

CHAPTER 4

THERMOPHYSICAL PROPERTIES OF SOLVENTS

4.1 Introduction

The determination of thermophysical properties of solvents is imperative for developing an understanding on the nature of their constituent molecular behavior. The knowledge of solvent properties also executes an essential function in the design and development of many kinds of products, processes and industrial equipments. The solvent properties not only provide an insight for the type of intramolecular interactions such as van der waals forces, columbic forces and hydrogen bonding, but also help to know the interactions between solute and solvent i.e., intermolecular. Before incorporating the selected solvents for an industrial application, it is essential to establish a fundamental understanding in their physical, chemical and thermodynamic properties. Therefore, the study conducted here has attempted to also measure some important physical properties of both solvents used namely aqueous solutions of alkanolamines and ionic liquids (ILs). The measured thermophysical properties of solvents include density, viscosity, surface tension, refractive index and thermal decomposition. The effect of temperatures on all the measured physical properties of solvents is investigated for a wide range. The values for the thermal expansion of solvents are derived from the experimental densities of the corresponding solvent. The main motive behind the measurement of thermophysical properties of the studied solvents is to understand their behavior and to develop a relationship between the solvent characteristics and their potential capabilities towards selective absorption of gases such as carbon dioxide (CO₂) and methane (CH₄).

4.2 Thermophysical properties of solvents

Thermophysical properties including density (ρ), isobaric coefficients of thermal expansion, viscosity (η), surface tension (σ), refractive index (nD), and thermal decomposition were measured for various types of solvents over a wide temperature range at atmospheric pressure. The studied solvents are namely aqueous solutions of *N*-Methyldiethanolamine (MDEA) with concentrations 32.28 and 48.80 (wt.%), aqueous Piperazine (PZ) solutions with concentrations 1.74, 5.16 and 10.35 (wt.%), PZ activated aqueous MDEA solutions i.e., 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 and 48.80/10.35 (wt.%) and Imidazolium based ILs i.e., 1-hexyl-3-methyl imidazolium tetrafluoroborate ([C₆mim][BF₄]), 1-hexyl-3-methyl imidazolium hexafluorophosphate ([C₆mim][PF₆]) and 1-hexyl-3-methyl imidazolium bis(trifluoromethylsulfonyl)imide ([C₆mim][Tf₄N]).

4.2.1 Density

The densities of aqueous MDEA solutions with concentrations 32.28 and 48.80 (wt.%), aqueous PZ solutions with concentrations 1.74, 5.16, 10.35 (wt.%), and PZ activated aqueous MDEA solutions i.e., aqueous blends MDEA/PZ solutions 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.%) have been measured using a digital density meter (DMA 5000, Anton Paar) for a temperature range of 298.15 K to 338.15 K at a regular interval of 5 K. Further details of the density meter are given in Section 3.2.4.1. The calibrated density meter was verified by measuring the densities of distilled water and pure MDEA prior to its utilization for measuring densities of aqueous solutions of alkanolamines. The experimental densities of distilled water, pure MDEA, aqueous solutions of MDEA and PZ are shown in Table A-1 of Appendix A, and PZ activated aqueous MDEA solutions are presented in Table A-2 of Appendix A along with their values of percentage absolute average deviations (100AAD) based on the Equation 4.1.

$$100AAD = \frac{1}{N_p} \sum_{i=1}^{N_p} 100 |(\rho_{calc} - \rho_{exp}) / \rho_{exp}|_i \quad (4.1)$$

where, ρ_{calc} and ρ_{exp} calculated and experimental densities respectively, and N_p is number of data points. A comparison between the experimental densities of distilled Water and pure MDEA for this work and the published literature is shown in Figure 4.1. A good agreement between the densities of pure solvents i.e., water and MDEA in this work and the literature was observed.

The effect of temperature on the densities of aqueous MDEA solutions and aqueous PZ solutions is illustrated in Figures 4.2. The effect of temperature on the densities of PZ activated aqueous MDEA solutions are shown in Figure 4.3. A linear decrease in the densities for all the concentrations of the studied aqueous alkanolamine solutions was observed with the increase in temperature.

The densities of 32.28 wt.% aqueous MDEA solutions are lower than its 48.80 wt.% solutions at all measured temperatures. Similarly, for all the temperatures studied, the densities of aqueous PZ solutions was also observed to be in decreasing order of 10.35, 5.16 and 1.74 (wt.%). The densities of MDEA + water were found to be significantly higher with the increase in amine concentration. However, in case of PZ + water, the increase in PZ concentration had insignificant effect on their densities. The effect of PZ addition in both concentrations of aqueous MDEA solutions on their densities has been demonstrated in Figure 4.3. The densities of PZ activated aqueous MDEA solutions were observed to be lower than aqueous MDEA solutions in case of both the studied concentrations of MDEA i.e., 32.28 and 48.80 wt.%. For example, the density of MDEA + water with concentration of 32.28 wt.% decreased from 1027.273 to 1024.783 (kg.m⁻³) at 298.15 K with the addition of 1.74 wt.% of piperazine. The overall precision in the experimental density measurements was found to be better than $\pm 3 \times 10^{-2}$ kg.m⁻³ for all aqueous alkanolamine solvents.

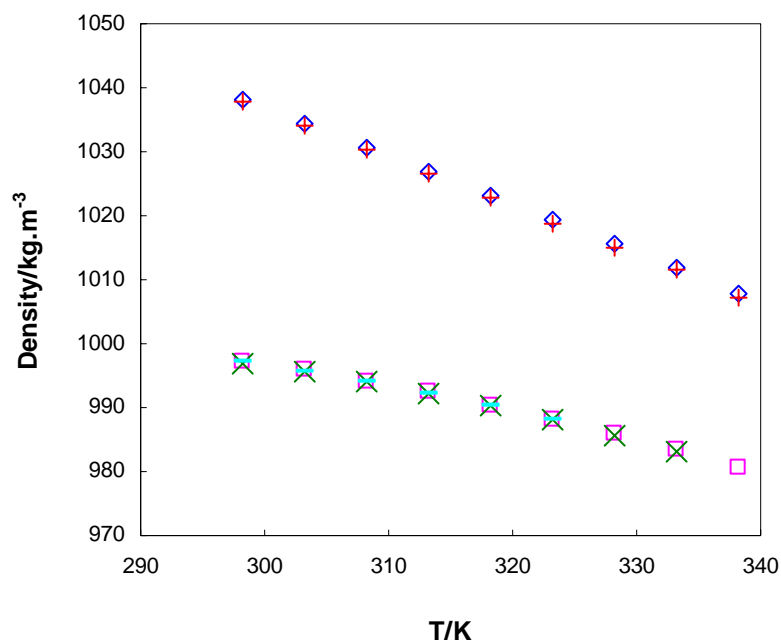


Figure 4.1: Comparison of densities for water.

[this work (\square), Al-Ghawaz et al. (1989) (\times), Alvarez et al. (2006) (---), for MDEA, this work (\diamond), Bernal-García et al. (2003) ($+$)]

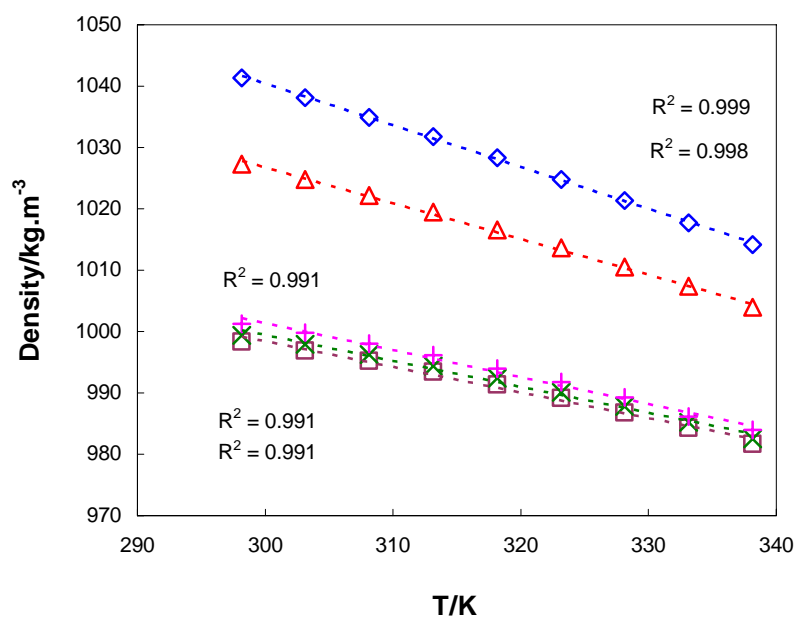


Figure 4.2: Effect of temperature on densities of aqueous MDEA and PZ solutions.

[for (MDEA + water) wt.%, 32.28 (Δ), 48.80 (\diamond), and (PZ + water) wt.%, 1.74 (\square), 5.16 (\times), 10.35 ($+$), correlation (----) using Equation 4.2]

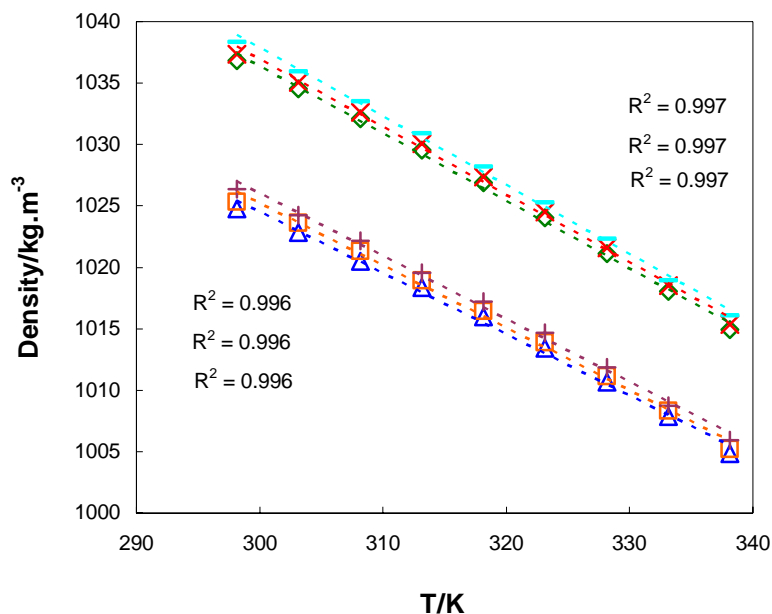


Figure 4.3: Effect of temperature on densities of (MDEA + PZ + water).

