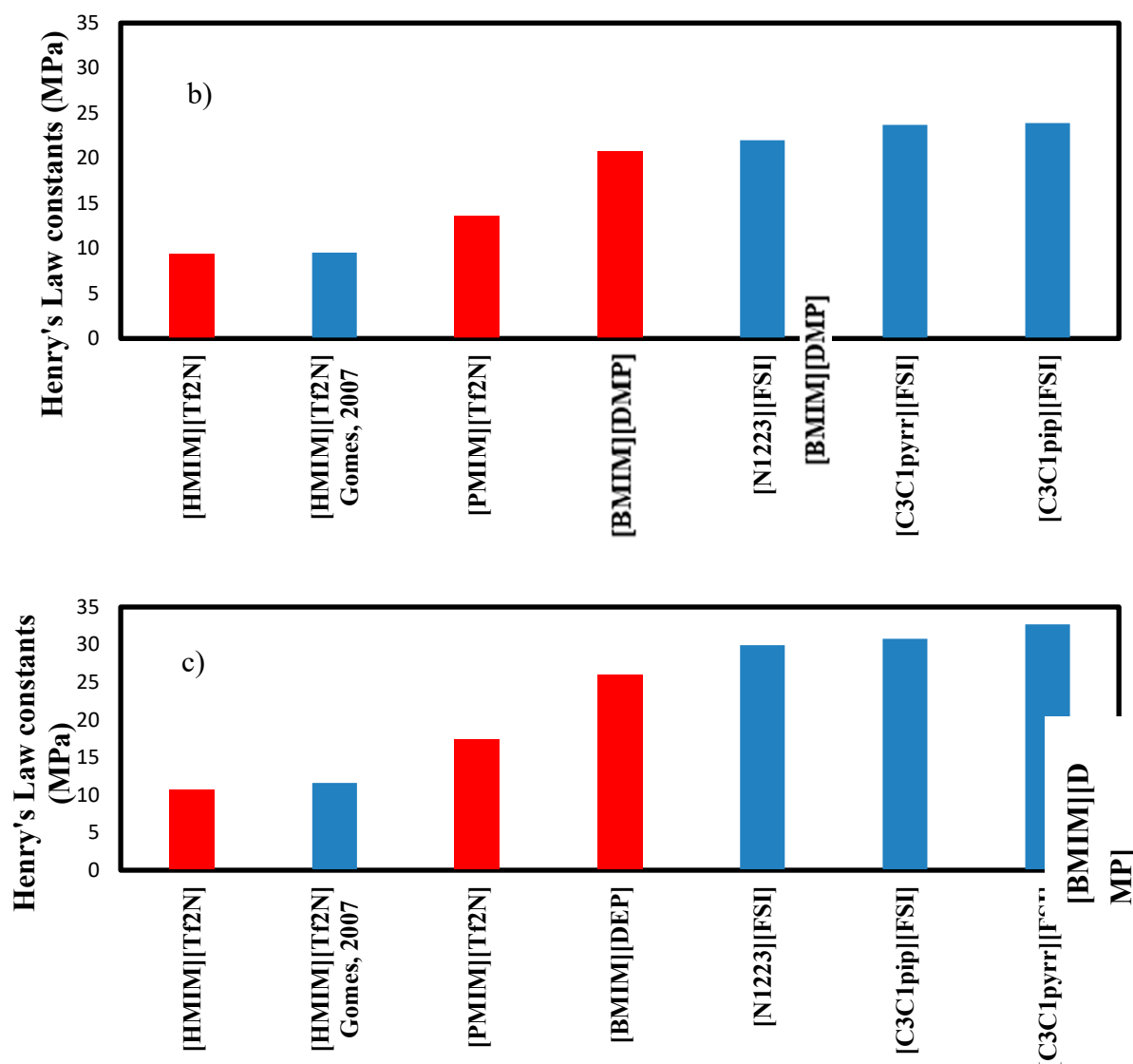
Figure 7. Comparison of Henry's law constants for C_2H_6 in ILs at: a) 303.15 K b), 323.15 K and c) 343.15 K; red: ionic liquids used in this work and blue: other ILs obtained from the literature summarized by (Nath & Henni) [5].

