

CHAPTER III EXPERIMENTAL

3.1 Materials

3.1.1 Ionic Liquids

Five different conventional ionic liquids, listed in Table 3.1 with their acronyms, structures, molecular weights and purity, were used in this work. All of them were ordered from Sigma-Aldrich Ltd. Each ionic liquid will be discussed about the amount, purity, impurities, colour, appearance, as well as some reported physical and chemical properties based on their MSDS for more detail.

1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆], CAS Number: 174501-64-5) with an assay of $\geq 97.0\%$ (HPLC) was available in our laboratory with the amount of 50 g. It is a clear liquid with light yellow colour. The reported density is 1.38 g/cm³ at 20 °C. It is utilized to validate the solubility apparatus and measurement method with published data.

Triethylsulfonium bis(trifluoromethylsulfonyl)imide ([S₂₂₂][Tf₂N], CAS Number: 321746-49-0) with an assay of $\geq 99.0\%$ (NMR) was ordered for 5 g and obtained as an electrochemical grade. It has total impurities of ≤ 200 ppm water. Anion traces such as bromide (Br⁻), chloride (Cl⁻), fluoride (F⁻), and nitrate (NO₃⁻) are all observed to be ≤ 10 mg/kg. It is in liquid state with melting point of -35.5 °C.

Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([deme][Tf₂N], CAS Number: 464927-84-2) with an assay of $\geq 98.5\%$ (T) was also ordered in the form of 5 g and obtained as an electrochemical grade. Total impurities are reported to be ≤ 500 ppm water. Bromide (Br⁻), chloride (Cl⁻), fluoride (F⁻), phosphate (PO₄³⁻), and sulfate (SO₄²⁻) are found to be ≤ 10 mg/kg, whereas nitrate (NO₃⁻) is ≤ 20 mg/kg. It is a clear liquid with light yellow colour similar to [bmim][PF₆], but it appears less viscous.

1-Propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([pmim][Tf₂N], CAS Number: 216299-72-8) produced by BASF with an assay of $\geq 98.0\%$ (H-NMR) was purchased in the form of 100 g. Total impurities are investigated to be $\leq 0.5\%$ water. It is in clear liquid form with its melting point less than -20 °C. It is investigated to be colourless and basic with pH of 6.5 at 10g/L at 25

°C. Its boiling point and flash point are present higher than 200 °C and 100 °C, respectively. The density of [pmim][Tf₂N] is 1.45 g/cm³ at 20 °C, and it can be soluble in methanol.

1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([amim][Tf₂N], CAS Number: 655249-87-9) was obtained with a weight of 5 g and an assay of $\geq 98.5\%$ (HPLC). Total impurities are investigated to be $\leq 1\%$ water. It is a clear yellowish liquid.

Last, 1-Butyl-4-methylpyridinium tetrafluoroborate ([4mbp][BF₄], CAS Number: 343952-33-0) with an assay of $\geq 97.0\%$ (T) was ordered in the amount of 5 g. It is in more viscous liquid form when compared to others and its colour is dark brown. The reported density of [4mbp][BF₄] is 1.20 g/cm³ at 20 °C.

Table 3.1 Studied ionic liquids

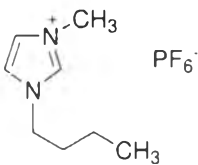
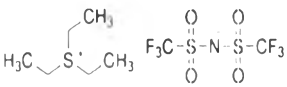
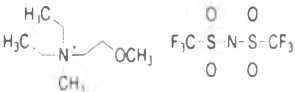
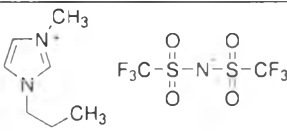
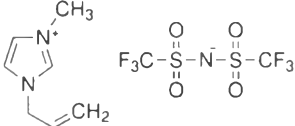
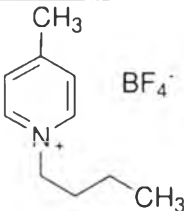
Acronym	Structure	Ionic liquids	Purity
[bmim][PF ₆]		1-Butyl-3-methylimidazolium hexafluorophosphate, Sigma-Aldrich Ltd. (CAS Number: 174501-64-5) MW: 284.18 g/mol	≥97.0% (HPLC)
[S ₂₂₂][Tf ₂ N]		Triethylsulfonium bis(trifluoromethylsulfonyl)imide, Sigma-Aldrich Ltd. (CAS Number: 321746-49-0) MW: 399.39 g/mol	≥99.0% (NMR)
[deme][Tf ₂ N]		Diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide, Sigma-Aldrich Ltd. (CAS Number: 464927-84-2) MW: 426.40 g/mol	≥98.5% (T)
[pmim][Tf ₂ N]		1-Propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Sigma-Aldrich Ltd. (CAS Number: 216299-72-8) MW: 405.34 g/mol	≥98.0% (H-NMR)
[amim][Tf ₂ N]		1-Allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, Sigma-Aldrich Ltd. (CAS Number: 655249-87-9) MW: 403.32 g/mol	≥98.5% (HPLC)

