CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

The details of various materials such as specifications, purity and supplier information has been included in this section. Moreover, the details related to the preparation of and purification of the studied solvents has also been the interest of the following section.

3.1.1 Solvents

The various solvents which have been used in the present research work include alkanolamines, ionic liquids (ILs) and common organic solvents.

3.1.1.1 Alkanolamine solutions

N-Methyldiethanolamine (MDEA) with a stated purity of 99.5% (GC, area%) and Piperazine (PZ) with stated purity of 99.9% was supplied by Merck Sdn Bhd (Malaysia) which were used without further purification. The aqueous MDEA solutions i.e., MDEA + water, aqueous PZ solutions i.e., PZ + water as well as PZ activated aqueous MDEA solutions i.e., MDEA + PZ + water of desired compositions were prepared gravimetrically using an analytical balance (Mettler Toledo, model AS120S) with a precision of ±0.0001 g. The possible uncertainty in the mole fraction calculations was estimated to be around ±0.0001. All the measurements for each sample were performed in duplicate, and the values are reported as an average.

3.1.1.2 Ionic liquids (ILs)

Ionic liquids (ILs), such as 1-hexyl-3-methylimidazolium tetraflouroborate; $[C_6mim][BF_4]$ and 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[C_6mim][Tf_2N]$ containing both water and chloride contents ≤ 100 ppm whereas 1-hexyl-3-methylimidazolium hexaflourophosphate; $[C_6mim][PF_6]$ with water contents ≤ 100 ppm and chloride contents ≤ 10 ppm, were purchased from Merck Sdn Bhd, Malaysia. All the ILs obtained were of high purity (HP) grade with quoted purity of ≥ 99%. Prior to their use for characterization and gases solubility measurements, all the ionic liquids were dried in a vacuum drier.

3.1.1.3 Organic solvents

The organic solvents such as Ethanol (absolute) with purity > 99.4% was obtained from Fischer scientific, 1-Propanol with purity = 99.5% and 1-Butanol with purity = 99.5% were obtained from Merck Sdn Bhd, Malaysia. Methanol with purity = 99.8% was obtained from Aldrich while 2-Propanol with purity > 99% and Acetone with purity = 99.5% were obtained from CALEDON, Brightchem Sdn Bhd, Malaysia. All the organic solvents were used without further purification.

3.1.1.4 Gases

Purified gases such as carbon dioxide (CO_2) with purity 99.9% minimum (moisture < 10 vpm, hydrocarbons < 1 vpm), Methane (CH_4) with purity > 99.995%, Nitrogen (N_2) with purity 99.999%, Air containing oxygen (O_2) 21%, moisture (H_2O) < 2 ppm, carbon monoxide (CO) < 0.5 ppm, CH_4 < 5 ppm and CO_2 < 0.5 ppm, Helium (He) with purity 99.999% minimum (moisture and O_2 < 3 vpm each and CO, CO_2 , CH_4 < 1 vpm each) were purchased from MOX-Linde gases Sdn Bhd, Malaysia. The binary mixtures of CO_2 and CH_4 with purities; a) 20.47 and 79.53 (mol%), b) 40.01 and 59.99 (mol%) of analytical grades for GC calibration purpose, were purchased from SOXAL, Oxygen Air Liquide Pte Ltd, Singapore.

3.2   Methods

The equipments which are used in this research work could be divided as: i) Analytical equipments for the measurement of thermophysical properties of solvents and composition of gaseous mixture and ii) High pressure gas solubility cell. The details of equipments in terms of their specifications, experimental capabilities, calibration methods, operating pinciples and measuring procedures are described as follows:

3.2.1   Piperazine solubility in water

Piperazine (PZ), a secondary cyclic diamine, is one of the most recently used 'activator' in combination with aqueous MDEA solutions to achieve relatively high rates of CO_2 absorption. However, the solubility of PZ in water is limited due to the formation of piperazine hexahydrate ($C_4N_2H_{10} \cdot 6H_2O$) crystals (monoclinic pseudo-tetragonal) which melt at 317 K (Schwarzenbach, 1968). Therefore, the extent of PZ solubility limit in water was investigated by adding a known quantity of anhydrous PZ (solid crystals) in a round bottom flask containing 20 mL of distilled water. The aqueous PZ samples were placed in a thermostated water bath shaker (Polyscience, 28L B/S/C) with temperature uniformity of ±0.2 K. To ensure proper mixing of PZ in water, the apparatus was operated at a shaking speed of 160 cycles.min^{-1}. Anhydrous PZ solid crystals were added in water until the saturation or equilibrium was achieved. The shaker was then stopped and the sample solutions were allowed to settle down before testing the samples for their limited solubility.