[for (MDEA + PZ + water) wt.%; 32.28/1.74 (\diamond), 32.28/5.16 (\times), 32.28/10.35 (—), 48.80/1.74 (Δ), 48.80/5.16 (\square), 48.80/10.35 (+), correlation (----) using Equation 4.2]

The densities of ILs; $[\text{C}_6\text{mim}][\text{BF}_4]$, $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ have been measured using a digital density meter (DMA 5000, Anton Paar) for a temperature range of 298.15 K to 338.15 K. The overall precision in the experimental density measurements for all the studied ILs has been found to be better than $\pm 2 \times 10^{-2} \text{ kg.m}^{-3}$. The experimental densities of all the studied ILs are presented in Table A-3 of Appendix A. The values for the density of $[\text{C}_6\text{mim}]$ based ILs with different types of anions was found to be in the decreasing order of $[\text{Tf}_2\text{N}]$, $[\text{PF}_6]$ and $[\text{BF}_4]$. The effect of temperature on the densities of ILs was plotted in Figure 4.4 which reveals that the densities of all ILs decrease with the increase in temperature. In general, the densities of ILs were found to be higher than aqueous alkanolamine solutions which shows the impact of structural difference for both kinds of solvents i.e., ILs are solely composed of ‘ions’ whereas aqueous alkanolamine solutions are molecular solvents. Moreover, the molar masses of ILs are approximately 3 to 4 time higher than MDEA or PZ e.g., molar mass of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ is $447.42 \text{ g.mol}^{-1}$ while molar mass of MDEA is $119.16 \text{ g.mol}^{-1}$.

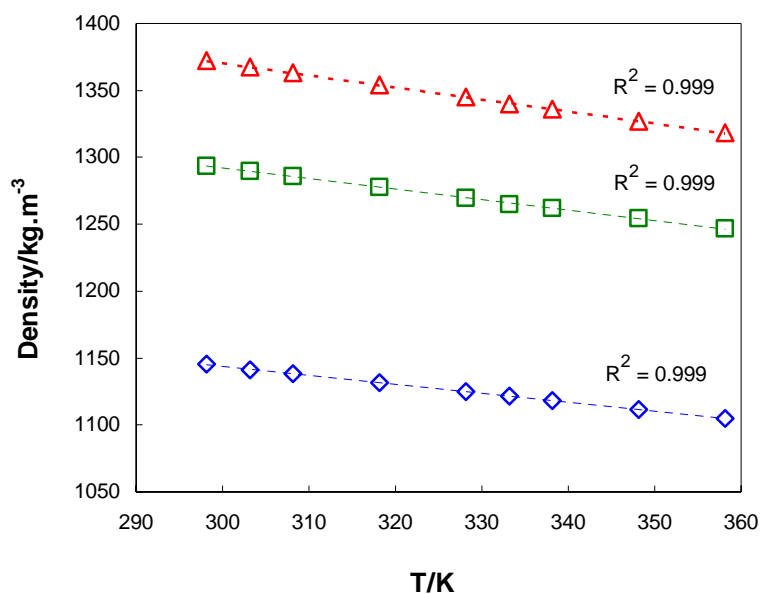


Figure 4.4: Effect of temperature on the experimental densities of ILs.

{for ILs; [C₆mim][BF₄] (◇), [C₆mim][PF₆] (□), [C₆mim][Tf₂N] (△), correlation (----) using Equation 4.2}

The experimental linear relationship observed for the effect of temperature on the densities of water, pure MDEA, all the compositions of MDEA + water, MDEA + PZ + water and ILs was correlated using Equation 4.2.

$$\rho = A_0 + A_1 T \quad (4.2)$$

where, A_0 and A_1 are the fitting parameters which were estimated using a method of least square and presented in Table A-4 of Appendix A, along with the values of standard deviations (SD) calculated using Equation 4.3.

$$SD = \left[\sum_i^{n_{dat}} (Z_{exp} - Z_{cal})^2 / n_{dat} \right]^{1/2} \quad (4.3)$$

where, n_{dat} , number of experimental data points, Z_{exp} and Z_{cal} are experimental and calculated density values respectively.

The densities of ILs at pressures up to 100 bar were also estimated for the entire range of studied temperatures from 298.15 K to 338.15 K using an extended group contribution method as proposed by Gardas et al. (2008):

$$\rho = \frac{M}{NV(a + bT + cP)} \quad (4.4)$$

where, ρ is density (kg.m^{-3}), M is molar mass (kg.mole^{-1}), N is Avogadro's constant (6.02214×10^{23}), V is molar volume ($^{\circ}\text{A}^3$), T is temperature (K) and P is pressure (bar). The constants of equation 4.4 i.e., $a = 8.005 \times 10^{-1}$, $b = 6.652 \times 10^{-4} \text{ K}^{-1}$ and $c = -5.919 \times 10^{-4} \text{ MPa}^{-1}$ were taken from Gardas et al. (2008), which were deduced after analyzing approximately 800 data points with 95% confidence level. The imidazolium based ILs are considered to behave as 'physical solvents' because they are presumed to contain cavities in their structure. Therefore, it is important to know the effect of pressure on the densities of ILs in order to develop an understanding for its role in their absorption behavior at high pressures.

The predicted density values for ILs; $[\text{C}_6\text{mim}][\text{BF}_4]$, $[\text{C}_6\text{mim}][\text{PF}_6]$ and $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$ are presented in Tables A-5, A-6 and A-7 respectively in Appendix A at pressures range of 1 bar to 100 bar and temperature range of 298.15 K to 358.15 K. The effect of pressure up to 100 bar on the densities of ILs which are predicted using equation 4.4 is shown in Figure 4.5 at temperature 333.15K. In general, it has been observed that the density of ILs slightly increase with an increase in pressure. A good agreement between the predicted density values of this work and experimental densities of Gardas et al. (2007) for the IL; $[\text{C}_6\text{mim}][\text{PF}_6]$ has been observed as shown in Figure 4.5 with a percent deviation of $\pm 0.18\%$.

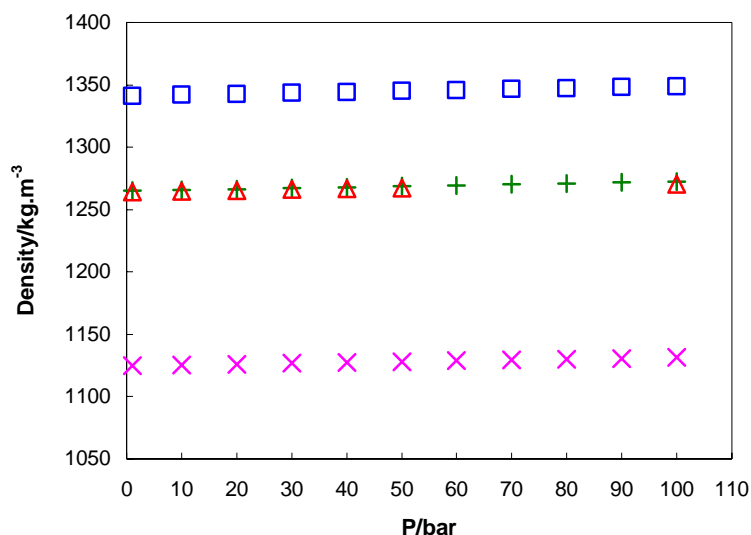


Figure 4.5: Effect of pressure on the densities of ILs at 333.15K.

[this work; [C₆mim][BF₄] (×), [C₆mim][PF₆] (+), [C₆mim][Tf₂N] (□), and Gardas et al. (2007); [C₆mim][PF₆] (Δ)]

4.2.2 Coefficients of thermal expansion

The isobaric coefficients of thermal expansion (α_p) of all the solvents were calculated from their experimental density data using the following empirical correlation (Pereiro et al., 2006):

$$\begin{aligned}\alpha_p &= -1/\rho \cdot (\partial\rho/\partial T)_p \\ &= -A_1/(A_0 + A_1 T)\end{aligned}\quad (4.5)$$

where α_p is thermal expansion coefficient, ρ is the density of solvents, T is the temperature and A_0 and A_1 are fitting parameters taken from Table A-4 of Appendix A. The values for isobaric thermal expansion coefficients of water, MDEA, and aqueous alkanolamine solutions are presented in Table A-8, and for ILs in Table A-9 of Appendix A. It can be observed that the values of isobaric thermal expansion coefficients for all the solvents do not change considerably. Therefore, the variation of volume expansion of the solvents studied here could be considered as independent of temperature for the

temperature range of 298.15 K to 338.15 K. However, the extent of volume expansion for ILs was observed to be slightly higher than aqueous alkanolamine solutions. In case of ILs the percent thermal expansion was found to be in decreasing order of $[\text{C}_6\text{mim}][\text{Tf}_2\text{N}]$, $[\text{C}_6\text{mim}][\text{BF}_4]$ and $[\text{C}_6\text{mim}][\text{PF}_6]$ i.e., 3.8%, 3.75%, 3.57%. The coefficients of thermal expansion values for aqueous MDEA solutions were found to be higher than aqueous PZ solutions. However, in case of PZ activated aqueous MDEA solutions the maximum thermal expansion of 2.23% was observed with amine concentration of 48.80/10.35 wt.%.

4.2.3 Viscosity

The viscosities for aqueous MDEA solutions, aqueous PZ solutions and PZ activated aqueous MDEA solutions were measured using Ubbelohde viscometers at temperature range of 298.15 K to 333.15 K. Further details related to calibrations and measuring procedure of the viscometers are given in Section 3.2.4.2. The maximum estimated uncertainty in calculating dynamic viscosities of MDEA + water, PZ + water and MDEA + PZ + water was within ± 0.04 mPa.s, after including the uncertainty of both the density and kinematic viscosity values. The temperature control accuracy during viscosity measurement of aqueous alkanolamine solutions and ILs was found to be better than ± 0.01 K. The viscosity measurements for all types of the studied aqueous alkanolamine solutions were made in triplicate and the average values are presented in Table A-10 of Appendix A, along with the calculated values of percent average absolute deviations (AAD) by equation 4.1. The viscosities of aqueous MDEA and PZ solutions have been found to be increasing with an increase in respective amine concentration. In general, the viscosities of PZ activated MDEA solutions were found to be slightly higher than aqueous MDEA solutions. However, the viscosities of aqueous MDEA solution with concentration 48.80 wt.% significantly increased with the addition PZ with concentration 5.16 and 10.35 wt.%.