Table 3.1 Studied ionic liquids (cont.)

Acronym	Structure	Ionic liquids	Purity
[4mbp][BF ₄]		1-Butyl-4-methylpyridinium tetrafluoroborate, Sigma-Aldrich Ltd. (CAS Number: 343952-33-0) MW: 237.05 g/mol	≥97.0% (T)

3.1.2 Gases

Carbon dioxide (CO₂) as a research grade was delivered by Praxair Products Inc, with a purity of 99.99%. The gas cylinder has a weight of 27.2 kg with a two-stage regulator which can be adjusted to the pressure of 300 psi and the outlet connection should be 1/4" (or) 1/8" Swagelok.

3.2 Experimental Procedures

3.2.1 Density Measurement

Densities of the ionic liquids at different temperatures ranging from 5 °C to 80 °C (278.15 K to 353.15 K) were experimentally measured using an Anton Paar density meter (DMA 4500). This apparatus determines a liquid density or concentration, which is based on the principle of oscillation of U-tube to ensure highly accurate density values. The temperature range for the operation is from 0 °C to 90 °C. Results such as density, temperature, specific gravity, % concentration, etc. will be displayed. After initialization of the density meter, a desired temperature (5-80 °C) had to be set beginning with 5 °C and approximately 2 mL of a sample was slowly injected through the inlet using a 3-mL syringe. While injecting, the sample would flow through the oscillating U-tube inside the apparatus and then left out at the outlet. In order not to waste the sample, another syringe was required to block the outlet. The density value would be attained automatically when reaching the desired temperature. After use, the oscillating U-tube had to be rinsed by injecting distilled water, acetone and methanol, respectively. Then, air was pumped through the inlet to

push the solvents off and temperature would be set at 90 °C to evaporate the residual solvents. The DMA 4500 density meter can be illustrated in Figure 3.1.



Figure 3.1 The DMA 4500 density meter.

3.2.2 Gas Solubility Measurement

Gas solubility measurements were performed using a gravimetric microbalance (Hiden Isochema Ltd, IGA-003). The IGA is well-designed to integrate computer control and measurement of weight change, pressure and temperature together, leading to completely automatic and reproducible determination of gas sorption-desorption isotherms and isobars in diverse operating conditions. The schematic diagram of the IGA-003 gravimetric microbalance is shown in Figure 3.2, and the experimental set-up of the IGA-003 for static gas operation is depicted in Figure 3.3. The microbalance has a weight range of 0-100 mg with a resolution of 0.1 μg . A stainless steel (SS316N) reactor is able to operate up to 20 bar and 500 °C. The microbalance is, in general, composed of a sample bucket containing the liquid

and counter weight components placed inside a stainless steel pressure-vessel, which are designed symmetrically to minimize buoyancy effects. In the experiment, approximately (65 to 75) mg of ionic liquid sample were loaded to the sample container and the reactor was then installed. After waiting for stability, the thermostat was then attached to the reactor and the external water jacket was connected. The sample was dried and degassed by fully evacuating the reactor to 10^{-8} bar. While performing ultra-high vacuum, the sample was heated to approximately 70-75 °C for at least 10 h by the water jacket connected to a remote-controlled constant-temperature bath. The sample weight slowly decreased since trace amounts of water and other volatile solvents were removed. Once the sample weight had stabilized for at least 60 min, the sample dry weight was recorded. The percent weight losses for the five ionic liquids were calculated during the treatment. These weight losses were attributed to the losses of residual water present in the ionic liquids.