The total amount of PZ was determined after taking out a small quantity of the solution from upper portion of the flask and titrated with 2M HCl to an endpoint pH of 2. The total amine contents of the solution in the absence of other basic species are usually determined with acid titration to pH 2-4. The solubility of PZ in distilled water was measured at a temperature range of 278 K to 343 K and the experimental data is presented in Table 3.1. As mentioned earlier that the limitation of PZ solubility in water may be explained due to the formation of PZ hexahydrate crystals. This fact is reinforced

with the appearance of a discontinuity in PZ solubility at around 313 K, as shown in Figure 3.1. The experimental solubility values of PZ in water appeared to be in good agreement with the literature values i.e., in the present work, PZ solubility at 293 K is found to be 148.16 g.L^{-1}, which is in close proximate to the reported value of Merck (Piperazine, MSDS) i.e., 150 g.L^{-1}.

Table 3.1: Solubility of piperazine (PZ) in water.

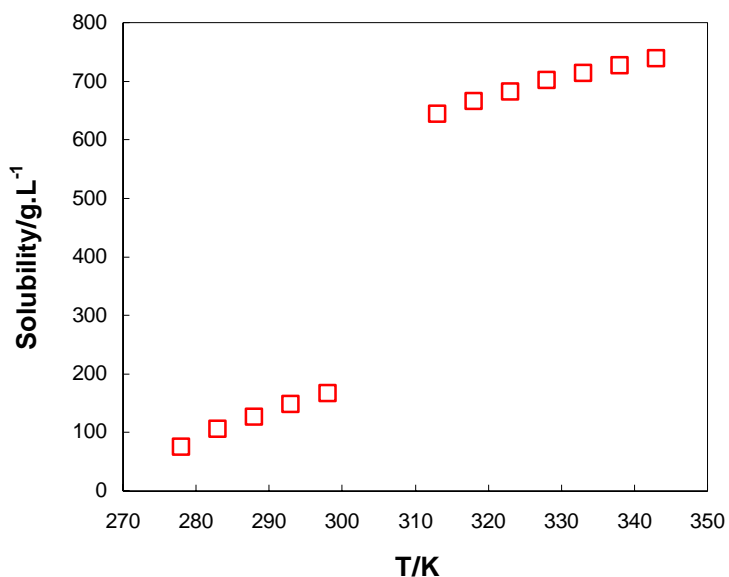| T /K	PZ solubility		
	g.L^{-1}	Molarity/moles.L^{-1}	Mole fraction
278	74.9418	0.87	1.5×10^{-2}
283	105.9522	1.23	2.2×10^{-2}
288	126.6258	1.47	2.5×10^{-2}
293	148.1608	1.72	3.0×10^{-2}
298	167.1116	1.94	3.4×10^{-2}
313	644.3272	7.48	0.121
318	665.8622	7.73	0.124
323	682.2288	7.92	0.127
328	702.0410	8.15	0.130
333	714.1006	8.29	0.132
338	727.0216	8.44	0.134
343	739.0812	8.58	0.136

Figure 3.1: Solubility of anhydrous solid crystals of PZ in distilled water at temperatures (273 to 343) K.

3.2.2   Purification of ILs

The imidazolium based ILs are usually contaminated with water and chloride contents as an impurity. The contents of water in ILs originate from two sources i.e., during washing step of the IL synthesis process and due to the hygroscopic nature of ILs. The chloride contents in ILs are usually added up in the ion exchange step of their process of synthesis. The purification or treatment of ILs is required to remove the water and chloride prior to their use for each set of measurements. For this purpose, the studied ILs were dried in a vacuum drier to remove water and to some extent the chloride contents which are dissolved in water. The quantification of impurities associated with ILs, is a crucial task in assessing the reliability of physical constants and solvent properties. However, in most of the published work related to thermophysical properties of ILs, the extent of their 'purity' has not been systematically verified; hence the reliability of published data for 'pure' IL is questionable (Berthier et al., 2004). Moreover, a considerable effect on the physical properties of ILs has also been reported due to the presence of chloride and water contents in ionic liquids (Seddon et al., 2000). Therefore, it is extremely important to measure and report the presence of impurity contents associated with ILs during their characterization, which would lead to generate more reliable and accurate physiochemical database of ionic liquids.