3.4. CO_2/C_2H_6 Selectivity in the Three Ionic Liquid Systems

One of the major criteria for a potential solvent for the use of gas solubility is the following: high removal efficiency. High selectivity towards CO_2 and low energy requirement. There isn't much research done when it comes to the selectivity between gases. When CO_2 is captured, it is not the only gas being absorbed. Other gases are absorbed such as N_2O, O_2, SO_2, H_2S, CH_4 and many other hydrocarbons. Therefore, with that in mind, it is crucial to study the effect of selectivity on ionic liquids. The selectivity of the ionic liquids used in this work was estimated as the ratio between Henry's Law constant of CO_2 and C_2H_6. The equation used to estimate the selectivity is the following:

$$S_{CO_2/C_2H_6} = \frac{H_{C_2H_6}}{H_{CO_2}} \tag{24}$$

The values of the selectivities are presented in Table 6, CO_2/C_2H_6 selectivity of the ionic liquids is not significantly high, however, they decrease as the temperature rises. The data obtained for the Henry's Law constant of CO_2 was taken from previous research we performed measuring the CO_2 solubility in [HMIM][Tf2N], [BMIM][DMP] and [PMIM][Tf2N]. [12] The study revealed that the three solvents were among the best in capturing CO_2. The three ionic liquids followed this rank in terms of

increasing CO_2 solubility: [HMIM] [Tf2N] > [PMIM][Tf2N] >[BMIM][DMP] as reported in reference [12]. The study confirmed that [HMIM][Tf2N] is an excellent solvent for CO_2 capture. [PMIM][Tf2N] was also found to have a high capacity for CO_2 among ILs published in the literature.

The selectivities of the 3 ionic liquids studied are compared to those found in the literature and presented in Figures 8–10 at the three temperatures studied.

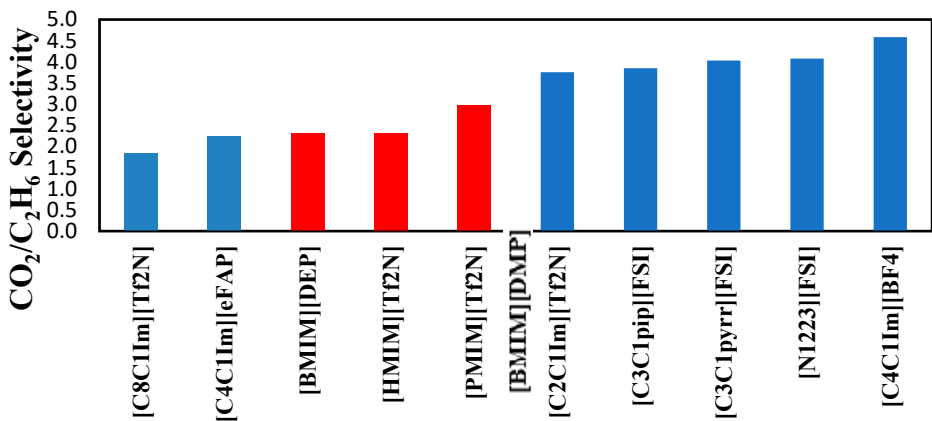**Table 6.** CO_2/C_2H_6 selectivity of the ionic liquids used in this work.

	Temperature (K)		
	303.15	323.15	343.15
Solvents			
[HMIM][Tf2N]	2.47	2.32	2.07
[BMIM][DMP]	3.19	2.30	2.01
[PMIM][Tf2N]	3.87	2.98	2.79
Selexol	0.550	0.569	0.531

For a comprehensive comparison, we have added in the table data related to Selexol, a widely used and efficient physical solvent (a mixture polyethylene glycol dimethyl ethers). Selectivity values were reported by Rayer et al. (2012).[13]

