Physicochemical Properties of Protic Ionic Liquids and Their Binary Mixtures with Molecular Solvents as Fuel Cell Electrolytes

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1.0 Introduction

Ionic liquids (ILs) are liquids that consist exclusively or almost exclusively of ions with asymmetric, flexible and charge-localized structures. As their name implies, they are liquid over a wide range of temperature. Their melting temperature is near room temperature or by convention below 100°C.[1-3] To date, ILs are generally classified into two broad categories, i.e., aprotic ionic liquids (AILs) and protic ionic liquids (PILs).[4] The PIL subgroup is defined when the selected IL is formed by simple transfer of a proton from a Brönsted acid to a Brönsted base rather than an alkyl group like AILs.[4-5]

Recently PILs have attracted much attention as candidate of electrolytes for fuel cells due to their proton-conductivity, high thermal stability, and low vapor pressure.[6–11] Several tertiary amine base ionic liquids were used as proton-conducting nonaqueous electrolytes for fuel cells.[8–11] The elucidation of the factors controlling the transport properties (viscosity, ionic conductivity, and self-diffusion coefficients of ions) of IL is important for rational design for electrolytes, as the transport properties of ILs play crucial roles in determining the performance of batteries.[12–14] Recent experimental and theoretical studies on AILs show that the transport properties are controlled by several factors.[15–18] The size and shape of ions are important for diffusivity of ions. The diffusion of ions becomes slow as the size of ions increase.[19] The inter-action between cation and anion affects the transport properties of ILs significantly.[15] The magnitude of the attraction between cation and anion is one of the important factors controlling the diffusion of ions in ILs.

To design any process involving ILs on an industrial scale, it is necessary to know some thermo physical properties.[5,20,21,22] Furthermore, these experimental data provide also useful fundamental information about molecular interactions and are also applied to evaluate thermodynamic models.[23,24] Thus, the huge task ahead is preparation of PILs with tunable structures and physicochemical properties. Although applications of PILs are well-known, a detailed knowledge of the thermodynamic behavior of (PILs + molecular solvent) mixtures has not yet received a particularly large share of the literature based on ILs studies, [25–36] and is still limited.[25-27]

The relatively high viscosities of pure ILs in comparison with traditional solvents has resulted in limited commercial use to date. This problem is partially resolved by mixing ILs with alcohol or organic solvents.[26-28] In fact, the main advantage of using (PIL + molecular solvent) binary mixtures is to decrease the viscosity and increase the conductivity of the

solution, which leads to lowering the energy requirements for any engineering process.[28,29] There has been an upsurge of interest in the preparation of PILs and definition of the parameters responsible for their characteristic properties. However, typical PILs are very expensive due to high cost in production and preservation. PILs based mixed solvents have the potential to offer a novel route for tailoring properties of these designer solvents. To-date, there are very few attempts were made to investigate physicochemical properties of PILs-based binary mixtures though there are enormous studies in case of typical AILs, although applications of PILs are well-known. Relatively high viscosities of pure PILs in comparison with traditional solvents have resulted in limited commercial use to date. Therefore, it is very interesting to prepare binary mixtures of PILs and alcohol with a wide range of composition to make a systematic investigation for task-specific applications.

1.1 Classification of ILs

ILs can be classified in different types. Following is the classification given by Angell *et al.*[30]

a) Protic ILs: When the IL is formed by the proton transfer from a Bronsted acid to a Bronsted base, it is called protic IL. An example of PIL is pyrolidinium acetate, [Pyrr]Ac.

b) Aprotic ILs: If the cations and anions of IL have no active proton then the IL is called an aprotic IL. For example, 1-ethyl-3-methylimidazolium tetrafluoroborate, [EMIM]BF_4

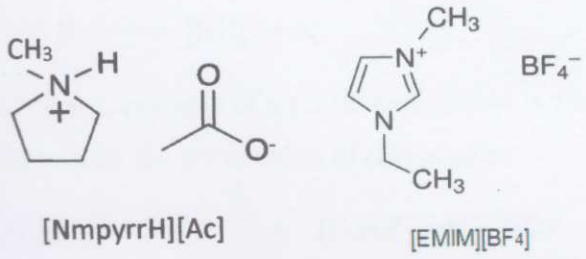


Figure 1.1: *Structure of N-methylpyrrolidinium acetate, [NMpyrr]Ac and 1-ethyl-3-methylimidazolium tetraflouroborate, [EMIM]BF_4.*

c) Inorganic ILs

The third and distinct class of IL is the one that consists entirely of inorganic entities. These are obtained, in both aprotic and protic forms, by taking advantage of the same packing problems that lead to low-melting ILs of the organic cation type. There are fewer examples of such ILs. Inorganic ILs are formed mostly as a consequence of the mismatch of large anions like tetrachloroaluminate or iodide with small cations like Li^+. Of them there are aprotic examples,

lithium chlorate (melting point 115°C). The protic example would be hydrazinium nitrate, (melting temperature, T_m = 80°C).

d) Solvate (chelate) ILs

A fourth class may be considered, although it contains nonionic entities. This is the liquid state of various ionic solvates. In these systems, molecules usually thought of as solvent molecules are bound tightly to high field cations and have no solvent function. These form a largely unstudied class of ILs that needs to be recognized because the class includes cases of multivalent cation salts that would not ordinarily be able to satisfy the criterion of T_m< 100°C. The first recognized members of this class were molten salt hydrates, like $Ca(NO3)_2.4H_2O$, whose mixtures with alkali metal salts were found to be almost ideal mixtures.[31]

Among them we are interested in protic ionic liquids. This study is based on PILs and the double salt based on them. So there will be a detailed discussion on PILs.