The purification of ILs with respect to the removal of water contents was performed in a Vaccum dryer. All the samples were placed for 3 days in a dryer in which temperature was maintained at 313 K and a vacuum of 76 cm of Hg. Later, all the samples were tested for their water and chloride contents. The water contents of ILs were investigated using a coulometric Karl Fischer titrator, DL-39 (Mettler Toledo), using a hydranal coulomat AG reagent (Riedel-de Haen). The chloride contents of all ILs were determined using an autotitrator (model DL-55, Mettler Toledo) with 0.005 M silver nitrate ($AgNO_3$) as the titrant. Each measurement was made in triplicate and the values are reported as an average with an accuracy of ±5%.

The water and chloride contents of the dried ILs are shown in Table 3.2. The water and chloride contents in ILs were found to be in decreasing order of [C$_6$mim][PF$_6$], [C$_6$mim][BF$_4$], [C$_6$mim][Tf$_2$N]. These results reveal that the presence of different anions of imidazolium based ILs has significant effect in making association with water and halide contents.

Table 3.2: Water and chloride contents of ILs after purification.

Impurities (ppm)	[C$_6$mim][BF$_4$]	[C$_6$mim][PF$_6$]	[C$_6$mim][Tf$_2$N]
water contents	324	456	268
chloride contents	34	45	28

3.2.3 Miscibility of ILs with organic solvents

The miscibility of ILs with various organic solvents such as methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, acetone and water was carried out at 298.15 K under atmospheric pressure. The equimolar compositions of binary mixtures of ILs and organic solvents were prepared in closed vials and thoroughly stirred for 2 hours to ensure the attainment of liquid-liquid equilibrium (LLE). The extent of miscibility i.e., partial or complete miscibility or immiscibility of two liquids was observed visually based on: i) formation of a homogeneous solution, ii) change in the original volume of the respective liquid and iii) presence of two distinct layers. The temperature of sample vials was regulated using a Polyscience temperature controller bath (model 9510) with an uncertainty of ±0.01 K.

The miscibility measurements of ILs with various organic solvents were carried out to find an appropriate solvent which could be utilized for rinsing the solubility cell after each experimental gas solubility measurement. The extent of miscibility i.e., partial or complete miscibility or immiscibility of two liquids was visually observed and shown in Table 3.3.

Table 3.3: Miscibility of several organic solvents including water in ILs at 298.15K under atmospheric pressure.

Solvent	[C_6mim][BF_4]	[C_6mim][PF_6]	[C_6mim][Tf_2N]
Methanol	Miscible	Miscible	Miscible
Ethanol	Miscible	Miscible	Miscible
1-Propanol	Miscible	Immiscible	Miscible
2-propanol	Miscible	Immiscible	Miscible
1-Butanol	Miscible	Immiscible	Miscible
Acetone	Miscible	Miscible	Miscible
water	Partially miscible	Immiscible	Immiscible

Almost all the studied ILs appeared to be miscible with lower to higher alcohols and acetone. However, [C_6mim][PF_6] has shown immiscibility with higher alcohols (1-propanol, 2-propanol and 1-butanol). The results for miscibility behavior of [C_6mim][PF_6] are found to be in good agreement with Pereiro et al. (2006). The complete immiscibility of [C_6mim][PF_6] and [C_6mim][Tf_2N] with water depicts their hydrophobic character. Although the IL with [BF_4] anion also falls in the category of air and water stable ILs, however, the partial misciblility of this IL with water shows its high hygroscopic nature.

3.2.4 Thermophysical properties of solvents

In this research, thermophysical properties of ILs and pure MDEA, aqueous solutions of MDEA, PZ and MDEA + PZ were determined in terms of density, viscosity, surface tension, refractive index and thermal stability for a wide temperature range under atmospheric pressure. All the measured thermophysical properties were also correlated based on the outcomes of experimental results.

3.2.4.1 Density

The density of pure MDEA, aqueous solutions of MDEA, PZ and MDEA + PZ and ILs was measured using a density meter (model DMA 5000, Anton Paar, Austria). The density meter consists of an oscillating U-tube made up of borosilicate glass as a

measuring cell in a thermostated jacket. The operating principle of the density meter is based on the oscillations of U-tube at its fundamental frequency which is a function of system mass as follows:

$$\tau = 2\pi\sqrt{\frac{\rho V + m}{C}}$$ (3.1)

where, τ is oscillation period, ρ is sample density, V is cell volume, m is cell mass and C is spring constant. After simplifying equation (3.1) by taking squares on both sides and substituting $H = \frac{4\pi^2 m}{C}$ and $G = \frac{4\pi^2 V}{C}$ in equation (3.2), the sample density could be directly related to the oscillation period as represented in equation (3.3).