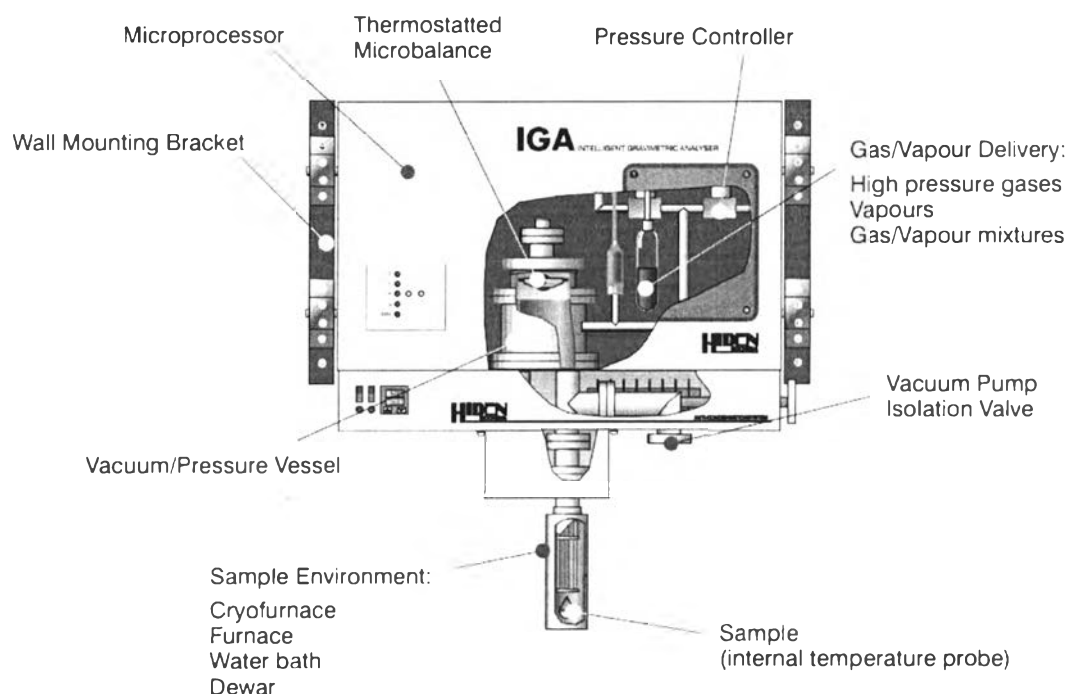


Figure 3.2 Schematic diagram of Hiden Isochema IGA-003 gravimetric microbalance (Hiden Isochema, UK).