Overall, the ranking of the CO_2/C_2H_6 is the following: [PMIM][Tf2N] > [BMIM] [DMP] > [HMIM][Tf2N]> Selexol. As the lowest selectivity is the one preferred, among the three ionic liquids studied [HMIM][Tf2N] was the best. As shown below, these ILs do not possess the best selectivities. Selexol seems to have a good selectivity as a physical solvent. More details about the solvents in Figures 7–9 can be found in reference [5].
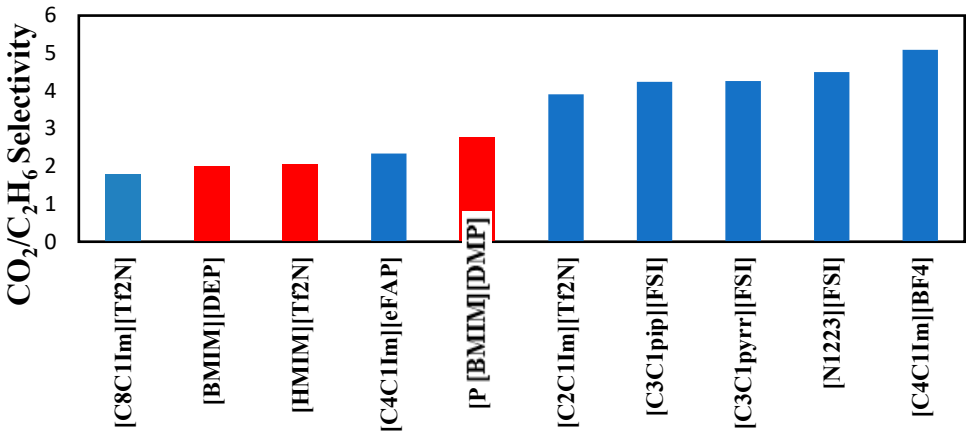
Figure 8. Comparison of CO_2/C_2H_6 selectivity in several ionic liquids reported by Nath and Henni (2020) [5] at 303.15 K.

Figure 9. Comparison of CO_2/C_2H_6 selectivity in several ionic liquids reported by Nath and Henni (2020) [5] at 323.15 K.
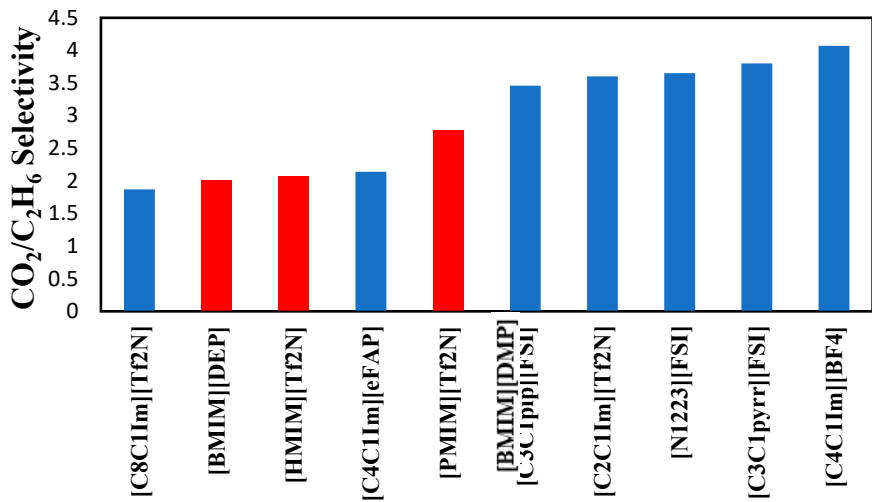
Figure 10. Comparison of CO_2/C_2H_6 selectivity with other ionic liquids reported by Nath and Henni (2020) [5] at 343.15 K.

4. Materials and Methods

4.1. Materials

Table 7 lists the structures, acronyms, suppliers, purities, and water content of all of the solvents and solutes used in this study. The manufacturers of the chemicals provided the information related to the purities of the solvents listed in the same table.

Table 7. List of all the solvents and solutes used in this study, structures, acronyms, suppliers, purities, and water content.