The effect of temperature on the viscosities of all concentrations of aqueous alkanolamine solutions i.e., MDEA + water, PZ + water and MDEA + PZ + water is demonstrated in Figures 4.6 and 4.7 respectively. It has been observed that the viscosities of all the

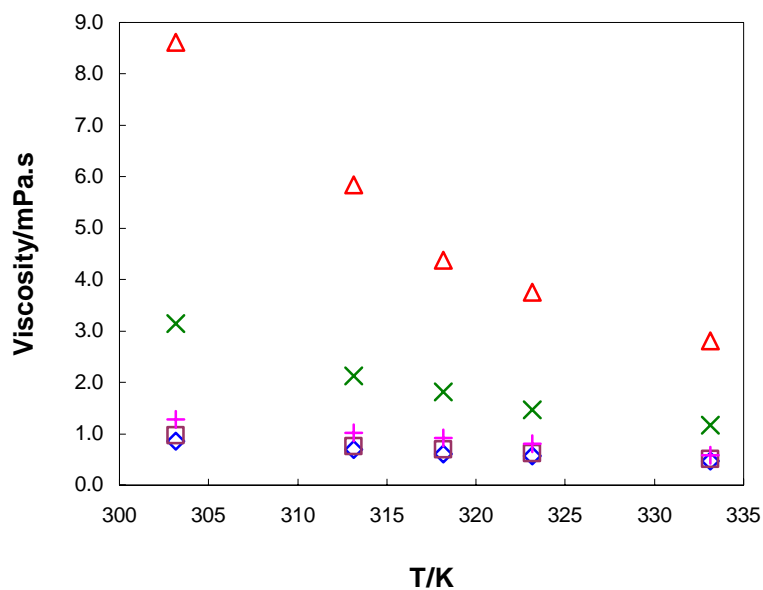


Figure 4.6: Effect of temperature on viscosities of aqueous MDEA and PZ solutions.
[for (MDEA + water) wt.%; 32.28 (x), 48.80 (Δ), and (PZ + water) wt.%; 1.74 (◇), 5.16 (□), 10.35 (+)]

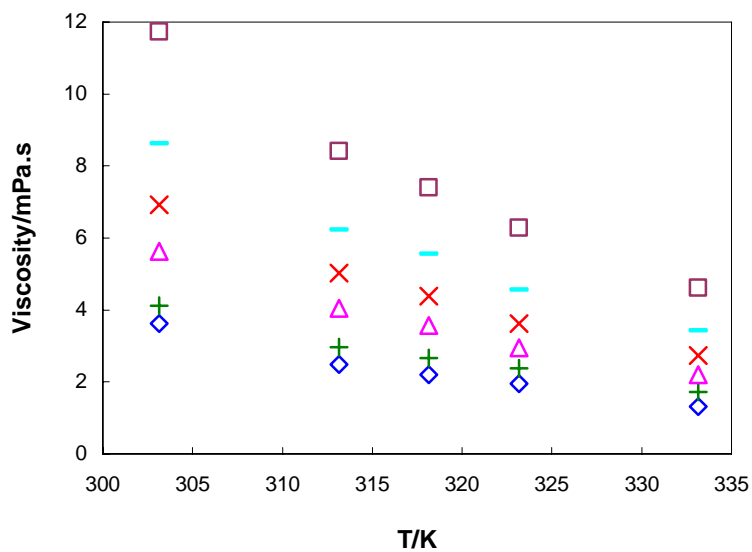


Figure 4.7: Effect of temperature on viscosities of PZ activated aqueous MDEA solutions.
[for (MDEA + PZ + water) wt.%; 32.28/1.74 (◇), 32.28/5.16 (+), 32.28/10.35 (Δ), 48.80/1.74 (x), 48.80/5.16 (—), 48.80/10.35 (□)]

samples of aqueous alkanolamine solutions decreased exponentially with an increase in temperature.

The viscosities of ILs were measured using a cone and plate viscometer (Brookfield) at temperature range of 298.2 K to 348.2 K. Further details of the viscometer which has been used to measure viscosities of ILs are given in Section 3.2.4.2. The viscosity results of ILs are reported as an average agreeing to within ± 10 mPa.s. The temperature control accuracy during viscosity measurement of ILs was found to be better than ± 0.2 K. The viscosity measurements for all types of ILs were made in triplicate and the average values are presented in Table A-11 of Appendix A, along with the calculated values of percent average absolute deviations (AAD) by Equation 4.1. The viscosity values of ILs show that they are highly viscous in comparison to aqueous alkanolamine solutions. For example, the viscosity of IL; [C₆mim][PF₆] at 298.15 K has been measured as 607 mPa.s which is very much higher than the viscosity of 48.80 wt.% aqueous MDEA solution i.e., 8.86 mPa.s. The viscosity of ILs was found to be in decreasing order of [C₆mim][PF₆], [C₆mim][BF₄] and [C₆mim][Tf₂N] at all the investigated temperatures.

The effect of temperature on the viscosities of all the studied ILs is illustrated in Figure 4.8, which reveals an exponential decrease in the viscosities of ILs with an increase in temperature. The maximum decrease in the viscosity of ILs for the temperature range of 298.2 K to 348.2 K was found to be for [C₆mim][PF₆].

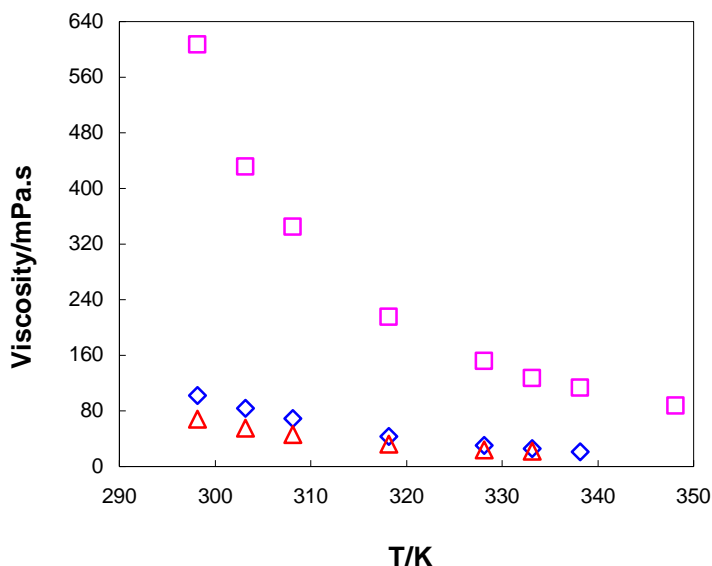


Figure 4.8: Effect of temperature on viscosities of ILs.

{for ILs; [C₆mim][BF₄] (◇), [C₆mim][PF₆] (□), [C₆mim][Tf₂N] (△)}

After careful analysis of the experimental data for the viscosities of all types of studied solvents has been correlated using the following equation:

$$\log \eta = A_0 + A_1/T \quad (4.6)$$

where, η is viscosity, A_0 and A_1 are fitting parameters which were estimated with a method of least squares and T is temperature. The values for the fitting parameters of Equation 4.5 are presented in Table A-12 of Appendix A along with the values of standard deviations using Equation 4.3. The log of experimental viscosities vs reciprocal of temperature for all concentrations of aqueous alkanolamine solutions are plotted in Figures 4.9 and 4.10, and for ILs in Figure 4.11 along with their correlated values. A satisfactory agreement between the experimental and correlated values for the viscosities of all the solvent was obtained with high values of their correlation coefficients.

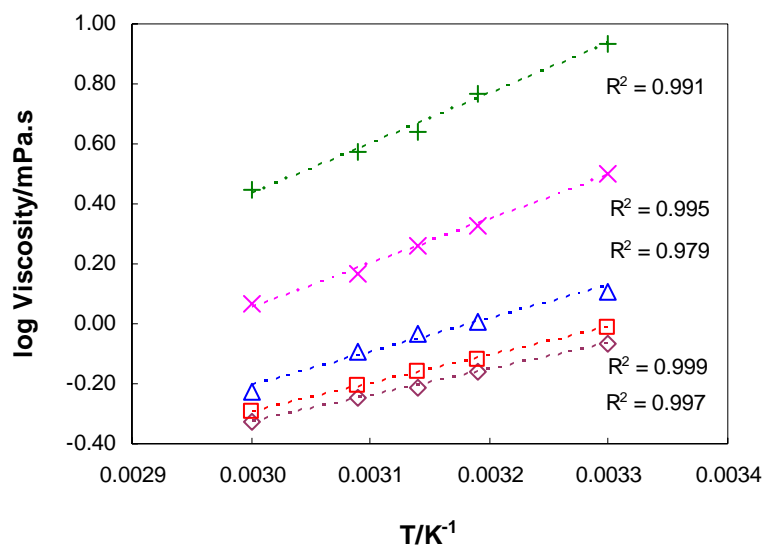


Figure 4.9: Plot for log of viscosities of aqueous MDEA and PZ solutions versus reciprocal of temperature.

[for (MDEA + water) wt.%; 32.28 (x), 48.80 (+) and (PZ + water) wt.%; 1.74 (◇), 5.16 (□), 10.35 (Δ), correlation (----) using Equation 4.5]

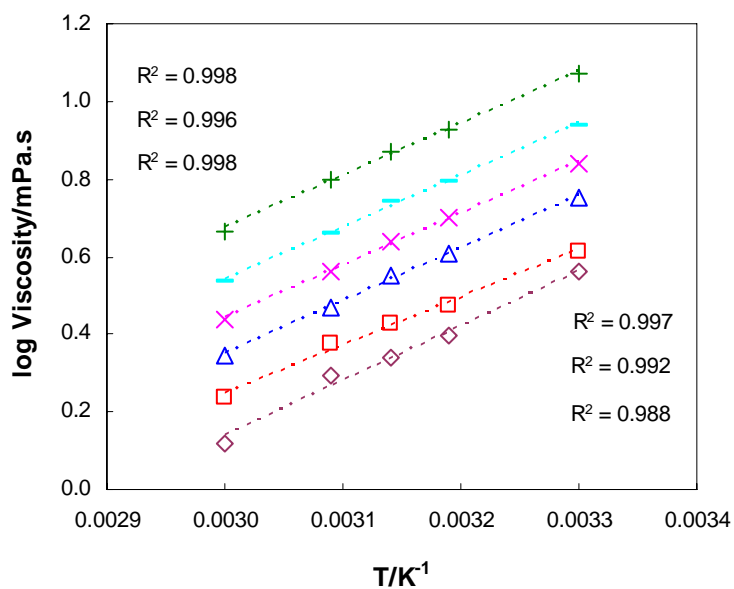


Figure 4.10: Plot for log of viscosities of PZ activated aqueous MDEA solutions versus reciprocal of temperature.