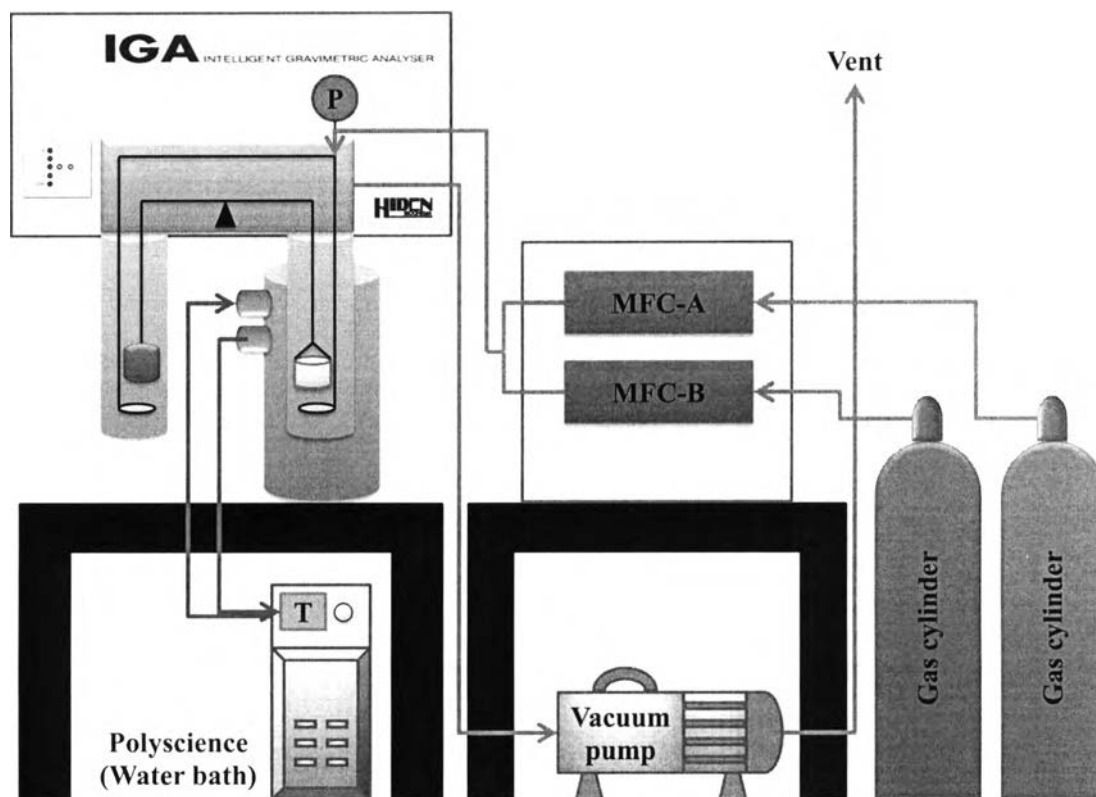


Figure 3.3 IGA-003 configuration set for static gas operation.

The IGA-003 can operate in both dynamic and static modes. Static mode operation introduces gas into the top of the balance away from the sample, and both the admittance and exhaust valves control the set point pressure. All absorption measurements in this work were performed in static mode. The sample temperature was measured with a thermocouple located inside the reactor next to the sample container. The water jacket maintained the set point temperature automatically to within accuracy of ± 0.1 K. Three temperatures of 40, 50 and 60 °C (313.15, 323.15 and 333.15 K) were set as isotherms. Once the temperature status showed that it reached the set point and the weight was stabilized after waiting for 1-3 h, several pressure levels up to 20 bar (0.1, 0.5, 1.0, 2.0, 4.0, 7.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0 bar) were used in the present work. To ensure sufficient time for gas-liquid equilibrium, the ionic liquid samples were maintained at set point for minimum time of 2 h with maximum time-out of 4 h.

The IGA method exploits the relaxation behavior following pressure and temperature changes to simultaneously evaluate the time-dependent absorption and asymptotic uptake. The real-time processor was used to determine the end-point for each isotherm. The percent relaxation used as an end point for the real-time analysis was 99%. The minimum weight change for real-time analysis was set at 1 mg, the acceptable deviation of the model from the acquired data was set at 7 mg, and the target interval for weight acquisition was set at a typical value of 1 mg. The temperature variation during an isotherm was maintained less than 0.1 K/min. The gas solubility measurement procedure could be simplified in detail as presented below.

3.2.2.1 Preparation of Sample, Accessories and Program

1. Rinse the bucket with distilled water by pinching it tightly and turning upside down
2. Rinse the bucket with methanol and then soak it in methanol for 5-10 min
3. Dry the bucket at 110 °C for 10-15 min to evaporate the solvent out
4. Cool down the bucket to room temperature
5. Weigh the bucket (the bucket weight: $0.6326x-0.6327x$ g)
6. Be ready with the ionic liquids, transfer pipettes, clean and dry bucket, weight of the bucket, bucket holder, tissue paper, copper gasket and the density of ionic liquids at temperature of the experiment
7. Inspect the equipment physically (diaphragm pump is running, gas cylinder and regulator fully open, sufficient water in water bath, stuffs like black o-ring, nuts and bolts, spanner, etc. in place)
8. Open IGASwin icon on desktop
9. Click on machine mode and this will lead to Idle window

3.2.2.2 *Sample Loading*

1. Click on New Sample icon on toolbar
2. Confirm to load sample and provide password
3. Select small sample
4. Buoyancy table will pop up and then provide sample density as well as weight of sample container
5. Fill in the form in lab book (title, sample, form, etc.) and click on green button to open sample loading window
6. Lower the reactor and load empty bucket using the bucket holder
7. Re-attach the reactor as draught shield (only 2 bolts) and wait for stability (no red arrow on the stability meter)
8. Click “Record empty pan reading” button
9. Lower the reactor and load the sample (put between 65-75 mg of the sample at the bottom of the bucket in the middle)
10. Re-attach the reactor as draught shield, wait for stability and click “Finished” button
11. Seal the reactor with the 6 nuts and bolts in diagonal fashion
12. Put the o-ring and steel ring on the reactor and then attach the thermostat with the reactor
13. Put the clamp to fasten the steel o-ring with the thermostat
14. Attach the polyscience (water bath)
15. Lab book will be shown again with the weight of the sample
16. Record the weight of the sample and time to calculate the percent weight loss during sample treatment
17. Stay in Idle window