Compounds	Structure	Abbreviation	Suppliers and Purities	Water Content
Ethane		C_2H_6	Praxair (99.99%)	-
1-Hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide		[HMIM][Tf2N]	Sigma-Aldrich (≥98.0%)	-
1-Butyl-3-methylimidazolium dimethylphosphate		[BMIM][DMP]	IoLiTec (>98.0%)	< 2500 ppm
1-Propyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide		[PMIM][Tf2N]	Sigma-Aldrich (≥99.0%)	≤ 0.5 wt%
1-Butyl-3-methylimidazolium hexafluorophosphate		[BMIM][PF6]	Sigma-Aldrich (≥97.0%)	-

4.2. Solubility Measurement

The gas solubility experiments were performed with the use of an IGA-003 (Intelligent Gravimetric Analyzer, Hidden Isochema Ltd). The machine measures the weight change of a liquid sample once a gas/gas mixture has been injected into the system. The IGA-003 can run at a maximum pressure and temperature of up to 2.0 MPa and 773.15 K, respectively.

For each isotherm experiment, around 50 to 90 mg of ionic liquid sample was inserted into the sample container to determine the solubility of the gas in the ionic liquid. A Grant water bath was used to regulate the temperature of the sample. For each experiment, the sample was degassed for around 10 hours at high temperatures and under a deep vacuum before beginning the isotherm process to remove any contaminants that may have been in the sample. Throughout the degassing process, the temperature of the sample was kept constant at 349.15 K.

Once the sample weight stabilized after being degassed for over 10 hours, the operating temperature was reduced to the isotherm condition using a Grant water bath. The ionic liquid sample was kept under this condition for at least an hour to ensure that the sample weight was at equilibrium. Once the weight of the sample has been stable, the isotherm process can be initiated by choosing a list of pressures at which the gas solubility is to be measured. Once all the necessary parameters have been selected in the IGA computer software, C_2H_6 is then injected into the chamber using the mass flow controller (MFC). The system's pressure is kept constant at a pre-set pressure until the system

reaches equilibrium. The IGA-003 records all real-time data such as weight, temperature and pressure.

Measurement of the density of the solvent is a required input in the experimental procedure. We reported the values of the densities of the 3 solvents in reference. [12] The density values decreased in the following order: [PMIM][Tf2N] > [HMIM][Tf2N] > [BMIM][DMP]. [BMIM][DMP] was reported to have a high viscosity value of 409.88 mPa·s at 303.15 K. [12]

Figure 10 shows the setup for the IGA. Each instrument used in this work was numerically labelled. The setup consists of (1) a computer; (2) a microbalance; (3) Gas cylinder (4) Mass Flow control; (5) Water bath.
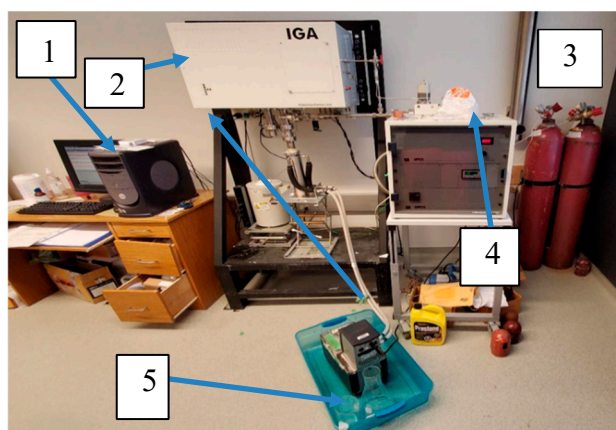

Figure 11. IGA-003 setup.

4.3. Thermodynamic Modelling

The Solubility data of C_2H_6 in ILs obtained in this work were correlated using the Peng-Robinson Equation of State (PR-EoS) as shown in Eq. (1) [14]; where a_m is the intermolecular attractive force and b_m is the van der Waals co-volume factor. The PR- EoS combined with three different mixing rules were used to build this model. The three mixing rules are the following:
1. Single binary interaction parameter based on van der Waals one (vdW1),
2. Two binary interaction parameters based on van der Waals two (vdW2),
3. Wong-Sandler mixing rules combined with the NRTL model (WS-NRTL).

$$P = \frac{RT}{v-b_m} - \frac{a_m(T)}{v(v+b_m)+b_m(v-b_m)} \tag{1}$$

4.3.1. Van der Waals Mixing Rule

For this case, van der Waals created two different mixing rules to estimate mixture parameters (a_m and b_m), van der Waals one (vdW1) and van der Waals two (vdW2) [14–16]. In the vdW1 mixing rule, only one parameter (l_{ij}) is regressed whereas, for vdW2 two binary interaction parameters are obtained (l_{ij} and k_{ij}). The parameter a_m for both vdW1 and vdW2 mixing rules was estimated using Eq. (2). By using the temperature dependence binary interaction parameter, k_{ij} , a_{ij} can be estimated with Eq. (5). The co-volume factor b_m for both vdW1 and vdW2 is estimated with Eq. (3) and Eq. (4), respectively. By using the interaction parameter (l_{ij}) b_{ij} can be estimated with Eq. (6).