[for (MDEA + PZ + water) wt.%; 32.28/1.74 (◇), 32.28/5.16 (□), 32.28/10.35 (Δ), 48.80/1.74 (x), 48.80/5.16 (—), 48.80/10.35 (+), correlation (----) using Equation 4.5]

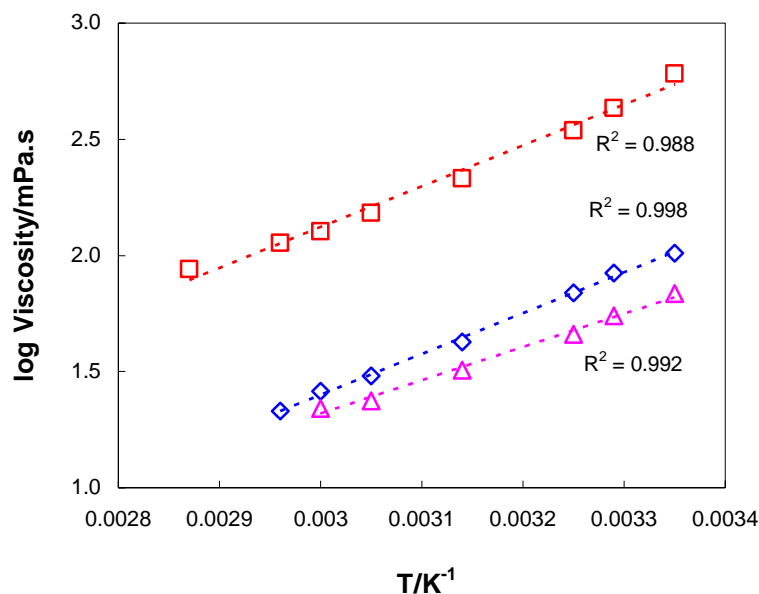


Figure 4.11: Plot for log of viscosities of ILs vs reciprocal of temperature.

{for ILs; [C₆mim][BF₄] (◇), [C₆mim][PF₆] (□), [C₆mim][Tf₂N] (△), correlation (----) using Equation 4.5}

4.2.4 Surface tension

The surface tension of solvents has great importance in gas-liquid interactions which could affect the extent of gases solubility in solvents. The liquid surface tension results due to the presence of unequal cohesive forces at its surface. As the surface ions of any liquid are not surrounded with other ions on all sides like the ions in the bulk of liquid which tends to pull the surface layer downward and creates a tension at the surface of liquid.

The experimental surface tension values of aqueous MDEA and PZ solutions, and PZ activated aqueous MDEA solutions have been measured using a pendant drop interfacial tension meter (IFT 700, VINCI Technologies) with a precision of $\pm 0.03 \text{ mN.m}^{-1}$ at temperature range of 303.15 K to 333.15 K with an accuracy of $\pm 0.2 \text{ K}$. Further details related to the calibration of tensiometer and the measuring procedure is given in section 3.2.4.2. The surface tension measurements were performed in triplicate and the average values are presented in Table A-13 of Appendix A along with the calculated values of

percent average absolute deviations using equation 4.1. The surface tension values for all the studied concentrations of aqueous alkanolamine solutions have been found to be in decreasing order of PZ + water, MDEA + PZ + water and MDEA + water. A decrease in surface tensions of all the studied aqueous alkanolamine solutions has been observed with an increase in the concentration of respective amine.

The surface tensions of ILs; [C₆mim][BF₄], [C₆mim][PF₆] and [C₆mim][Tf₂N] have been measured using a spinning drop video tensiometer (SVT 20, Dataphysics) at temperature range of 298.15 K to 338.15 K with an accuracy of ± 0.03 K. Further details related to the calibration of tensiometer and the measuring procedure is given in Section 3.2.4.3. The surface tension measurements were performed in triplicate and the average values are presented in Table A-14 of Appendix A, along with the calculated values of percent average absolute deviations using Equation 4.1.

In general, the values of surface tensions for ILs appeared to be higher than most of the conventional organic solvents such as hexane with surface tension 18 mN.m^{-1} but lower than water with surface tension 72 mN.m^{-1} at 298.15 K (Lide, 2001). The surface tension values for imidazolium based ILs are more close to the compounds that have intermolecular interactions like phenol i.e., 40.9 mN.m^{-1} . A linear decrease in the surface tension values of all the ILs with similar type of cation but different anion has been observed with an increase in temperature. Moreover, with the reduction in anion size of ILs the surface tension values decreased i.e., surface tension of [C₆mim][PF₆] with molecular volume of 401°A^3 is higher as compared to [C₆mim][BF₄] with molecular volume of 367°A^3 . However, the surface tension of [C₆mim][Tf₂N] is lower than ILs with [BF₄] and [PF₆] anions even though its molecular volume is much higher i.e., 542°A^3 , which indicates the influence of wide structural variance of [Tf₂N] anion on its surface tension values. In comparison to aqueous alkanolamine solutions the surface tension values for ILs are low at all the investigated temperatures.

A linear decrease in the surface tensions of all solvents has been found with an increase in temperature. The effect of temperature on surface tensions of MDEA + water, PZ + water, and MDEA + PZ + water is shown in Figures 4.12 and 4.13 respectively. The

effect of temperature on the surface tensions of ILs is illustrated in Figure 4.14. Based on the experimental outcomes, the dependency of surface tensions of all the studied solvents on temperature has also been correlated with the empirical Equation 4.7.

$$\sigma = A_0 + A_1/T \quad (4.7)$$

where, σ is surface tension, A_0 and A_1 are fitting parameters which were estimated with a method of least squares and T is temperature. The values for the fitting parameters of Equation 4.6 are presented in Table A-15 of Appendix A, along with the values of standard deviations calculated using Equation 4.3. A satisfactory agreement between the experimental and correlated values for surface tensions of all the solvents has been obtained high values of their correlation coefficients as presented in Figures 4.12, 4.13 and 4.14.

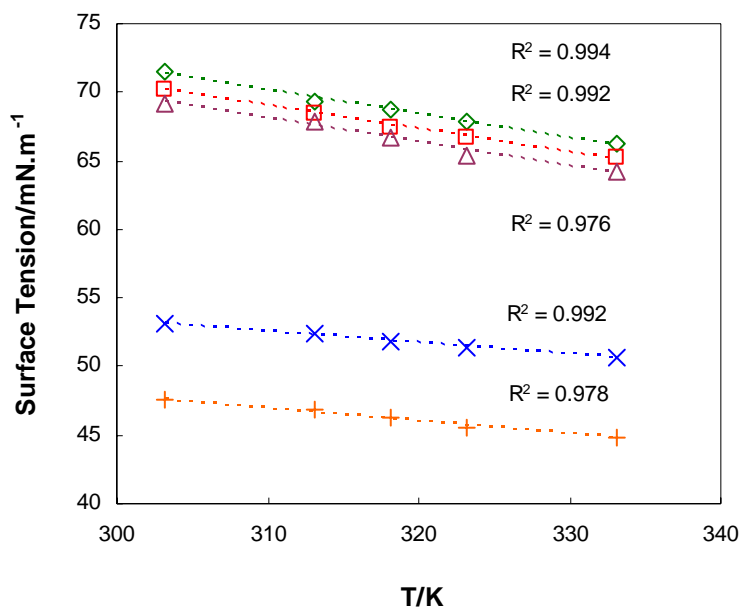


Figure 4.12: Effect of temperature on surface tension of aqueous MDEA and PZ solutions.

[for (MDEA + water) wt.%; 32.28 (×), 48.80 (+), (PZ + water) wt.%, 1.74 (◇), 5.16 (□), 10.35 (△), correlation (----) using Equation 4.6]

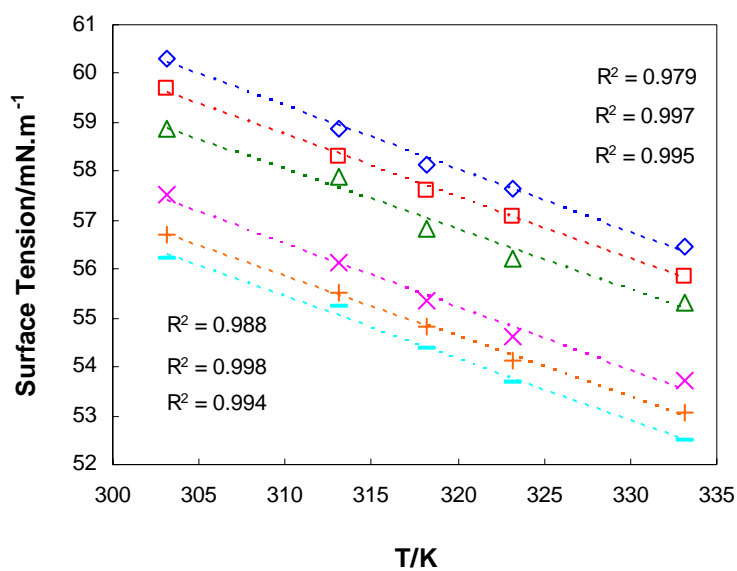


Figure 4.13: Effect of temperature on surface tension of PZ activated MDEA solutions.