3.2.2.3 *New Application Set-up*

1. Click on New Application icon
2. IGA-003 window will be appeared with the static mode
3. Select “Pressure control only”, “Gas supply via MFC”, “SS316N” and “Water bath”
4. Select stream, gas and the inlet port to MFC from gas cylinder
5. Define gas flow rate (197 mbar/min)
6. Warning regarding gas cylinder connections and regulators will be appeared
7. Select Idle mode
8. Stay in Idle window

3.2.2.4 *Drying and degassing*

1. Run chart and click on pressure set icon on toolbar
2. Select outgas and define the flow rate (200 mbar/min)
3. Wait at least 30 min until the pressure status box shows green outgas
4. Click on temperature set icon on toolbar and set temperature at 70-75 °C
5. Wait at least 10 h to ensure that all contaminants are evaporated
6. Start checking whether the weight of the sample is stabilized (straight line) and keep checking water in water bath
7. Click on temperature set icon and enter the experimental temperature for the isotherm
8. Wait until the temperature status box shows set point and a new weight is stabilized for 1-3 h
9. Check water in water bath again
10. Save and end the chart
11. Stay in Idle window

3.2.2.5 Isotherm

1. Check out the density of ionic liquids and the bucket weight again by clicking set up and then buoyancy
2. Click Set up, Isotherm and then Static
3. Give the 13 pressures for solubility measurement (0.1, 0.5, 1.0, 2.0, 4.0, 7.0, 9.0, 10.0, 11.0, 13.0, 15.0, 17.0, 19.0 bar) in sorption window
4. Give nothing in desorption window
5. Provide real time parameters (Mode, Minimum time, Time out and Wait until)
6. Click “Edit sequence” and convince that the experimental temperature is set
7. Click Run, Isotherm and then Static
8. Enter the title for the isotherm, select “Begin with Sorption Scan” at initial options and select “Outgas Sample” at End State
9. Check out what you have programmed before clicking continue
10. Confirm that kinetic data will be saved for the following device: Total weight, Pressure, etc.
11. Confirm that the water bath temperature will be set to the experimental temperature
12. Now the machine will execute what is programmed and determine the isotherm for all the pressures and then outgas sample
13. Stay in Idle window after isotherm experiment is done

3.2.2.6 Sample Removal

1. Check temperature status whether temperature is below 50 °C. If not, set temperature below 50 °C and leave it until the set point is reached

2. Click on Remove Sample, confirm to remove sample and then provide password
3. Not confirm to evacuate/decontaminate the chamber
4. No warning will be appeared if temperature is below 50 °C
5. Remove the polyscience by first removing the water bath pipes from the thermostat, removing the clamp and loosen the steel ring and black o-ring, lowering the thermostat, wiping the reactor with tissue if it is wet and then removing the steel and black o-ring
6. A warning of pressure status will be appeared because the system pressure is not between 0.915 and 1.015 bar
7. Open air admittance valve slowly, wait for pressure to rise and then click on continue when the pressure approaches atmosphere
8. Close air admittance valve
9. Remove SS316N reactor
10. Use the bucket holder to remove the bucket from the reactor, keep it on the table and replace another empty bucket
11. Re-attach the reactor as draught shield
12. The data of pressure and mass fraction will be collected

3.2.3 Buoyancy Correction and Data Treatment

Although the gravimetric microbalance provides a direct method for measuring gas solubility, a number of gravitational forces must be taken into account in the solubility calculations due to a buoyancy effect. The buoyancy effect will be significant especially at low temperature and high pressure since the gas density is high. These gravitational balance forces introduced at high pressure originate from changes in the buoyant forces as well as the balance sensitivity due to changes in pressure and temperature, aerodynamic drag forces created by the flow of gases, and volumetric changes of the sample due to expansion.