$$\tau^2 = 4\pi^2\left(\frac{\rho V + m}{C}\right)$$ (3.2)

$$\rho = \left(\tau^2 - H\right)/G$$ (3.3)

The sample viscosity influences the density measurement through 'damping' effect on the oscillations of U-tube measuring cell and appears to move oscillation nodes slightly which increases the cell volume. The combined error due to these two factors can be presented by equation (3.4) as follows:

$$k \approx 0.05\sqrt{\eta}$$ (3.4)

where, k ; is the error (kg.m^{-3}) and η ; is the sample viscosity (mPa.s). The influence of sample viscosity on the measured density is automatically corrected by the apparatus through an internal software which applies equation 3.5 valid for samples having viscosity < 700 mPa.s.

$$\rho = A\tau^2.(1+D.damping+E.damping^2)-B+C.\tau^4 \qquad\qquad (3.5)$$

where, A, B, C, D and E are correlation coefficients. To determine the temperature with an accuracy of ±0.01 K, a built-in platinum resistance thermometer of the apparatus was used. The apparatus was calibrated by measuring the density of Millipore quality water at regular intervals according to supplier instructions. The calibrated apparatus was also verified using few pure organic liquids of known densities and found to be with in the adjusted uncertainty of the apparatus. The procedure adopted for the density measurements of all the samples can be configured in the following steps:

i)   *Cleaning and drying of measuring cell:*

A suitable solvent (volatile, capable to dissolve residues) i.e., ethanol in this case, was injected several times in the measuring cell using a syringe to remove the residues of the sample. Later, dry air was blown through the measuring cell using a built in air pump for approximately 10 minutes.

ii)   *Measurement settings:*

The execution of accurate density measurement entirely depends on the measurement settings which includes equilibrium mode, viscosity correction and temperature scan steps. The settings for density measurement of all samples were adjusted to work at 'medium equilibrium mode' with automatic viscosity correction 'method of < 700 mPa.s' and '5 K step increment of temperature' within the initial and final temperature range.

iii)   *Density measurement:*

The predefined quantity of sample (approx. 2mL) was filled in a syringe and slowly injected in U-tube measuring cell (0.7mL) ensuring that there is no bubble in the cell by

viewing through the optical window. The preset method was activated to start the density measurement of and recorded in data memory.

3.2.4.2 Viscosity

The viscosities of pure MDEA, aqueous solutions of MDEA and PZ, and aqueous MDEA + PZ solutions were measured using four calibrated Ubbelohde viscometers (sizes 1, 1C, 1B, and 2). During the calibration and viscosity measurements, viscometers were immersed in a thermostatic bath (Tamson, TVB445) with a built-in circulation stirrer for uniform temperature distribution. The bath temperature was regulated with a Pt-100 temperature probe to within 0.01 K. The viscometers containing samples were kept in a thermostatic bath at least for 15 minutes to allow them to equilibrate and to obtain the set point temperature. Later, the time required for samples to flow between the marked points of viscometer i.e., efflux time was measured manually with a digital stopwatch with an accuracy of 0.01 seconds. The kinematic viscosity values were obtained by multiplying efflux time (seconds) with the respective viscometer constant using the following equation:

$$v = Ct \tag{3.6}$$

where, v is the kinematic viscosity in centistokes (cSt), C is the viscometer constant in cSt/s and t is the efflux time in seconds (s). The dynamic viscosity of alkanolamine samples was calculated by multiplying the kinematic viscosity values with the corresponding density values of the samples. The maximum estimated error in calculating dynamic viscosity was within ±0.03 mPa.s, after including the uncertainties of both the density and kinematic viscosity values.

The dynamic viscosities of all ILs were measured using a cone and plate (L-series) viscometer (CAP 2000, Brookfield). The viscometer was calibrated using few standard calibration fluids according to the instructions given by the supplier. The viscometer was placed in a dry environment to avoid the effects of presence of high humid air. The

viscosity measurements were carried out as soon as the samples were placed on viscometer plate. The IL samples were considered to be no more in contact with the external environment, immediately after the cone was tightly pressed on plate. All the viscosity measurements for ILs were performed at viscometer rotational speed of 900 rpm. The cone numbers (1 to 4) which are recommended for viscosity range (21 to 1667) mPa.s, were utilized for the viscosity measurement of all IL samples.

3.2.4.3 Surface tension

The surface tension measurements of pure MDEA, aqueous solutions of MDEA, PZ and (MDEA + PZ) solutions were carried out using an interfacial tension meter, IFT 700 (VINCI Technologies). A pendant drop method was used for surface tension measurements, which allows forming of a regular drop suspended in a thermo-stated chamber. A camera connected to the computer, focuses and records the shape of the liquid drop to derive the interfacial properties through fast calculating system software.