[for (MDEA + PZ + water) wt.%; 32.28/1.74 (\diamond), 32.28/5.16 (\square), 32.28/10.35 (\triangle), 48.80/1.74 (\times), 48.80/5.16 ($+$), 48.80/10.35 ($-$), correlation (----) using Equation 4.6]

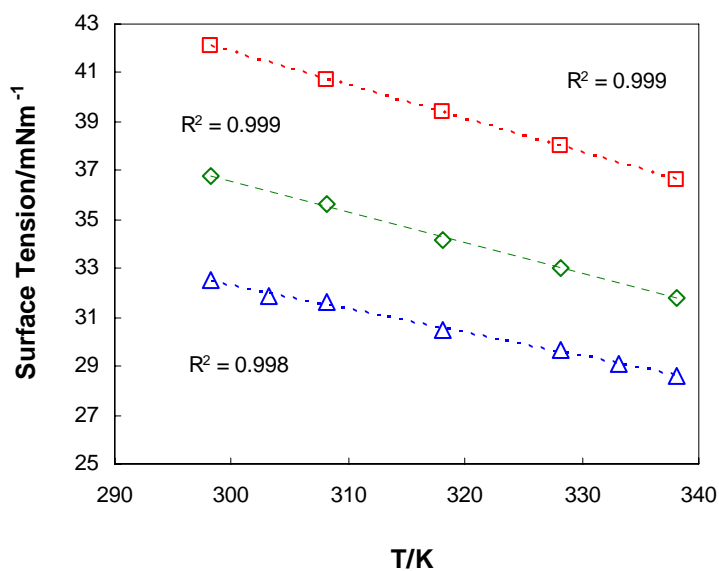


Figure 4.14: Effect of temperature on surface tension of ILs.

{for ILs; [C₆mim][BF₄] (\diamond), [C₆mim][PF₆] (\square), [C₆mim][Tf₂N] (\triangle), correlation (----) using Equation 4.6}

4.2.5 Refractive index

The refractive index (n_D) is the property of a material that changes the speed of light and computed as the ratio of the speed of light in a vacuum to the speed of light through the material. The refractive index is basically related to the polarizability/dipolarity of the medium and the derived excess molar refraction values could be used in the least squares energy relationships (LSERs) as a predictor of solute distribution (Abraham et al., 1999).

The refractive indices of all the solvents studied in this work have been measured using an ATAGO programmable digital refractometer (RX-5000 alpha) for a wide temperature range of 303.15 K to 333.15 K with a temperature control accuracy of ± 0.05 K. Further details of the apparatus related to calibration and procedure for measuring refractive indices are provided in Section 3.2.4.4. All the measurements for refractive indices of aqueous alkanolamine solutions and ILs were performed in triplicate with an uncertainty of $\pm 4 \times 10^{-5}$ and their average values are presented in Tables A-16 and A-17 of Appendix A respectively, along with the calculated values of percent average absolute deviations using Equation 4.1.

The refractive index values for aqueous solutions of MDEA and PZ have been found to be in decreasing order of MDEA + water and PZ + water for all the studied concentrations. However, the refractive indices of MDEA + PZ + water decreased with an increase in PZ concentration for a constant MDEA concentration. The experimental refractive index values for the studied ILs have been found to be higher than common organic compounds e.g., the refractive index of $[\text{C}_6\text{mim}][\text{PF}_6]$ is 1.41694 at 303.15 K which is higher than the refractive index value of ethanol i.e., 1.35923 (Poling et al., 2001). In comparison to aqueous alkanolamine solutions the refractive indices of ILs are found to be lower at all the investigated temperatures. The effect of temperature on the surface tensions of solvents is shown in Figures 4.16 (ILs), 4.17 (binary solutions of aqueous alkanolamines) and 4.18 (ternary solutions of aqueous alkanolamines).

A linear decrease in refractive indices of all solvents has been noticed with an increase in temperature. The effect of temperature on the values of refractive indices for MDEA +

water, PZ + water, and MDEA + PZ + water is shown in Figures 4.15 and 4.16, and for ILs in Figure 4.17. The dependency of refractive index of all the solvents on temperature has been found to be linear which is correlated with the following empirical equation:

$$n_D = A_0 + A_1 T \quad (4.8)$$

where, n_D is refractive index, A_0 and A_1 are fitting parameters which were estimated with a method of least squares and T is temperature. The values for the fitting parameters of Equation 4.7 are presented in Table A-18 of Appendix A, along with the values of standard deviations calculated using Equation 4.3.

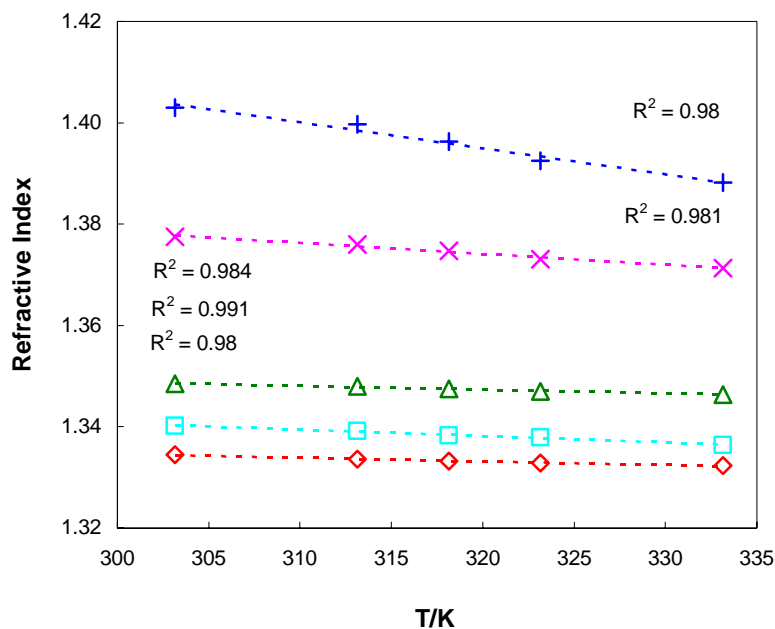


Figure 4.15: Effect of temperature on refractive indices of aqueous MDEA and PZ solutions.

[for (MDEA + water) wt.%; 32.28 (×), 48.80 (+), and (PZ + water) wt.%; 1.74 (◇), 5.16 (□), 10.35 (Δ), correlation (----) using Equation 4.7]

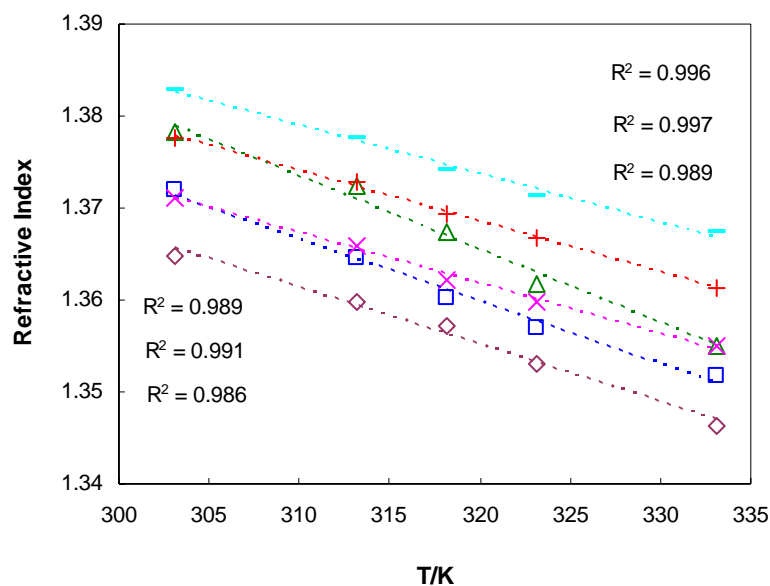


Figure 4.16: Effect of temperature on refractive indices of PZ activated MDEA solutions.

[for (MDEA + PZ + water) wt.%; 32.28/1.74 (\diamond), 32.28/5.16 (\square), 32.28/10.35 (\triangle), 48.80/1.74 (\times), 48.80/5.16 ($+$), 48.80/10.35 ($*$), correlation (----) using Equation 4.7]

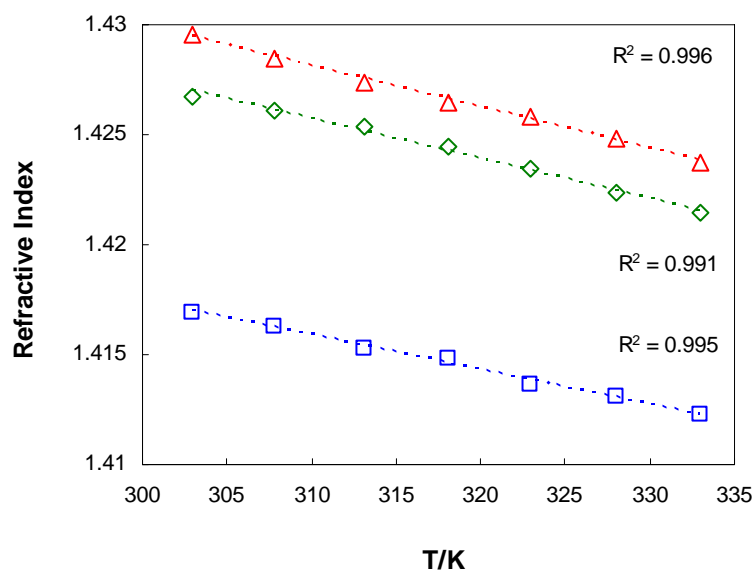


Figure 4.17: Effect of temperature on refractive indices of ILs.