1.2 Synthetic Route and Structure of PILs

Most research on ionic liquids has focused on AILs. These are generally salts consisting solely of cations, which are not protonated, and anions such as $[C_2mim]BF_4$ and $[C_4mim]NTf_2$. Protic ionic liquids are formed by proton transfer from an acid that can donate a proton, *i.e.* a Brönsted acid (HA), to a base that can accept a proton, *i.e.* a Brönsted base (B)

$$HA + B \longrightarrow [BH]^+ + A^-$$

The classic example of a protic ionic liquid is ethylammonium nitrate, $[C_2H_5NH_3]NO_3$, which is formed by the protonation of ethylamine:

$$C_2H_5NH_2 + HNO_3 \longrightarrow [C_2H_5NH_3]^+ + NO_3^-$$

Another example is 1-methylimidazolium tetrafluoroborate ($[Hmim]BF_4$), which is prepared by the reaction of 1-methylimidazole and tetrafluroboric acid.[32] Protic ionic liquids do not necessary consist of entirely of ions.[33] Such liquids may contain a small percentage of molecular species if the proton transfer is incomplete.

1.3 Unique Properties of PILs

Unique physic-chemical properties of PILs have gained increasing interest and attention in both academia and industries. The unique combination of ionic nature with the intrinsic physico-

chemical properties results in the following extraordinary features of some PILs having high ΔpK_a similar to their counterparts:

- ❖ PILs have negligible vapor pressure. So they do not evaporate at normal temperature.
- ❖ They own a wide liquid region. Thus PILs provide a large working temperature range (from -96 °C to 300 °C)
- ❖ PILs exhibit high thermal stability than molecular solvents.
- ❖ They have large electrochemical potential window (ca. 4V).
- ❖ They have excellent electrochemical stability.
- ❖ PILs show large ionic conductivity (ca.10 ms cm^{-1}) due to their ionic nature.

PILs have favorable solvating capacity for both polar and non-polar compound.

1.4 Objectives of work

With the incredible expansion of PILs, enormous interest has been focused on the determination and understanding of the physic-chemical properties of PILs. The important physicochemical properties may significantly affect by the amount of alcohol either deliberately added or absorbed. So, the knowledge of interactions between PILs and alcohol is very important for the utility PILs for various applications.

Therefore, this study was designed to achieve the following objectives

- to study the effect of alkyl chain of the alcohol and composition on the physico-chemical properties of PILs and their binary mixtures with alcohol
- to get an insight on the molecular interactions in the binary mixtures from excess thermodynamic properties
- to study the ionic nature of PIL and its binary mixtures through Walden plot

1.5 Present Work

In this study, PIL was prepared through neutralization of a tertiary amine, diethylmethylamine (dema) with trifluoroacetic acid (CF_3COOH). Binary mixtures of the PIL and four aliphatic alcohol varying alkyl chain lengths were prepared with a wide range of composition. Thermal stability of [dema]CF_3COO and their binary mixtures were measured by Thermogravimetric Analysis. Densities and viscosities of PILs with alcohol were measured at various temperatures by using combined meter. Conductivity of PIL-alcohol binary system of varying composition was measured at room temperature by

impedance spectroscopy. The excess molar volume and excess viscosities were derived by fitted with reported model to conform the presence and nature of the interactions between PIL and alcohol such as excess molar volume and viscosity data were fitted to Redlich-Kister polynomial equation. The viscosity and conductivity data were correlated through Walden plot. The ultimate target has been to evaluate the physicochemical properties of [dema]CF_3COO and its binary systems with alcohol, so that the features may endorse many efforts for the use of those binary mixtures in task specific applications.

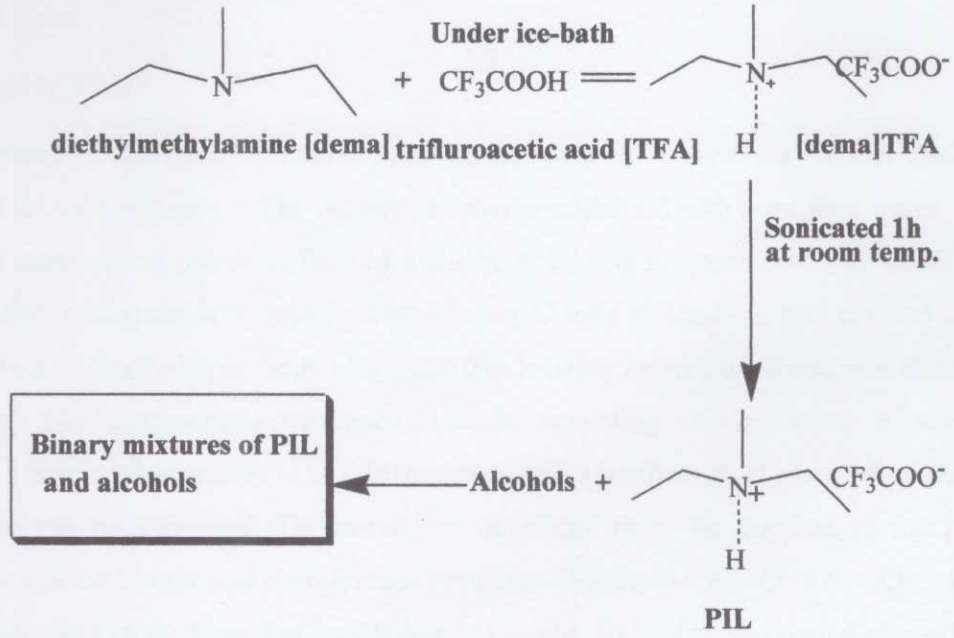
2.0 Experimental

2.1 Materials

Diethylmethylamine (>97.0%) was obtained from Sigma-Aldrich and trifluoroacetic acid (99.5%), Scharlar S.L., ethanol, 1-propanol, 1-butanol and 1-pentanol from Lab-Scan and were used without further purification.