A spinning drop video tensiometer (model; SVT 20) introduced by Dataphysics instruments (GmbH, Filderstadt) was used to measure the surface tension of all IL samples. The standard method of measuring surface tension was adopted in accordance with the supplier instructions which could be summarized in the following steps:

i)   Capillary and sample preparation:

The glass capillary was flushed several times with acetone to ensure the removal of residues of previous measurement and cleaned with dry compressed air. The cleaned capillary was filled with IL samples (2-3) mL, as outer phase (higher density fluid) from bottom to up and sealed carefully to ensure that there is no air bubble left inside the capillary which could greatly alter the surface tension measurements.

ii)   Measuring procedure:

The glass capillary was fixed inside the main fame of calibrated apparatus which is encapsulated by thermostat fluid (water). The capillary was initially started with a spinning revolution of 500 rpm and one drop of water was injected into the capillary as inner phase (lighter density fluid). To avoid the contact of injected water drop with capillary wall, it is recommended to rotate the capillary from 200 to 500 rpm. Later, the spinning rate of the capillary was gradually increased to 4000-6000 rpm (optimal/recommended range of rotational speed) with moderate steps of 200 rpm to obtain stable and clear image of water drop. Dynamic calibration for the image size of drop was performed through activating the camera "movement" in order to get reproducible results of stable and sharp drop. The "profile fit" mode of the operating software was activated to get a series of surface tension measurement results for the sample and the average values were reported. The calculations for the surface tension measurement were executed automatically by the software according to the principles of Laplace and Vonnegut (VG).

3.2.4.4 Refractive index

The refractive indices of pure MDEA, aqueous MDEA solutions, aqueous PZ solutions, PZ activated aqueous MDEA solutions and all room temperature ILs were determined using ATAGO programmable digital refractometer (RX-5000 alpha) with a measuring accuracy of $\pm\ 4\times10^{-5}$. The apparatus was calibrated at regular intervals and before each series of sample measurements through determining the refractive index of Millipore quality water. The calibrated apparatus was also verified by measuring the refractive index of pure liquids with known refractive index values. The measuring procedure for refractive index consists of placing a sample on cleaned prism and covering the prim with lid followed by pressing the START button to execute the result on LCD in few seconds.

3.2.4.5   Thermal decomposition

The thermal stability of pure MDEA, aqueous solutions of MDEA and PZ, PZ activated MDEA solutions and ILs were investigated using a thermogravimetric analyzer (TGA) PerkinElmer. This analytical technique is used to determine the thermal stability of materials and to assess the fraction of volatile components within it, by monitoring the weight change that occurs as the specimen material is heated. The measurement is normally carried out in air or in an inert atmosphere, such as Nitrogen (N_2), Helium (He) or Argon, and the weight is recorded as a function of increasing temperature. The effect of temperature on the decomposition of all the solvents was studied at a constant heating rate of $10^{o}C.min^{-1}$. All the samples were placed in a platinum pan and heated at constant rate to measure the percent weight loss in the presence of N_2 atmosphere supplied at the rate of $20 \ mL.min^{-1}$.

3.2.5   Gases solubility measurements

The solubility of pure CO_2 in MDEA + water with concentrations 32.28 and 48.80 (wt. 5), MDEA + PZ + water with concentrations 32.28/1.74, 32.28/5.16, 32.28/10.35, 48.80/1.74, 48.80/5.16, 48.80/10.35 (wt.%) and three imidazolium based ILs were experimentally measured at low temperatures and high pressure conditions The effect of CH_4 presence on the solubility of CO_2 was also determined for aqueous MDEA solutions and ILs using binary mixtures of CO_2/CH_4 as high pressures. The experimental solubility of gases in all the studied solvents was measured using high pressure gas solubility equipment.

3.2.5.1   High pressure gas solubility equipment

The high pressure gas solubility equipment (SOLTEQ, model BP-22) was specifically designed, fabricated and installed through SOLUTION Engineering Holdings Bhd. A digital picture and schematic diagram of the high pressure gas solubility equipment is shown in Figure 3.2, Figure 3.3, and Figure 3.4 respectively. The above mentioned

equipment is compatible to measure the solubility of wide range of gases such as CO_2, SO_2, H_2S, NO_2, O_2 and other constituents of natural gas (methane, ethane, propane, n-butane, iso-butane, n-pentane, iso-pentane) with any desired compositions in water, physical and chemical solvents. The equipment consists of four sections i.e., i) gas cylinders ii) data logging and acquisition system iii) main gases solubility measurement section and iii) gas and liquid analysis section. The details of various parts in these sections are as follows:

- There is a separate place allocated for the proper positioning of gas cylinders which are connected to the main solubility unit through pipelines.
- The auto-logging data acquisition system which is operated using PC through LABVIEW software.
- The main solubility measurement section consists of flow controllers with maximum flow rate capacity for $CO_2 = 6$ L.min.$^{-1}$ and for $CH_4 = 10$ L. min.$^{-1}$), a mixing vessel, gas solubility cells, thermostatic bath with water circulation system (JULABO), air driven gas booster pump (Haskel, model AG-15, USA), liquid dosing reciprocating metering pump (Eldex laboratories, Inc. USA) and gas evacuation system with a turbo molecular vacuum pump (Pfeiffer, model TSH 071 E)
- A gas chromatograph (Clarus 500, PerkinElmer) operated through Total chrom software and an autotitrator (Mettler Toledo, model DL 55) running with LabX pro software, from a single workstation.

Figure 3.2: A digital picture of high pressure gas solubility apparatus (SOLTEQ, BP-22).

Figure 3.3: A digital picture of mixing vessel and high pressure gas solubility cell assembly in BP-22 equipment.
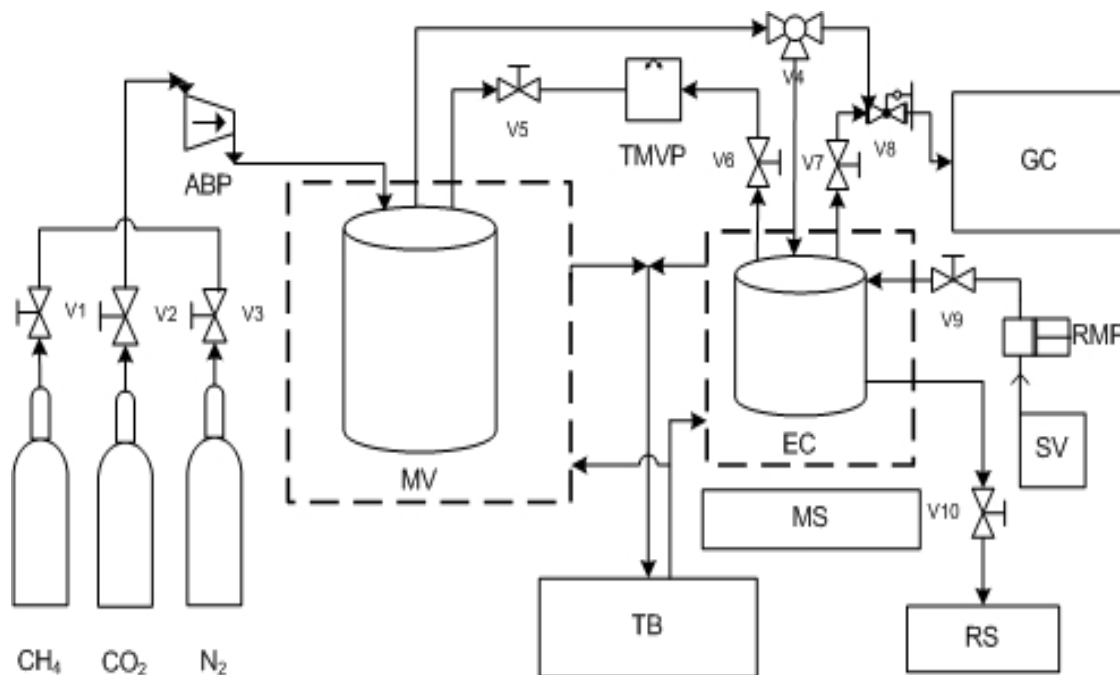
Figure 3.4: Schematic diagram of high pressure gas solubility equipment (SOLTEQ, model BP-22).

ABP: Air driven non lubricated gas booster pump

MV: Mixing vessel

TB: Thermostated bath

EC: Equilibrium cell

MS: Magnetic stirrer

GC: Gas chromatograph

TMVP: Turbo-molecular vacuum pump

SV: Sample vessel

RMP: Reciprocating metering pump

RS: Recovered solvent

3.2.5.2   Procedure for measuring CO_2 solubility in solvents

The experimental measurements for CO_2 and binary mixtures of CO_2 and methane (CH_4) i.e., 60/40 (B_{64}) and 40/60 (B_{46}) volume percent in all the studied solvents were performed using high pressure gas solubility equipment (SOLTEQ, model BP-22) at temperatures of 303.15 K, 318.15 K and 333.15 K and pressures up to 90 bar. The solubility measurements for CO_2 were also performed for recycled ILs in order to assess the loading capacity of ILs and effectiveness of the system through absorption-desorption cycle using high pressure gas solubility cell. The steps for the solubility measuring procedure are detailed as follows:

The pure CO_2 gas was filled in mixing vessel after opening the gas flow control valve at its full load and compressing it using air driven gas booster pump to a desired pressure. In case of binary mixtures of CO_2/CH_4 the desired volume percentage of each component was maintained through controlled opening of flow valves i.e., for B_{46} and B_{64} the CO_2 and CH_4 gases flow valves were opened in ratio of 2.4/6 and 3.6/4 respectively. A constant temperature of mixing vessel was ensured by immersing it in a thermostatic bath and maintaining a fixed flow of water through an auto circulation system.

The gas was transferred to solubility cell by opening valve (V4) steadily to make sure that there is no sudden gas expansion or quick increase in temperature. The gas solubility cell is also immersed in a thermostatic water bath to maintain a desired temperature. The temperature accuracy ±0.1 K for thermostatic water bath in which the mixing vessel and gas solubility cell are immersed was obtained using RTD (Pt-100).

A known volume of solvents (5 mL) were dosed in gas solubility equilibrium cell after opening valve (V9) using a pre-calibrated reciprocating metering pump at 900 rpm. The solubility calculations for CO_2 in solvents were made after achieving a constant pressure in equilibrium cell which was indicated within 1 to 4 hours for all the studied solvents. The equilibrium was assumed to be attained when the total pressure of the system reaches to a constant value and was maintained for at least one hour. A digital pressure transducer

(Druck, DPI-150) with an accuracy of ±0.01 bar was used to detect all initial and equilibrium system pressures in mixing vessel and solubility cell. The temperature of the gas phase (inside mixing vessel), and gas/liquid phase (inside solubility cell) was measured with a digital thermometer (YOKOGAWA 7653) with a precision of ±0.01 K.

The liquid samples of the studied solvents were withdrawn from the equilibrium cell. In this work, the solubility of gases in all the studied solvents was calculated using modified equation (for gas solubility on molality scale) of the form mentioned by Puranto et al., 1996.

$$m_g = \frac{\left\{P_i - (P_f - P^v)\right\}V_g \times 10^6}{RTV_l \rho_l} \qquad\qquad (3.7)$$

where, m_g is gas solubility (CO_2) in solvent (ILs) on molality scale i.e., moles.kg^{-1}, P_i and P_f are initial and final or equilibrium total pressures of system (bar), P^v is vapor pressure of solvent (for IL is taken as zero due to negligible vapor pressure), V_g is volume of gas (cm^{-3}), R is gas constant i.e., 83.1451 (bar.cm^3.mole^{-1}.K^{-1}), T is temperature (K), V_l is volume of solvent (mL) and ρ_l is density of solvent (kg.m^{-3}).

For the solubility measurements of pure CO_2 in alkanolamines, the liquid phase was also analyzed by a precipitation titration method using an automatic titrator (Metrohm 785 DMP Titrino). The amount of CO_2 in alkanolamine solutions was calculated on molality scale from the amounts of HCl found by titration method previously reported by Addicks et al. (2002). For the purpose of titration, the liquid sample (3 mL) was mixed with of 3.0 M NaOH (10 mL) to convert free dissolved CO_2 and HCO_3^- into nonvolatile ionic species such as carbonates (CO_3^{-2}). Then 50 mL of 0.3 M $BaCl_2$ was added in the solution for CO_3^{-2} to be precipitated as $BaCO_3$. The solution was heated for a few minutes to agglomerate the $BaCO_3$ particles and then cooled to ambient temperature it was filtered using a Millipore filter. Both the filter and filtrate are put into distilled water, and the $BaCO_3$ was dissolved by the addition of 0.1 M HCl and solution was boiled to remove

CO_2. After the solution was cooled to ambient temperature, it was titrated with 0.1 M NaOH to find the amount of HCl not used to dissolve $BaCO_3$. From the amounts of HCl found by titration and the amount added to dissolve the $BaCO_3$ particles, the amount of CO_2 in the solution was calculated.