{for ILs; [C₆mim][BF₄] (\diamond), [C₆mim][PF₆] (\square), [C₆mim][Tf₂N] (\triangle), correlation (----) using Equation 4.7}

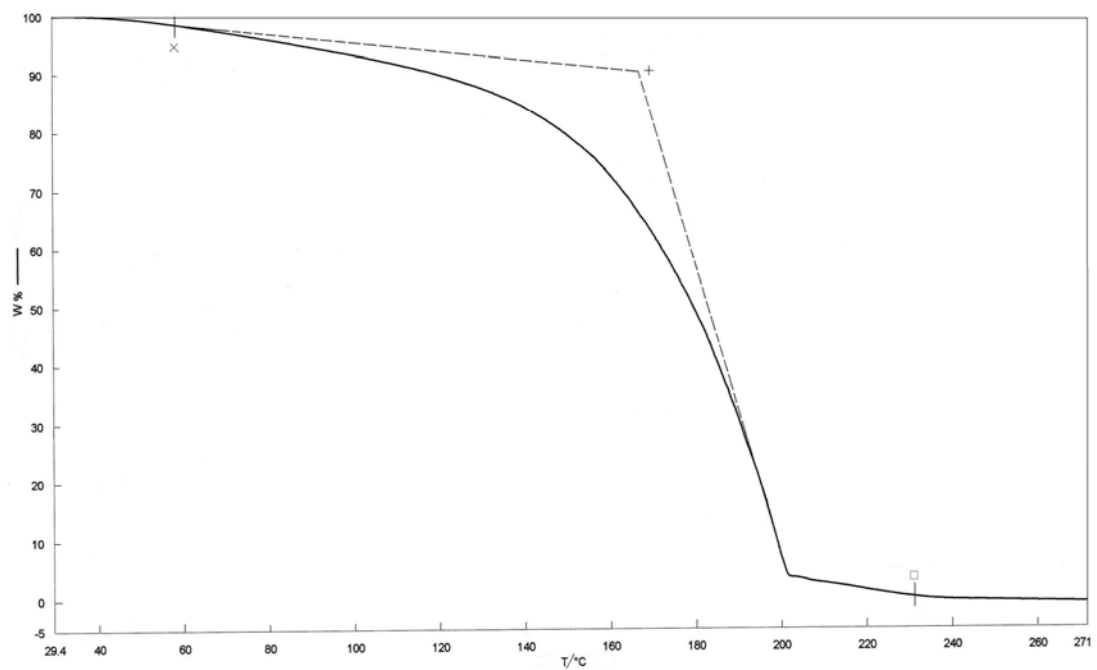
4.2.6 Thermal stability

The upper limit for the liquidus range of the solvents is usually represented by their values of thermal decomposition and reported as onset temperature (T_{onset}) using a technique known as thermogravimetric analysis. Moreover, to report the thermal stability in terms of ‘onset temperature’ has the advantage of its well defined reproducibility and ease of measurement. The information obtained through thermal analysis could be further used to evaluate the extent of thermal stability or thermal decomposition of materials and to estimate the compositional analysis of the material. Therefore, the thermal stability of all the solvents studied here, have been investigated using a thermogravimetric analyzer (TGA), which works on the principle of measuring the weight change of a material with increasing temperature. For this purpose, aqueous alkanolamine solutions were heated for a temperature range of 30°C to 300°C and ILs were heated for temperature range of 40°C to 700°C at a constant heating rate of 10°C.min⁻¹. The overall temperature accuracy was found to be better than $\pm 3^\circ\text{C}$ during the measurement of thermal stabilities of solvents with respect to their percent weight loss. The values for thermal decomposition of all the solvents are presented in Tables A-19 and A-20 of Appendix A respectively considering the following steps:

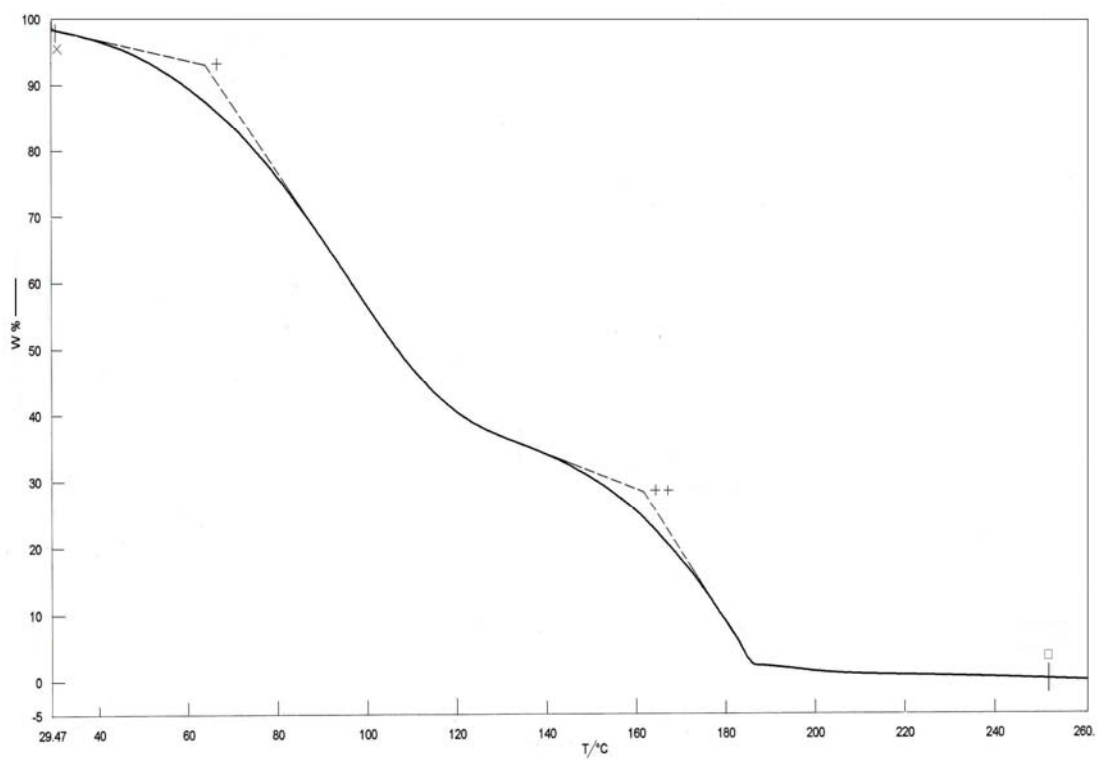
- (i) Start temperature (T_{start} i.e., start temperature for decomposition about one weight % loss)
- (ii) Onset temperature (T_{onset} i.e., intersection of the baseline weight and the tangent of the weight vs temperature curve as the decomposition occurs).
- (iii) Final decomposition temperature (T_f i.e., about one weight % loss).

The plots for thermal decomposition of pure MDEA and aqueous MDEA solutions with concentrations 32.28 and 48.80 (wt.%) as the percentage weight loss with increase in temperature are shown in Figure 4.18. The aqueous MDEA solutions have shown low temperature values at the start of decomposition as compared to pure MDEA. The onset temperature and two step degradation of aqueous MDEA solutions indicate that initially free water molecules were decomposed i.e., 64°C and 62°C followed by the degradation of MDEA molecules in second step i.e., 162°C and 173°C. Final decomposition

a)



b)



c)

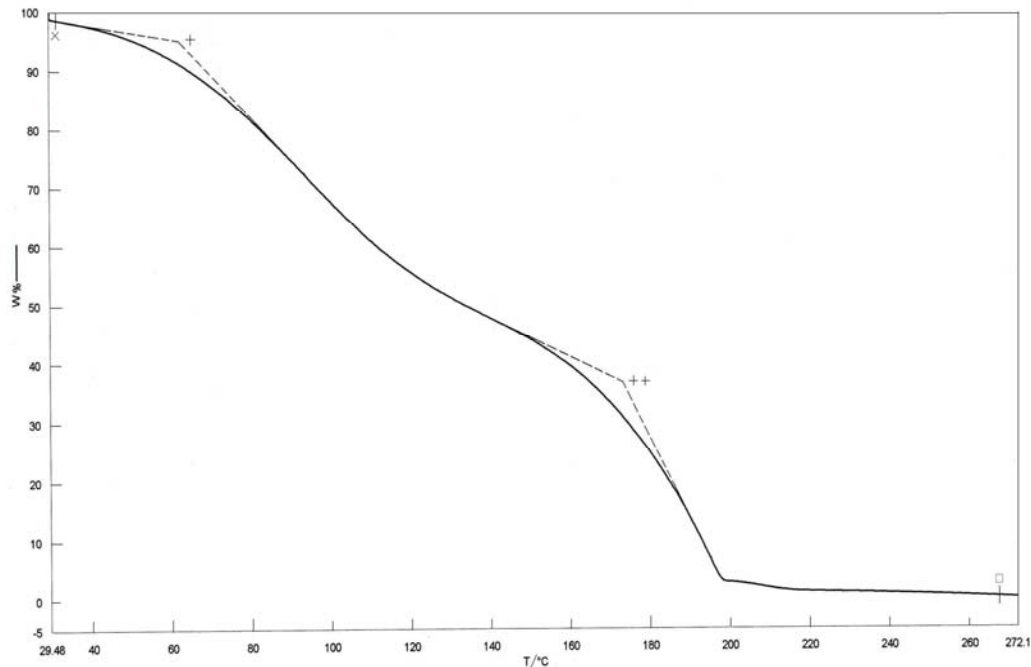


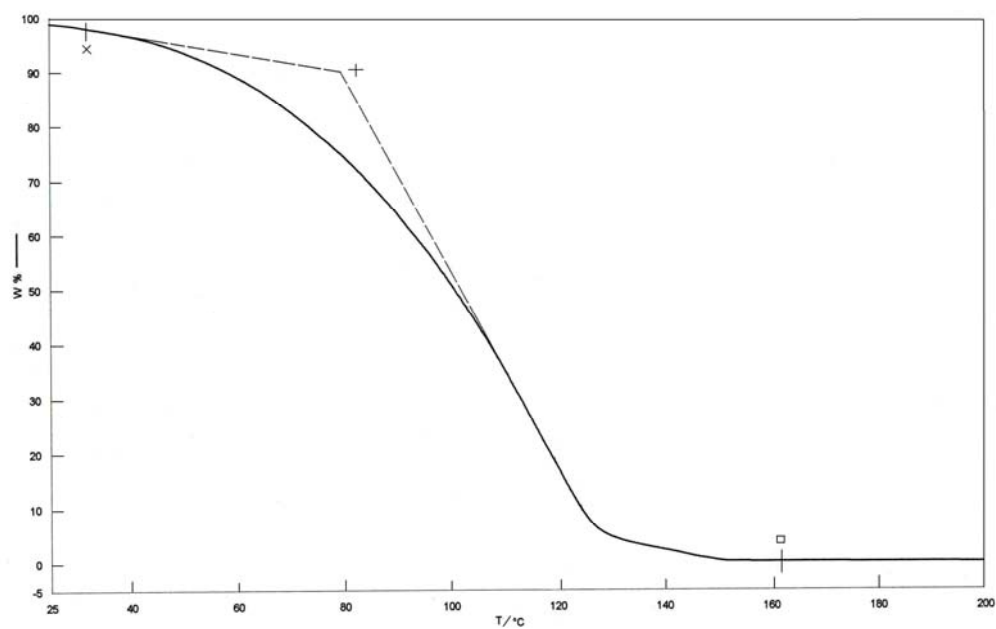
Figure 4.18: Plots for thermal decomposition as weight percent loss (W%) vs temperature ($T/^{\circ}\text{C}$).