The buoyancy correction follows from Archimedes' principle, which states that there is an upward force exerted on an object equivalent to the mass of fluid displaced. The upward force (C_b) due to buoyancy corresponds to equation 3.1 where the mass of gas displaced is equal to the product of the volume of the submerged object (V_i), the gas density (ρ_g) of gas at given (T,P) and the gravitational acceleration (g). For the constant volume of the object, V_i will be equivalent to the mass of the object (m_i) divided by the density of the object (ρ_i).

$$C_b = gV_i\rho_g(T, P) = g \frac{m_i}{\rho_i} \rho_g(T, P) \quad (3.1)$$

The buoyancy correction using IGA-003 consists of many important components for weighing the sample. The difference between the weight of the sample side (i) and that of the counterweight side (j) accounts for the weight measured by the balance. The microbalance components and their weights as well as densities are summarized in Table 3.2. The sample side consists of a sample container, sample ballast, an upper sample hang-down and a lower sample hang-down. Similarly, the counterweight side comprises a counterweight, a counterweight container, an upper counterweight hang-down and a lower counterweight hang-down. The mass balance expression as shown by equation 3.2 includes the summation of all components, the mass of absorbed gas (m_a) and a correction factor (C_f) due to the sensitivity of the balance.

$$\sum_{i=1} m_i - \sum_{j=1} m_j - \sum_{i=1} \frac{m_i}{\rho_i} \rho_g(T_i, P) - \sum_{j=1} \frac{m_j}{\rho_j} \rho_g(T_j, P) + m_s + m_a - \frac{m_s}{\rho_s(T_s)} \rho_g(T_s, P) - \frac{m_a}{\rho_a(T_s)} \rho_g(T_s, P) - C_f(T_s, P) = Reading \quad (3.2)$$

where m_s and m_a are the weight of dry sample (ionic liquid) and interacted gas, respectively. ρ_s and ρ_a represent the density of ionic liquids and that of gas at a sample temperature (T_s). The density of air (ρ_{air}) at ambient temperature and pressure should be subtracted from ρ_i and ρ_j for more precise accuracy since the components were initially weighed in air. Physical densities of ionic liquids at different temperatures were measured using the Anton Paar density meter (DMA 4500) as described. The amount of gas absorbed can be calculated by the difference between

the reported weight by the balance (*Reading*) and the net forces of the elements of the sample and counterweight side.

Table 3.2 Microbalance components for buoyancy correction

Object	Description	Weight (g)	Density (g/cm ³)	Temperature (°C)
s	Dry sample	m _s	ρ _s	-
a	Interacted gas	m _a	ρ _a	-
i ₁	Sample container	0.63275	7.393103	-
i ₂	Sample ballast	-	-	-
i ₃	Upper sample hang-down	0.3055	19.8	35
i ₄	Lower sample hang-down	0.06524	21	-
j ₁	Counterweight	0.81219	7.9	-
j ₂	Counterweight container	0	2.71	25
j ₃	Upper counterweight hang-down	0.239	19.8	35
j ₄	Lower counterweight hang-down	-	-	-

At the beginning, the constant volume of the ionic liquid sample is assumed. The buoyancy due to sample expansion needs to be included to correct the solubility. The volume of each component on the balance and the sample is required, which can be calculated by the weight and the density of each component and those of the sample. Due to the insignificant volumetric expansion of ionic liquid during gas absorption at measured pressures, the liquid is composed of moles of absorbed gas and those of ionic liquid. The volume of the ionic liquid can be estimated using an average molar volume of the liquid in equation 3.3:

$$\bar{V}_m(T, P) = \bar{V}_{IL}(1 - x) + \bar{V}_g x \quad (3.3)$$

where, $\bar{V}_{IL} = MW_{IL}/\rho_{IL}$, $\bar{V}_g = MW_g/\rho_g$ and x represents the molar fraction of gas in the solution. The volume of the liquid sample as expressed in equation 3.4 is determined by multiplying the number of moles of ionic liquid and absorbed gas in the liquid sample and the average liquid volume (\bar{V}_m).

$$V_m(T, P) = \tilde{V}_m(T, P) \left[\left(\frac{m_s}{MW_{IL}} \right) + \left(\frac{m_a}{MW_g} \right) \right] \quad (3.4)$$

Equation 3.5 expresses the total mass of the liquid sample during gas absorption, which can be substituted into equation 3.2 to account for the buoyancy change with respect to sample expansion.

$$V_m(T, P)\rho_g(T, P) = \frac{m_s}{\rho_s(T_s)}\rho_g(T_s, P) + \frac{m_a}{\rho_a(T_s)}\rho_g(T_s, P) \quad (3.5)$$

The amount of absorbed gas from equation 3.2 is solved simultaneously using equations 3.2, 3.3, 3.4 and 3.5. The corrected gas solubility data in terms of mole fraction (x) is calculated using equation 3.6.

$$x = \frac{n_g}{n_{IL} + n_g} \quad (3.6)$$

where n_g and n_{IL} represent the number of moles of gas and ionic liquid, respectively.