The analysis for composition of binary gaseous mixtures of CO_2/CH_4 was carried out using an online gas chromatograph with thermal conductivity detector (TCD) module. The gas chromatograph is connected to an auto-logging database system and operated through Totalchrom navigator (V 3.0) software. The gas sampling valve for the GC is integrated with a mixing vessel and solubility cell through a pressure reducing valve. The GC was calibrated using analytical grades for binary mixtures of CO_2 and methane. The composition of gases before and after absorption was determined using GC neglecting the presence of solvents in vapor phase. The solubility of CO_2 and methane in aqueous MDEA solutions and ILs is calculated based on the mole percent difference of gaseous mixture before and after achieving equilibrium and reported on molality scale i.e., moles of gas absorbed per kilogram of solvent.

The equilibrium cell was depressurized after each gas solubility measurement, purged with nitrogen and evacuated to 0.45 bar using a vacuum pump. The schematic flowcharts for the gas solubility measurements and cleaning procedure for solubility cell are shown in Figures 3.5 and 3.6 respectively.
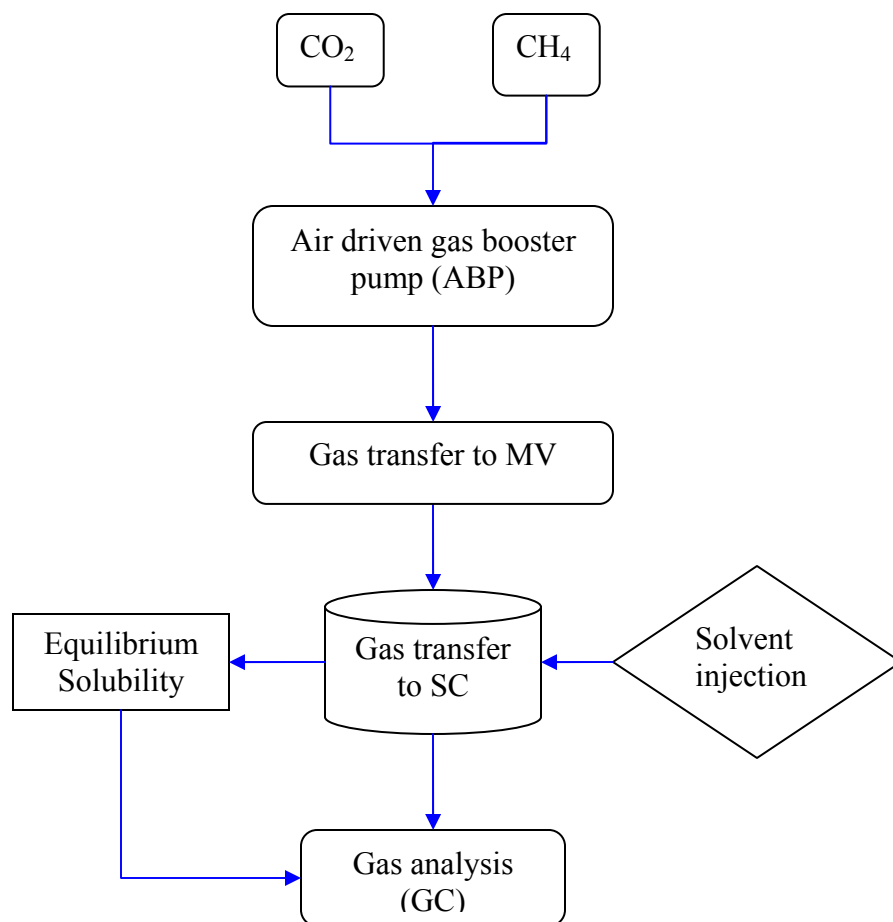
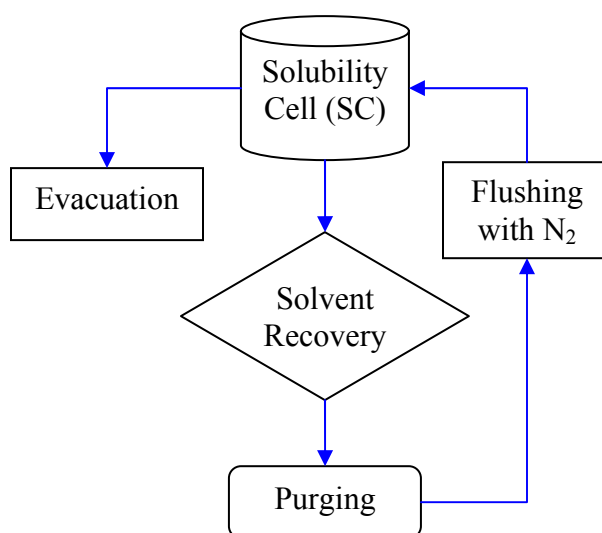**Figure 3.5:** Flowchart to perform gases solubility measurements.

Figure 3.6: Flowchart for cleaning of equilibrium solubility cell.