[for pure MDEA (a) \times , $T_{\text{start}} = 58.295^{\circ}\text{C}$ at 98.4606 (W%); $+$, $T_{\text{onset}} = 166.851^{\circ}\text{C}$ at 89.9677 (W%); \square , $T_f = 231.170^{\circ}\text{C}$ at 0.0968 (W%); and MDEA + water: (wt.%) = 32.28 (b), \times , $T_{\text{start}} = 29.460^{\circ}\text{C}$ at 98.4966 (W%); $+$, $1^{\text{st}} T_{\text{onset}} = 63.89^{\circ}\text{C}$ at 92.9528 (W%); $++$, $2^{\text{nd}} T_{\text{onset}} = 161.640^{\circ}\text{C}$ at 28.1363 (W%); \square , $T_f = 251.917^{\circ}\text{C}$ at 0.0969 (W%); (wt.%) = 48.80 (c) \times , $T_{\text{start}} = 31.388^{\circ}\text{C}$ at 98.4788 (W%); $+$, $1^{\text{st}} T_{\text{onset}} = 62.025^{\circ}\text{C}$ at 94.8941 (W%); $++$, $2^{\text{nd}} T_{\text{onset}} = 173.113^{\circ}\text{C}$ at 36.5520 (W%); \square , $T_f = 267.442^{\circ}\text{C}$ at 0.0972 (W%)]

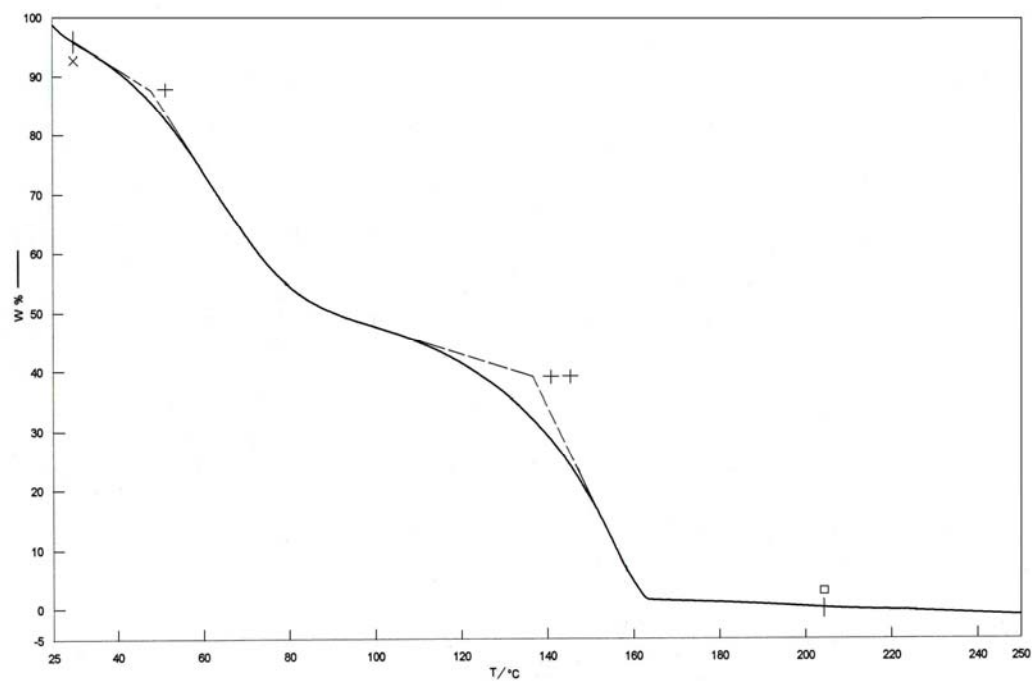
temperature (T_f) of aqueous MDEA solutions was found to be higher than pure MDEA which shows their strong hydrogen bonding interactions. The thermograms for the decomposition of aqueous PZ solutions with concentration 1.74 wt.% and PZ activated aqueous MDEA solutions with concentrations 32.28/1.74 and 48.80/1.74 (wt.%) have been shown in Figure 2.19. Thermograms for all the other compositions of alkanolamine systems are presented in Figures A-1, A-2 and A-3 of Appendix A. The one step degradation of aqueous PZ solutions shows the strong binding interactions between PZ and water molecules. The onset temperature and two step degradation of PZ activated aqueous MDEA solutions indicate that initially PZ molecules were decomposed followed by the degradation of MDEA molecules in second step.

The thermograms as percent weight loss with increase in temperature of ILs are shown in Figure 4.20. The ILs studied here have shown high thermal stability in comparison to alkanolamines e.g., the temperature at which 1.5 wt.% of IL; $[C_6mim][PF_6]$ is lost i.e., 320°C is much higher than 58°C observed in case of pure MDEA at same wt.% loss of sample. In general, the thermal stability of imidazolium based ILs was found to be almost 2 to 3 times more than all the studied aqueous alkanolamine solutions. For example, the T_{onset} of $[C_6mim][Tf_2N]$ is 461°C, which is 2.8 times higher than $T_{onset} = 162^\circ C$ of aqueous MDEA solution with concentration 32.28 wt.%. Similarly, the $T_{onset} = 461^\circ C$ of $[C_6mim][Tf_2N]$, which is 3.4 times higher than $T_{onset} = 137^\circ C$ of PZ activated aqueous MDEA solution with concentration 32.28/1.74 wt.%. Amongst the ILs the thermal stability has been found to be in decreasing order of $[C_6mim][Tf_2N]$, $[C_6mim][PF_6]$ and $[C_6mim][BF_4]$.

a)



b)



c)

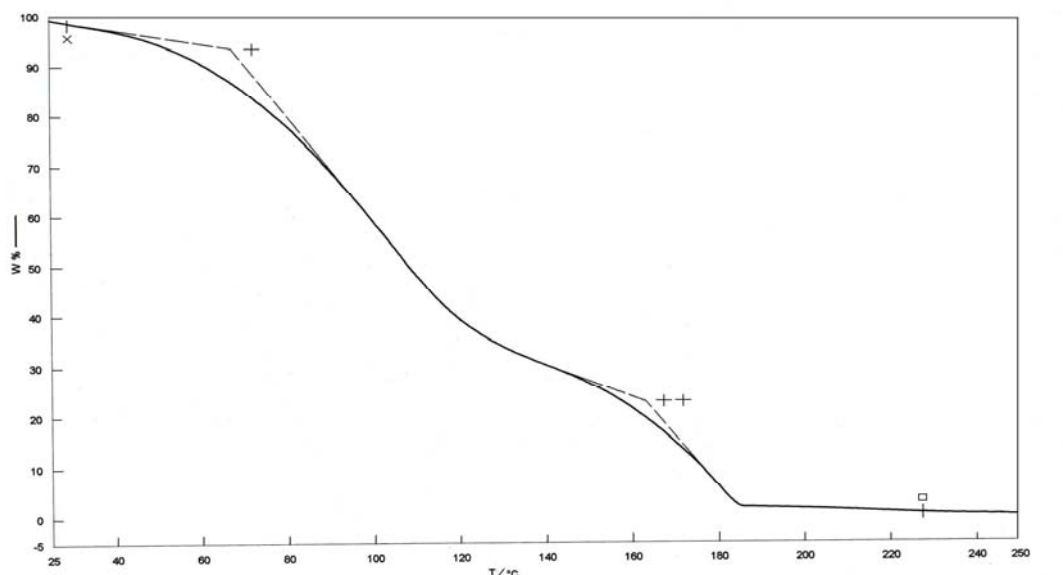
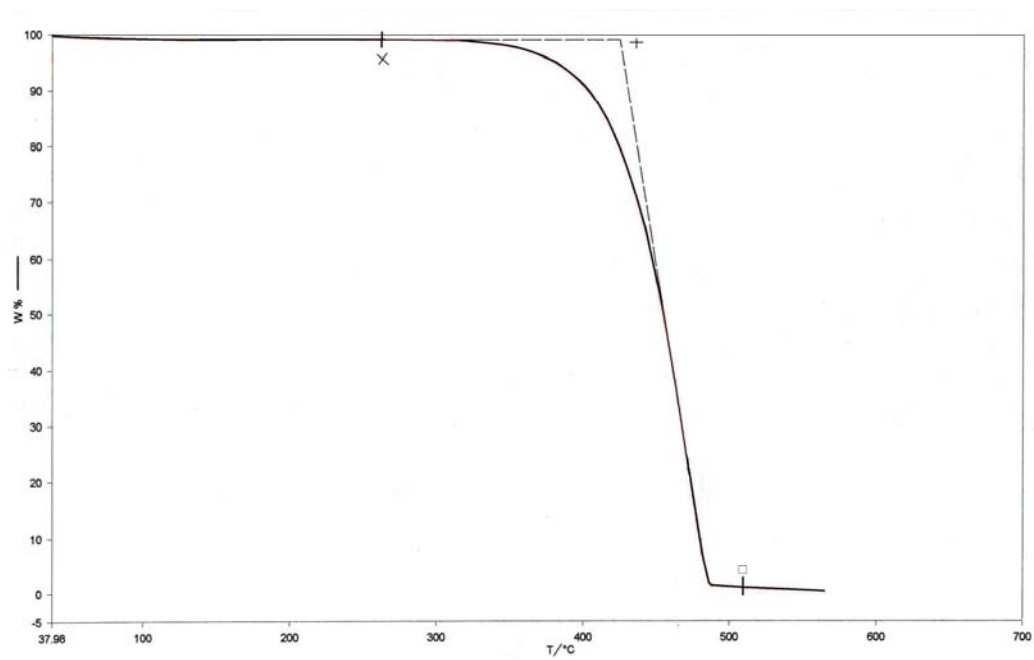


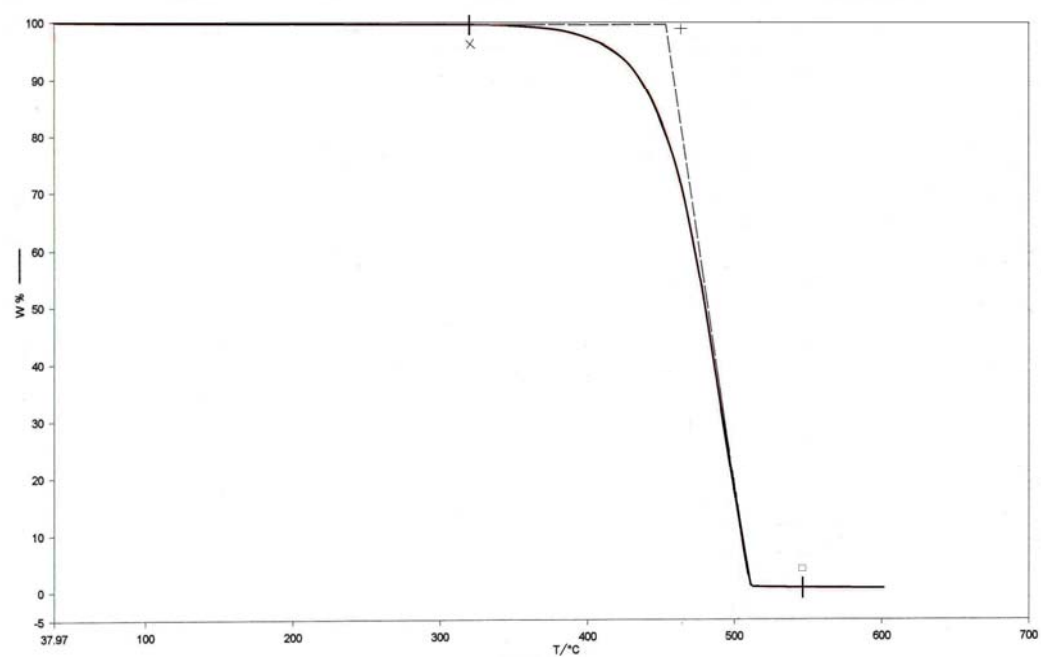
Figure 4.19: Plots for thermal decomposition as weight percent loss (W %) vs temperature ($T/^{\circ}\text{C}$)..