2.2 Preparation of PIL and Its Binary Mixtures

Diethylmethylamine trifluoroacetate, [dema]CF_3COO, was synthesized according to the **Scheme 2.1** by mixing trifluoroacetic acid with the dema in equimolar amounts in an individual vial kept in an ice bath and sonicated for 60 min then kept inside in an electrical desiccator. All the binary mixture of [dema]CF_3COO and alcohols were prepared in volume percentage by using micropipette. Each of binary mixtures was sonicated for 60 min.



Scheme 2.1: Synthesis of [dema]CF_3COO by neutralization reaction.

2.3 Instruments

2.3.1 Sonicator

A sonicator (LU-2 Ultrasonic cleaner, Labnics, USA) was used to prepare homogeneous binary mixtures of [dema]CF_3COO with alcohol. Each of the solution was sonicated for minimum 60 minutes to ensure homogeneous mixing of the components of the mixture.

2.3.2 FT-IR

FTIR spectra were recorded by Fourier transform spectrophotometer *Frontier*^{TM} by PerkinElmer in transmittance mode with 32 scans for each sample in the range between 1000 and 4000 cm^{-1} at 4.0 cm^{-1} resolution with a pair of rectangular CaF_2 windows with curved edges (Specac Model No.: GS20522). The uncertainty in measurements of this instrument is 1%.

IR (ATR) were measured by FTIR-8400S.IR (ATR) spectra of pure [dema]CF_3COO and alcohol were recorded at room temperature in the frequency range of 4000 to 700 cm^{-1}. The resolution were 4 cm^{-1}. Number of scan rate were 20 times.

2.3.3 Thermogravimetric and Differential Thermal Analyzer

Thermogravimetric measurements and differential thermal analysis of the pure PILs and their binary mixtures with alcohol were simultaneously carried out by Hitachi TG/DTA 7200 in N_2 atmosphere with a flow rate of 100 mL min^{-1}. Aluminum pans were used as sample holder and reference pans.

2.3.4 Density Meter

The densities of the binary mixtures were measured with Anton Paar (model DMA 4500) vibrating tube density meter. The density meter was calibrated with ultra pure water, and with dry air at atmospheric pressure. The repeatability of density measurement was 0.00001 gcm^{-3}. The density measurement is based on oscillating U-tube method. In this method sample is injected to a U-shaped borosilicate glass tube that is being excited to vibrate at a characteristic frequency. The characteristic frequency changes depending on the density of the sample. Through a precise determination of this frequency and a mathematical conversion, the density of sample can be measured. The density is calculated from the quotient of the period of oscillations of the U-tube and the reference oscillator. Density = $KA \times Q^2 \times f_1 - KB \times f_2$, where Q is the quotient of the period of oscillation of U- tube divided by the period of oscillation of the reference oscillator and f_1, f_2 are the correction terms for temperature, viscosity and non-linearity.

2.3.5 Microviscometer

Viscosities of the binary mixtures were measured with Lovis 2000 M/ME Microviscometer utilizing the rolling ball principle with an accuracy of $\pm 10^{-6}$ mPas. Capillaries with diameters 1.59 mm, 1.80 mm and 2.50 mm and a steel ball with maximum deviation of 0.2% was used for measurements. In the rolling ball principle, a ball rolls through a closed, liquid-filled capillary,

which is inclined at a defined angle. Three inductive sensors determine the rolling time of the ball between defined marks. The sample's viscosity is directly proportional to the rolling time. The microviscometer registers the rolling time. The inductive sensors allow the measurement of opaque liquids.

2.3.6 Impedance Spectroscopic Analyzer

The electrochemical impedance spectroscopic (EIS) measurements were performed using AutolabPGSTAT302N - High Performance Impedance Analyzer with the FRA32M module over a wide frequency range of 10 μHz to 32 MHz.

2.4 Measurements

2.4.1 Thermal Analysis

TGA of the PILs and binary mixtures were carried out simultaneously under N_2 atmosphere with N_2 gas flow rate of 100 mL min^{-1}. For every measurement, a programmed heating from 30 to 550°C with a heating rate of 10 °C $min^{-1}$was performed.

2.4.2 Density Measurement

A small amount of PILs and alcohol binary mixtures (less than 2 mL) was introduced into a U-shaped borosilicate glass tube. Density of each solution was measured from 30 to 70 °C. After raising the temperature to 70°C the sample was again cooled down to 30 °C. The density value obtained was found to be same as the initial value at 30 °C before the temperature was raised. After each measurement the U-shaped tube was cleaned with ethanol and ultrapure water.

2.4.3 Viscosity Measurement

A small amount of sample (<1 mL) was filled into a glass capillary by using a syringe which was introduced into a temperature controlled capillary block. This block was inclined at variable predefined angle. Angle of measurement and the diameter of capillary for sampling and ball have been selected depending on the approximate viscosity of the mixture. For PILs-alcohol solutions with PIL mole fraction 0.00 to 1.00 the measuring angle was 20° to 70° and the capillary used was 1.59mm, 1.80mm and 2.50 mm diameters.

2.4.4 Conductivity Measurement

Conductivity of PIL and alcohols binary mixtures was measured by impedance spectroscopic method. For this, the potentiostatic impedance spectra at 0.2V were recorded as a function of ac frequency over the range from 100 Hz to 32 MHz with ac potential amplitude of 0.5 mV. From

the Nyquist plot that is Z′ vs –Z″ plot for each sample, the R_s value was obtained. The cell constant was calculated using standard 0.01 M KCl solution and used to determine value of specific conductivity, κ from appropriate calculations. The temperature of the tested solutions was considered to be same as the room temperature.

3.0 Results

In this study, [dema]CF_3COO and its binary mixtures with aliphatic alcohols were prepared with a wide range of compositions and characterized them for investigating thermal behaviors, transport properties, molecular interactions. Detail results were mentioned in the following sections.