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$
$$b_m = \sum_i x_i b_i$$
$$b_m = \sum_i \sum_j x_i x_j b_{ij} \tag{4}$$

where,

$$a_{ij} = \sqrt{a_{ii}a_{jj}}(1 - k_{ij}) \tag{5}$$
$$b_{ij} = \frac{b_i+b_j}{2}(1 - l_{ij}) \tag{6}$$

where, a_{ii} and a_{jj} are the pure component intermolecular attractive force parameter, and b_i and b_j are the pure components co-volume factor parameters for the components (i and j).

4.3.2. Wong-Sandler Mixing Rule

The mixture's attractive force parameter, a, and co-volume parameter, b, can be calculated using Eqs. (7) and (8) [14], respectively, for Wong–Sandler mixing rules. In this paper, the Non-Random Two Liquid (NRTL) model is utilized to approximate the activity coefficient and Excess Gibbs Energy (Eqs. 13–19) [15]. The mixture parameters were estimated using three binary interaction parameters (k_{ij}, τ_{ij} and τ_{ji}), where τ_{ij} and τ_{ji} are the NRTL parameters. The energies g_{ij} and g_{jj} are the energies of interaction between molecules 'i' and 'j' [16–18] and are calculated using Eqs. (16)–(17). The value of α_{ij} in Eqs. (14) and (15) were set at 0.3 arbitrarily in this work.

$$a = RT \frac{QD}{1-D} \tag{7}$$

$$b = \frac{Q}{1-D} \tag{8}$$

where,

$$Q = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT}\right)_{ij} \tag{9}$$

$$D = \sum_i x_i \left(\frac{a_i}{b_i RT}\right) + \left(\frac{G^{ex}}{CRT}\right) \tag{10}$$

$$C = -\ln\left((1+\sqrt{2})/\sqrt{2}\right) \tag{11}$$

where, $\left(b - \frac{a}{RT}\right)_{ij}$ in Eq. (9) is defined in Eq. (12)

$$\left(b - \frac{a}{RT}\right)_{ij} = \frac{1}{2}\left[\left(b_i - \frac{a_i}{RT}\right) + \left(b_j - \frac{a_j}{RT}\right)\right](1 - k_{ij}) \tag{12}$$

$$\frac{G^{ex}}{RT} = x_i x_j \left(\frac{\tau_{ji} G_{ji}}{x_i + x_j G_{ji}} + \frac{\tau_{ij} G_{ij}}{x_j + x_i G_{ij}}\right) \tag{13}$$

$$G_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{14}$$

$$G_{ji} = \exp(-\alpha_{ij}\tau_{ji}) \tag{15}$$

$$\tau_{ij} = (g_{ij} - g_{jj})/RT \tag{16}$$

$$\tau_{ji} = (g_{ji} - g_{ii})/RT \tag{17}$$

$$\ln \gamma_i = x_j^2 \left[\tau_{ji} \left(\frac{G_{ji}}{x_i + x_j G_{ji}}\right)^2 + \frac{\tau_{ij} G_{ij}}{(x_j + x_i G_{ij})^2}\right] \tag{18}$$

$$\ln \gamma_j = x_i^2 \left[\tau_{ij} \left(\frac{G_{ij}}{x_j + x_i G_{ij}}\right)^2 + \frac{\tau_{ji} G_{ji}}{(x_i + x_j G_{ji})^2}\right] \tag{19}$$

4.4. Critical Properties Calculations

The critical parameters of the gas and the solvent examined must be known to be used in the model. The Modified Lydersen-Joback-Reid group contribution method was used to determine the critical temperature (Tc), critical pressure (Pc), and the acentric factor (ω) of the ionic liquids in this study using the spreadsheet provided by Valderrama and Rojas [19]. Table 8 lists the critical properties determined for this study's three ionic liquids and C_2H_6.