[for aqueous PZ wt.% = 1.74 (a), \times , $T_{\text{start}} = 31.927^{\circ}\text{C}$ at 97.9387 (W%); $+$, $T_{\text{onset}} = 79.402^{\circ}\text{C}$ at 89.8039 (W%); \square , $T_f = 160.681^{\circ}\text{C}$ at 0.0997 (W%); and (MDEA + PZ + water): (wt.%) = 32.28/1.74 (b), \times , $T_{\text{start}} = 29.737^{\circ}\text{C}$ at 95.9760 (W%); $+$, 1st $T_{\text{onset}} = 47.887^{\circ}\text{C}$ at 87.4634 (W%); $++$, 2nd $T_{\text{onset}} = 136.552^{\circ}\text{C}$ at 38.9671 (W%); \square , $T_f = 204.211^{\circ}\text{C}$ at 0.0953 (W%); (wt.%) = 48.80/1.74 (c), \times , $T_{\text{start}} = 29.211^{\circ}\text{C}$ at 98.5573 (W%); $+$, 1st $T_{\text{onset}} = 67.121^{\circ}\text{C}$ at 93.3463 (W%); $++$, 2nd $T_{\text{onset}} = 163.136^{\circ}\text{C}$ at 22.7240 (W%); \square , $T_f = 227.368^{\circ}\text{C}$ at 0.5125 (W%)]

a)



b)



c)

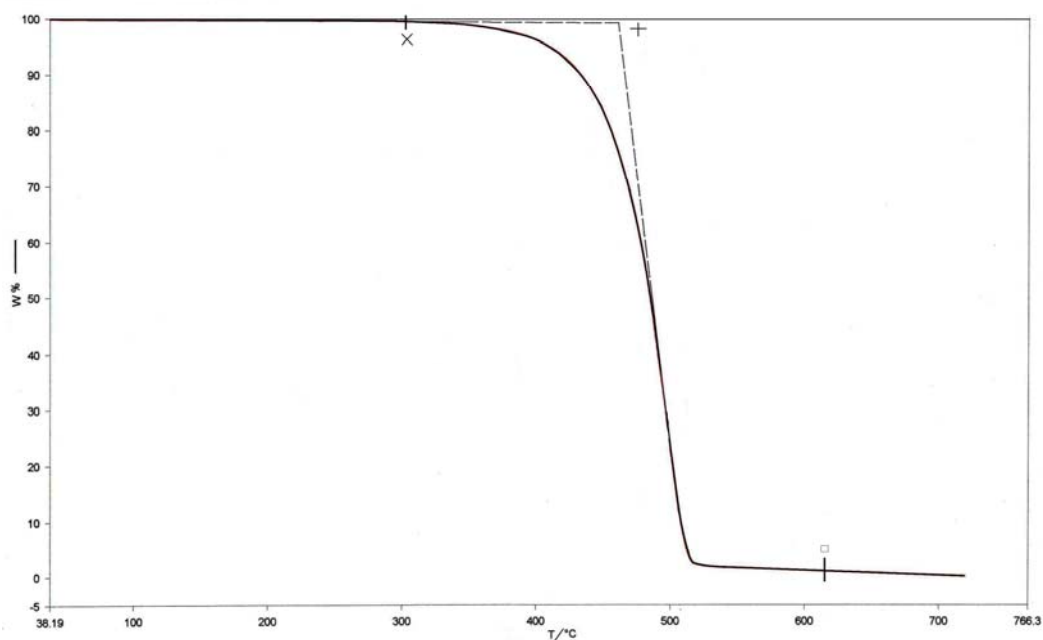


Figure 4.20. Plots for thermal decomposition as weight percent loss (W%) vs temperature (T/°C) for ILs.

[for ILs; [C₆mim][BF₄] (a) ×, T_{start} = 262.121°C at 98.9922 (W%); +, T_{onset} = 424.830°C at 98.8985 (W%); □, T_f = 509.478°C at 0.9347 (W%); [C₆mim][PF₆] (b), ×, T_{start} = 319.753°C at 99.4445 (W%); +, T_{onset} = 453.614°C at 99.3529 (W%); □, T_f = 546.300°C at 0.5025 (W%); [C₆mim][Tf₂N] (c) ×, T_{start} = 302.038°C at 99.4460 (W%); +, T_{onset} = 460.919°C at 99.1716 (W%); □, T_f = 615.295°C at 0.9407 (W%)]

4.3 Summary

In the present work, thermophysical properties including densities, isobaric coefficients of thermal expansion, viscosities, surface tensions, refractive indexes and thermal decompositions were measured over a wide temperature range at atmospheric pressure for solvents such as MDEA + water, PZ + water and MDEA + PZ + water with different concentrations, and imidazolium based ionic liquids. A summary of all the above mentioned experimentally measured physical properties of solvents are presented in

Table 4.1 at temperature of 303.15 K along with their of thermal decomposition values as T_{onset} using thermogravimetric analyzer.

The density of aqueous MDEA solutions was found to be higher as compared to aqueous PZ solutions for all the studied concentrations. The density of aqueous MDEA solution with concentration of 32.28 wt.% was found to be higher as compared to its concentration of 48.80 wt.%. However, the effect of PZ concentration on the density of its studied aqueous solutions appeared to be insignificant. The addition of PZ in both concentrations of aqueous MDEA solutions (ternary system) intended to slightly lower their densities as compared to binary solutions of MDEA with water. Generally, the density values for all the studied ILs were found to be higher than aqueous alkanolamine solutions.

Table 4.1: Summary for experimental density (ρ), viscosity (η), surface tension (σ) and refractive index (nD) of aqueous alkanolamine solutions and ILs at $T = 303.15$ K along with the thermal decompositions of all solvents as onset temperatures.

Solvents	Density	Viscosity	Surface tension	Refractive index	T_{onset}
	kg.m ⁻³	mPa.s	m.N.m ⁻¹		°C
MDEA + water (wt.%)					
32.28	1027.273	2.82	53.16	1.37748	65 and 162
48.80	1041.371	7.48	47.56	1.40298	64 and 174
PZ + water (wt.%)					
1.74	998.287	0.86	71.48	1.33449	79
5.16	999.360	0.97	70.24	1.34019	81
10.35	1001.285	1.28	69.10	1.34847	81
MDEA + PZ + water (wt.%)					
32.28/1.74	1024.783	3.62	60.32	1.36487	48 and 137
32.28/5.16	1025.327	4.11	59.70	1.37197	76 and 162
32.28/10.35	1026.382	5.62	58.86	1.37818	85 and 163
48.80/1.74	1036.829	6.93	57.52	1.37118	67 and 163
48.80/5.16	1037.365	8.63	56.72	1.37752	69 and 167
48.80/10.35	1038.328	11.74	56.23	1.38286	74 and 171
[C ₆ mim][BF ₄]	1141.03	84*	36.3	1.42672	425
[C ₆ mim][PF ₆]	1289.86	431*	41.4	1.41694	454
[C ₆ mim][Tf ₂ N]	1367.43	55*	31.9	1.42958	461

* At temperature of 303.2 K.

The viscosity of aqueous MDEA solutions was found to be slightly higher than aqueous PZ solutions for all the studied concentrations. The effect of amine concentrations was found to be insignificant on the viscosities of all the studied alkanolamine solutions. The viscosity values for all the studied ILs were found to be much higher as compared to all concentrations of aqueous alkanolamine solutions. The surface tension of aqueous PZ solutions was found to be much higher than aqueous MDEA solutions for all the studied concentrations. The effect of amine concentrations on surface tension values for aqueous MDEA and PZ solutions was insignificant. The surface tension values were found to be slightly increased with an addition of PZ in aqueous MDEA solutions. All the studied ILs were found to be having much lower surface tension as compared to all concentrations of aqueous alkanolamine solutions. The effect of amine concentration on refractive index values of all the studied alkanolamine solutions (binary and ternary systems) was found to be insignificant. The refractive index of ILs was found to be slightly higher as compared to aqueous alkanolamine solutions. The effect of temperature on the physical properties of all the solvents was investigated for a wide range. In general, the physical properties of all the studied solvents decreased with an increase in temperature.

The two onset temperature values obtained for degradation of both concentrations of aqueous MDEA solutions as shown in Table 4.1 indicate that the degradation of these solvents occur in two step. It can be summarized that in case of 32.28 and 48.80 (wt.%) aqueous MDEA solutions, initially free water molecules were decomposed i.e., 64°C and 62°C followed by the degradation of MDEA molecules in i.e., 162°C and 173°C respectively. However, in case of the one aqueous PZ solutions, the one step degradation shows the strong binding interactions between PZ and water molecules. The addition of PZ in aqueous MDEA solutions has insignificant effect on their trend and values of thermal decomposition. The imidazolium based ILs showed very high thermal stability with their onset temperature values reaches three times higher than all the studied aqueous alkanolamine solutions.