3.1 FT-IR Spectroscopic Study of PIL Alcohol Binary Systems

3.1.1 FT-IR (ATR) Spectra of [dema]CF_3COO and its Binary Mixtures with Alcohols

FTIR spectra of pure [dema]CF_3COO and alcohols were recorded at room temperature in the frequency range of 4000 to 700 cm^{-1}. The resolution were 4 cm^{-1} and number of scan rate were 20 times.

According to Figures (3.1, 3.2, 3.3, 3.4), FT-IR spectra for pure [dema]CF_3COO and its binary system with alcohols in the results section. According to figures, the absorption band were observed at 3016, 2996, 2666, 2508, 1676, 1476, 1409 , 1202, 1126, 1037 and 837 cm^{-1}. However, the absorption band were observed at 3016, 2996, 1676, 1409 for N-H streatching, C-H stratching, C=O streatching, C-O stretching respectively.

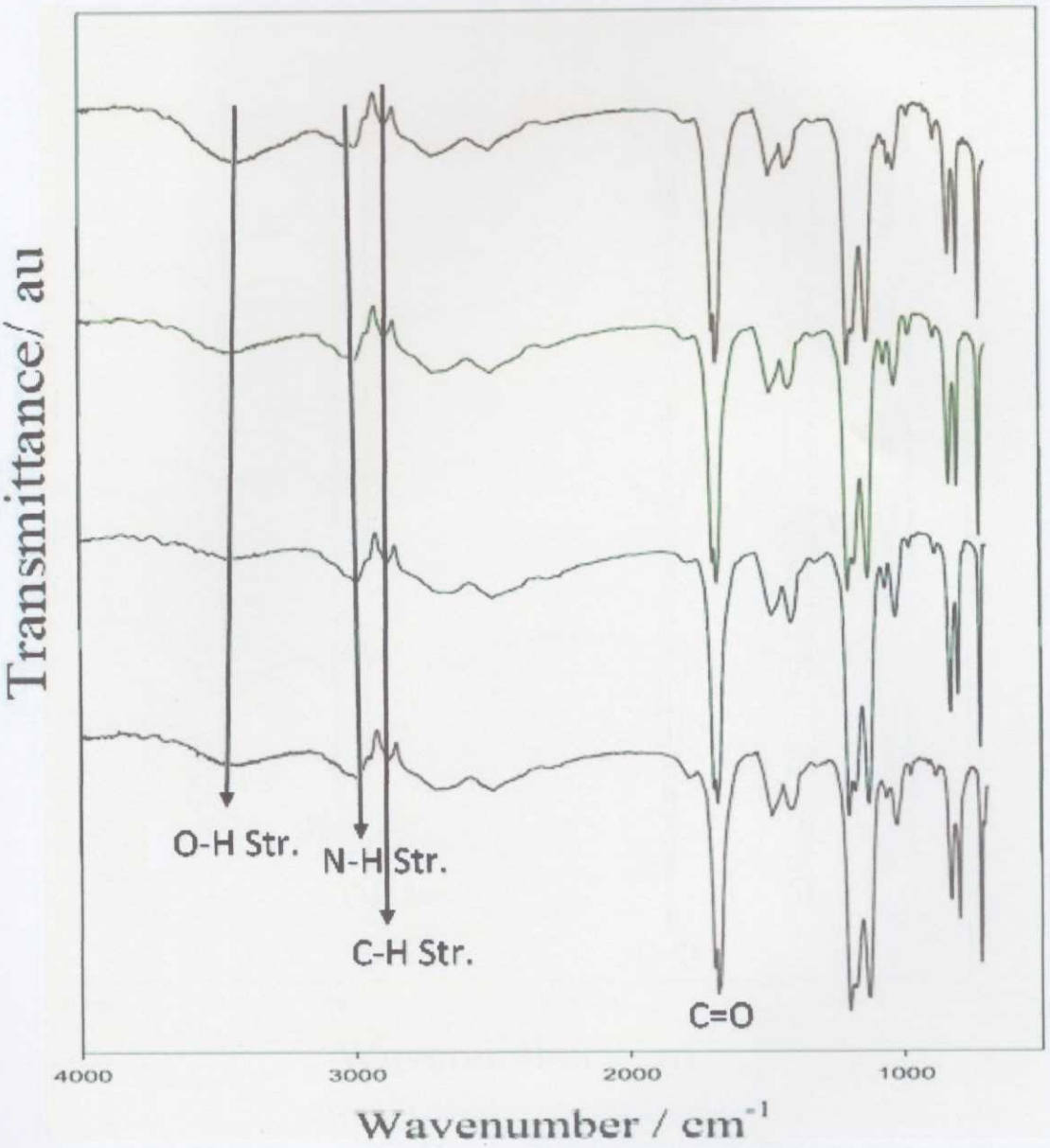


Figure 3. 1: FT-IR (ATR) spectra of [dema]CF_3COO – alcohols (PIL:Alcohol = 0.85:0.15) at room temperature.