Table 8. Molecular weights and critical properties of solutes and solvents used in this study.

Components	*MW (g/mol)*	T_c *(K)*	P_c *(MPa)*	*ω*
[HMIM][Tf2N]	447.4	1292.8	2.39	0.3893
[BMIM][DMP]	264.26	851	2.15	0.961
[PMIM][Tf2N]	405.3	1259.3	3.0	0.2575
C_2H_6	30.07	305.4	48.8	0.099

5. Conclusions

The purpose of this work was to screen three new ionic liquids measuring their capacity to absorb C_2H_6 at pressures up to 1.4 MPa and at temperatures ranging from 293.15 K to 343.15 K. Thermodynamic properties such as the enthalpies and entropies of absorption are reported and the data used to determine the selectivity values.

The ionic liquids selected were [HMIM][Tf2N], [BMIM][DMP] and [PMIM][Tf2N]. In an earlier publication, we reported that the density values of the solvents decreased in the following order: [PMIM][Tf2N] > [HMIM][Tf2N] > [BMIM][DMP].

As co-absorption of ethane is important in natural gas processing, Henry's Law constants for C_2H_6 were estimated at 303.15 K, 323.15 K and 343.15 K. As expected, they increased for all ILs as temperature increased. Overall, the ranking of the Henry's Law constants for C_2H_6 is the following: [BMIM][DMP] >[PMIM][Tf2N] > [HMIM][Tf2N] at all temperatures. [BMIM][DMP] is therefore found to be the IL that absorbs ethane the least. Compared to other ionic liquids, the three ionic liquids are not the best but [BMIM][DMP] seems to be the best option.

The overall ranking of the CO_2/ C_2H_6 selectivity is the following: [PMIM][Tf2N] > [BMIM] [DMP] > [HMIM][Tf2N]> Selexol. The most promising ionic liquid in terms of selectivity is therefore [HMIM][Tf2N] while Selexol presents much lower selectivity values

Solubility data were correlated using the Peng-Robinson equation of state (PR-EoS) and the binary interaction coefficients were reported. The average absolute deviations for the vdW1, vdW2 and WS-NRTL mixing rules when used in the ionic liquids for C_2H_6 were: 4.39%, 2.45% and 2.45%, respectively. The enthalpy and entropies of adsorption were calculated. Negative enthalpies were reported indicating an exothermic process of absorption.

Nomenclature

AAD	Average Absolute Deviation
[BF4]	Tetrafluoroborate
[BMIM][DMP]	1-Butyl-3-methyl-imidazolium dimethyl-phosphate
[N1223][FSI]	N-propyl-n-methyl-n,n-dimethyl-ammonium bis(fluorosulfonyl)imide
[C3C1PIP][FSI]	N-propyl-n-methyl-piperidinium bis(fluorosulfonyl)imide
[C3C1Pyrr][FSI]	1-Methyl-1-propylpyrrolidinium bis(fluorosulfonyl)imide
[C4C1Im] [BF4]	1-Butyl-3-methylimidazolium tetrafluoroborate
CO_2	Carbon Dioxide
C_2H_6	Ethane
DCN	Dicyanamide
EoS	Equation of state
[FSI]	Bis(fluorosulfonyl)imide
H	Henry's Law constant

[HMIM][Tf2N]	1-Hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide
IGA	Intelligent Gravimetric Analyzer
ILs	Ionic liquids
K	Kelvin
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
P_c	Critical pressure
PF6	Hexafluoro-phosphate
[PMIM][Tf2N]	1-Propyl-3- methylimidazolium bis(trifluoromethyl-sulfonyl)-imide
PR	Peng Robinson
RSO4	Alkylsulfate
T_b	Boiling point temperature
T_c	Critical temperature
vdW1	van der Waals one
vdW2	van der Waals two
WS-NRTL	Wong-Sandler mixing rules + Non-Random Two-Liquid model
x	Liquid mole fraction (moles gas/ moles gas + moles solvent)
y	Vapor mole fraction
Z_c	Critical compressibility factor

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