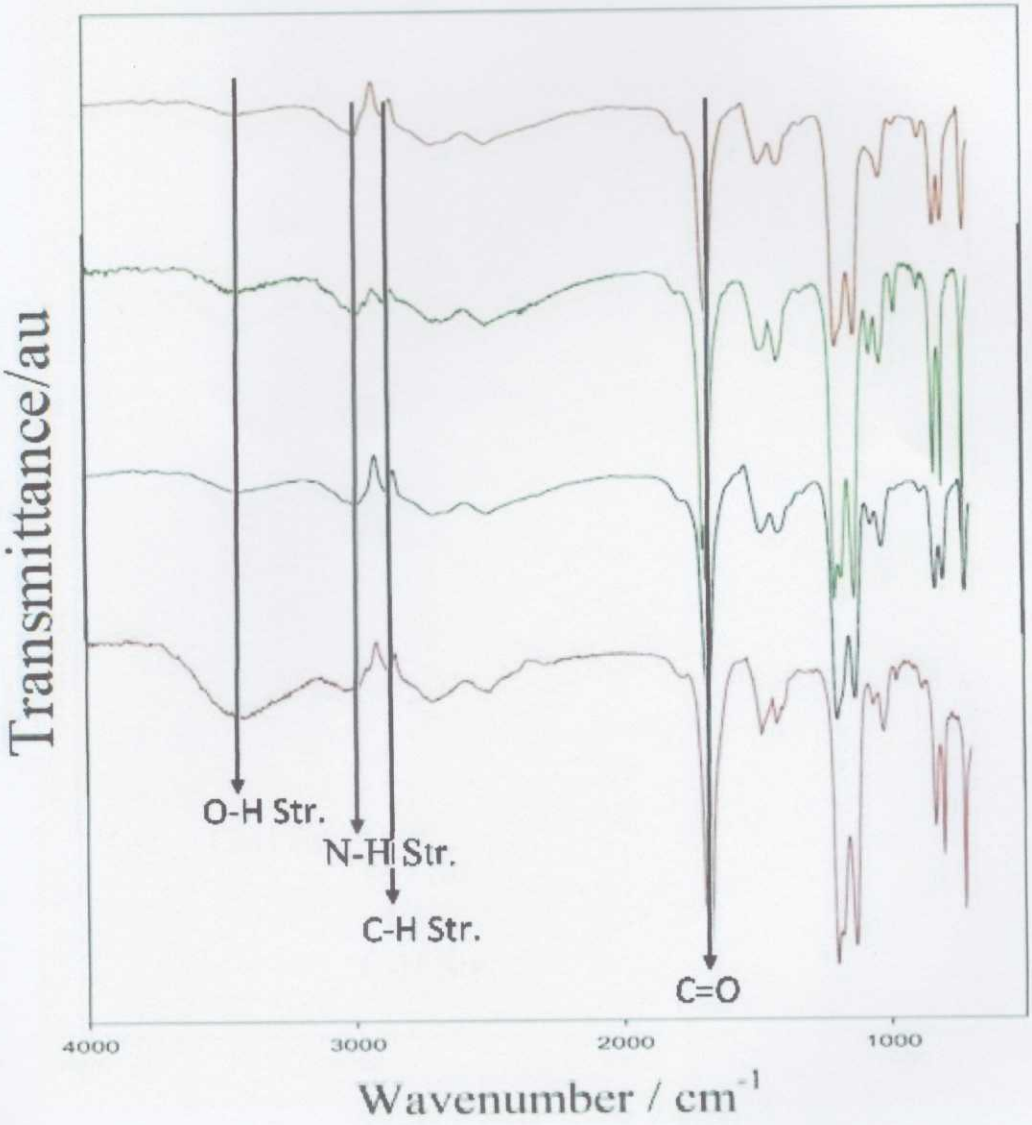


Figure 3.2: FT-IR (ATR) spectra of [dema]CF_3COO – alcohols (PIL:Alcohol = 0.75:0.25) at room temperature.

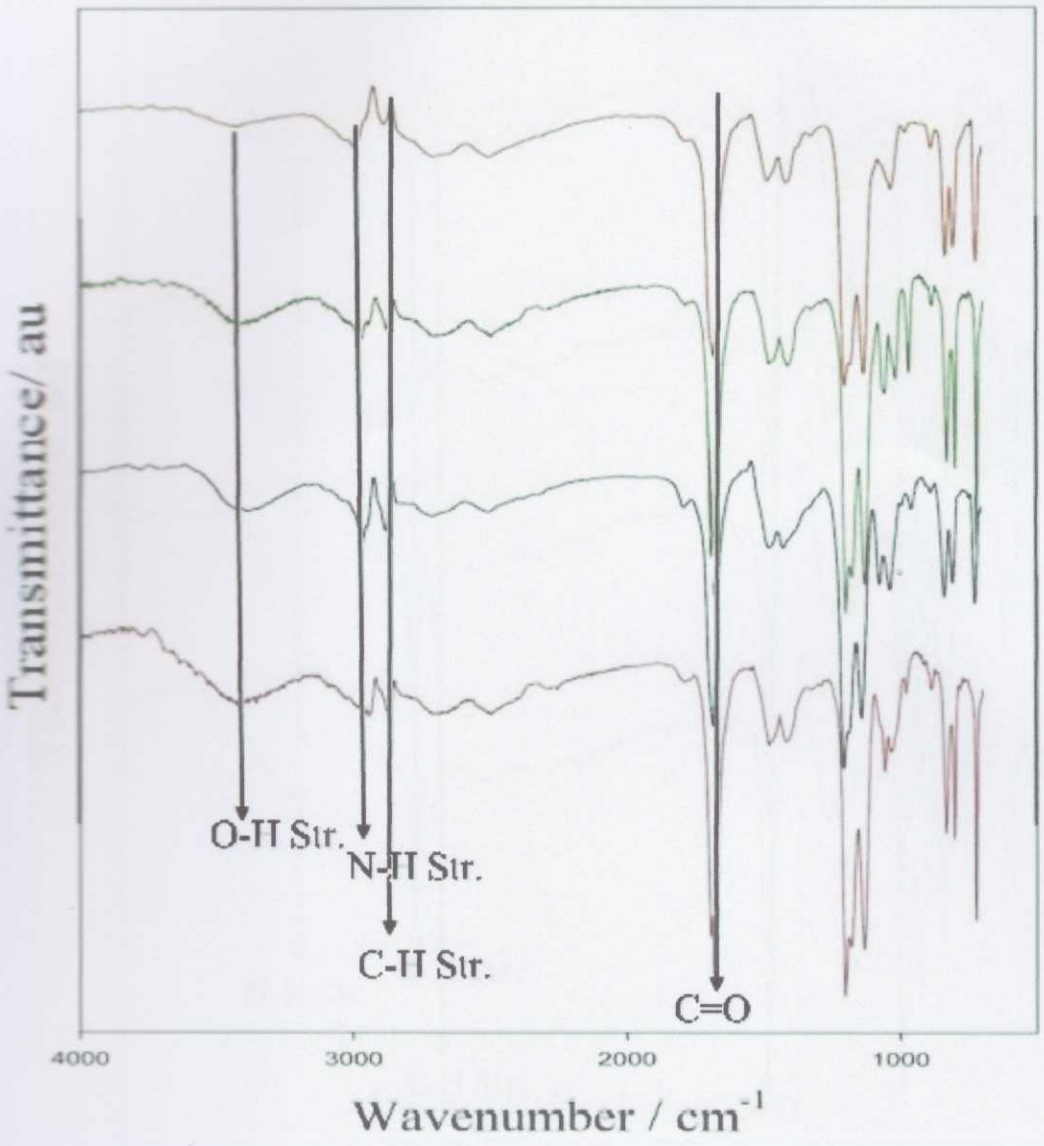


Figure 3.3: FT-IR (ATR) spectra of [dema]CF_3COO – alcohols (PIL:Alcohol = 0.50:0.50) at room temperature.

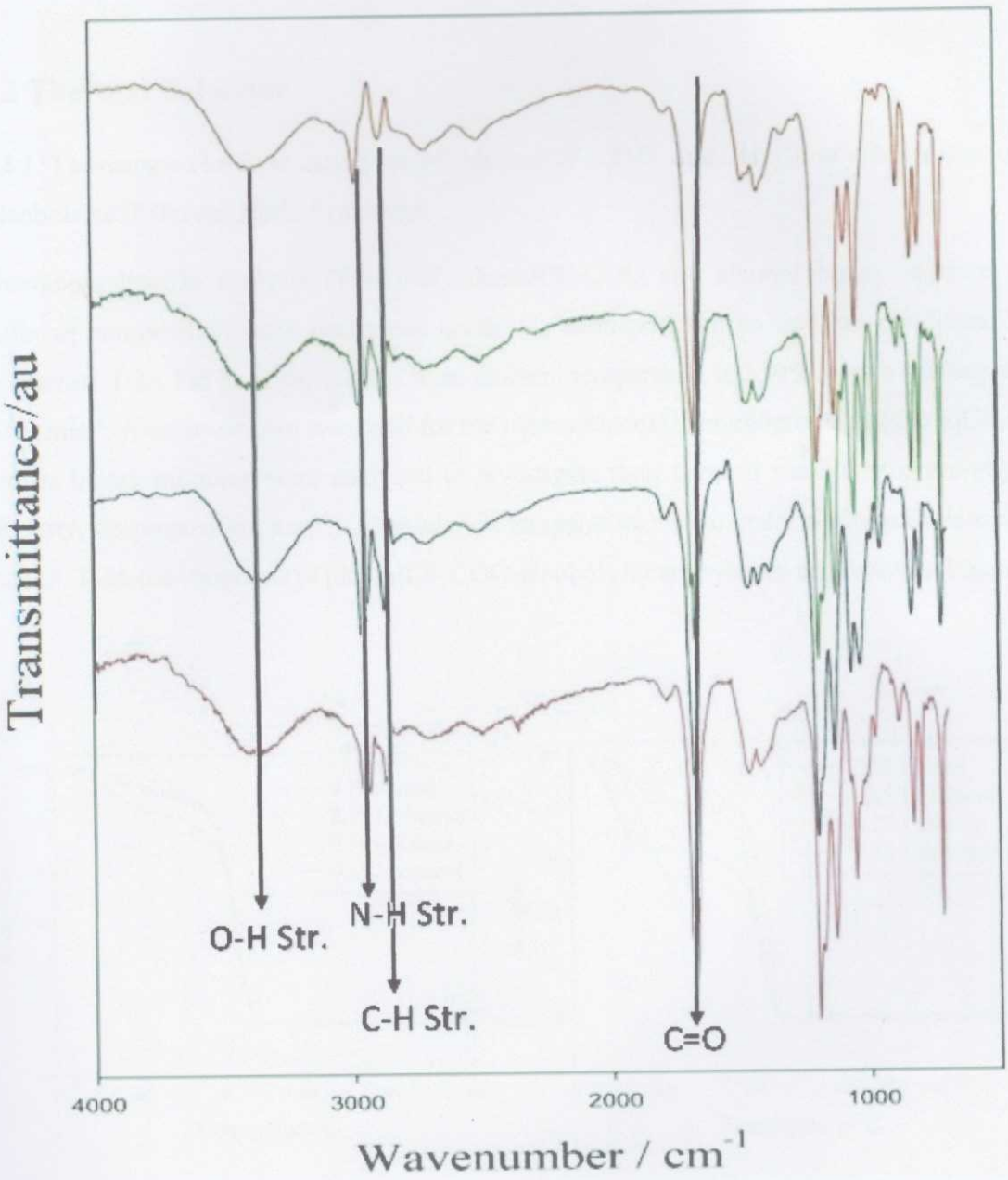


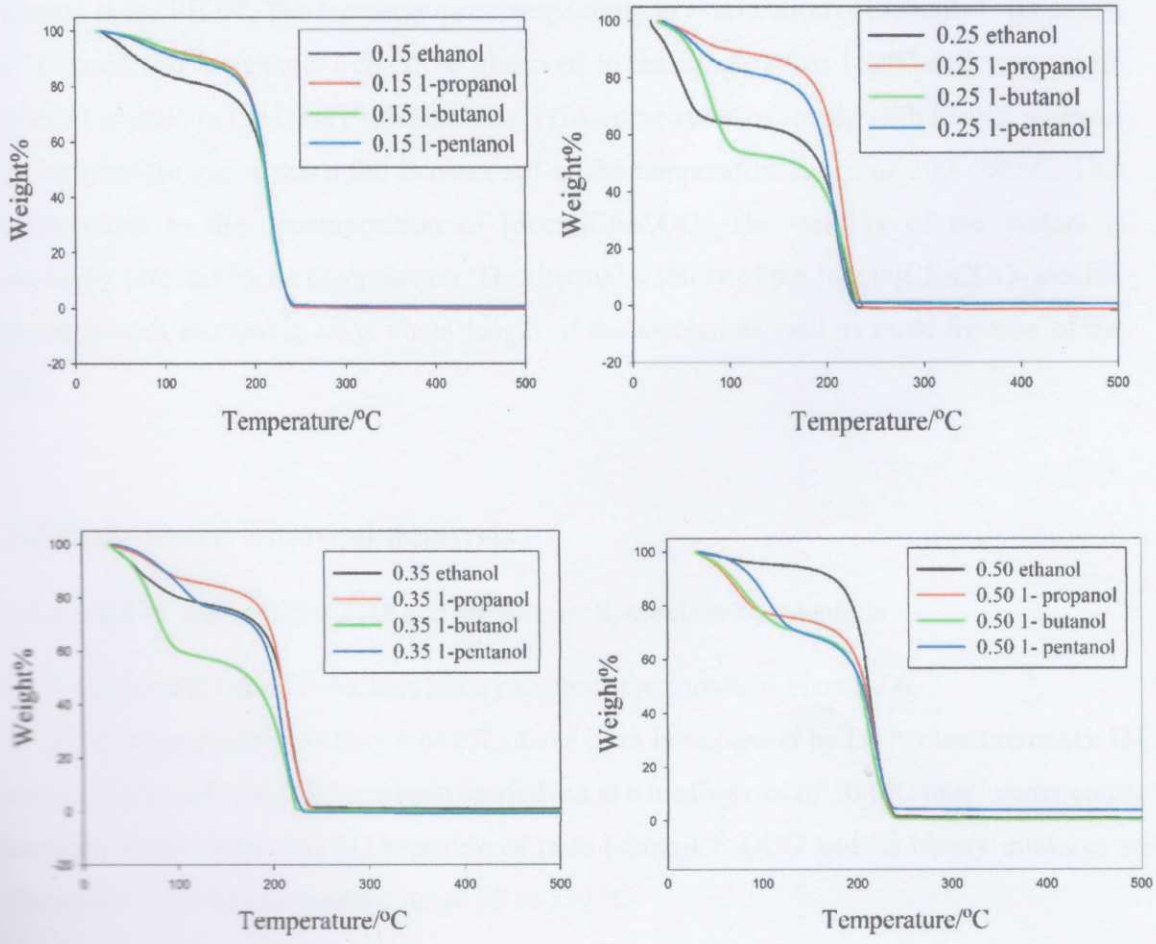
Figure 3.4: FT-IR (ATR) spectra of [dema]CF_3COO – alcohols (PIL: Alcohol = 0.25:0.75) at room temperature.

Other characteristic bands associated with the N-H bond are located around 1150 and 1300 cm^{-1} in [dema]CF_3COO. These rather strong bands originate from N-H out of plane bending deformation coupled with neighboring C-H bending. Detailed study of theN-H stretching and N-H out of plane bending deformationvibrations provides useful information about the dynamic nature of N-H protons relevant to proton conductivity.

3.2 Thermal Behavior

3.2.1 Thermogravimetric Analysis of [dema]CF_3COO and its Binary Mixtures of Alcohols at Different Mole Fractions

Thermogravimetric analysis (TGA) of [dema]CF_3COO and alcohol binary mixture (v/v) different composition were performed under N_2 atmosphere at an ambient condition. Non-isothermal TGA has been carried out from ambient temperature to 550°C with a heating rate of 10°C min^{-1}. Aluminium pan was used for the measurements. Thermograms of [dema]CF_3COO and its binary mixtures were analyzed to investigate their thermal stability, thermo-physical property, decomposition pattern, degradation temperature and to make a comparative study of the ILs. TGA thermograms of [dema]CF_3COO-alcohols binary systems are shown in Figure 3.5.



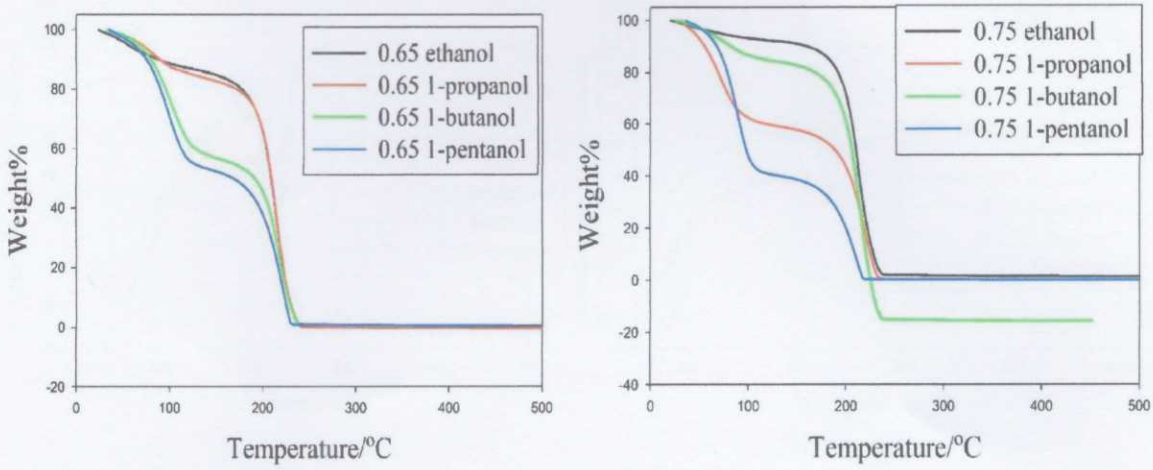


Figure 3.5: TGA curves for [dema]CF_3COO and its binary systems with different alcohols at different molar composition.

Two steps weight loss processes for each composition of [dema]CF_3COO- alcohol binary mixtures (v/v) could be observed from this figures. The first step due to loss of free alcohol present in the PILs[66]. The temperature corresponding to evaporation of ethanol, 1- propanol, 1- butanol and 1- pentanol could be observed in the range 80 to 110°C and varies with alcohol content in the binary mixture. The TGA curve remains steady with further increase in temperature and a sharp fall is observed in the temperature range of 200- 280°C. This corresponds to the decomposition of [dema]CF_3COO. The stability of the system is markedly affected by its composition. The thermal stability of the [dema]CF_3COO- alcohol changed with increasing alkyl chain length of the alcohol as well as mole fraction of the PIL.

3.3 Differential Thermal Analysis

3.3.1 DTA of [dema]CF_3COO and its Binary Systems with Alcohols

DTA of [dema]CF_3COO-alcohols binary systems are shown in Figure 3.6.

Thermal decomposition behavior of PILs have been investigated by DTA measurements. DTA curves of [dema]CF_3COO have been carried out at a heating rate of 10.0°C min^{-1} under constant nitrogen atmosphere. The DTA profile of pure [dema]CF_3COO and its binary mixtures with alcohols within the temperature range 30 to 550 °C

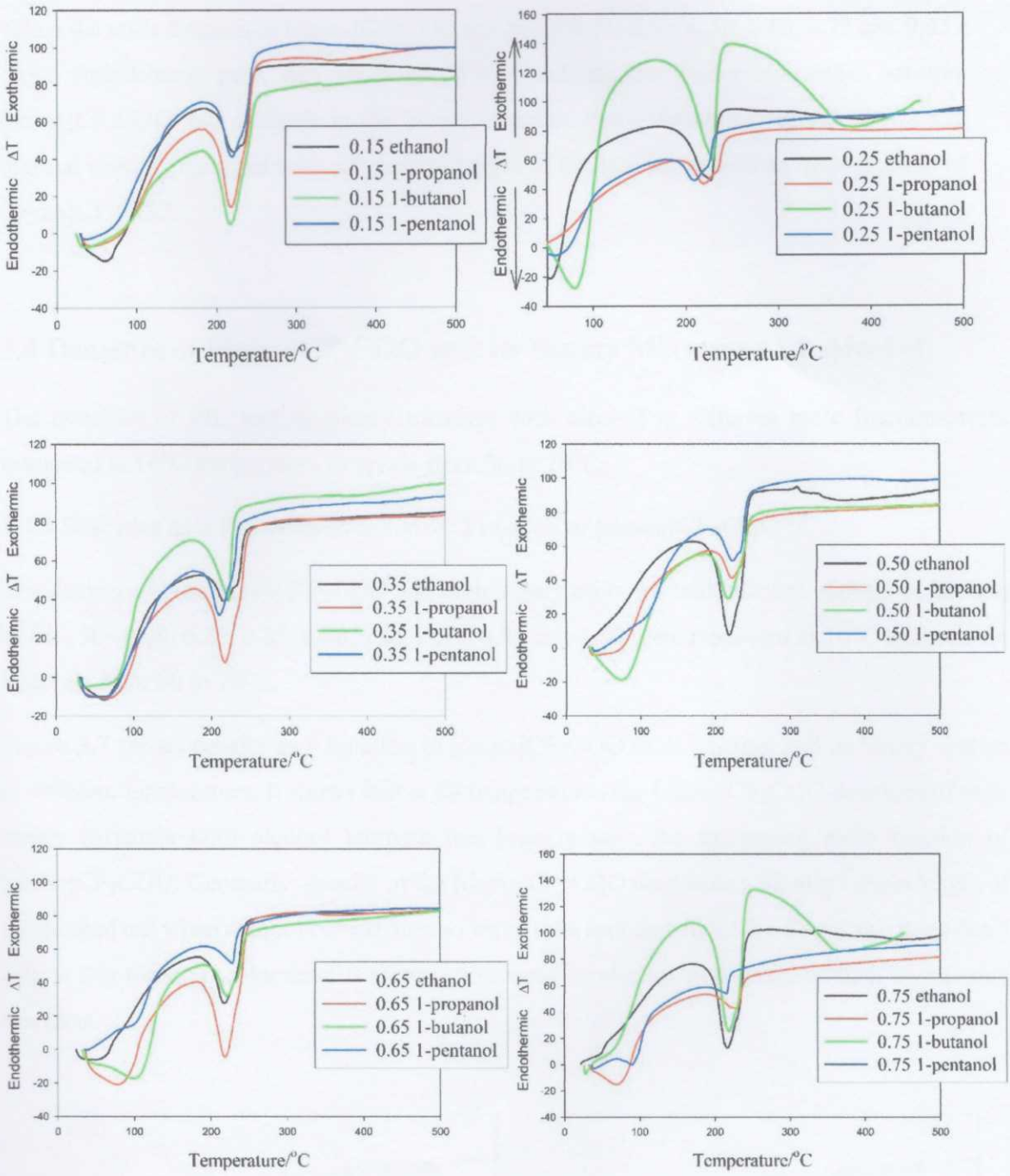


Figure 3.6: DTA profile of [dema]CF_3COO and its binary mixtures with different alcohol at different molar composition.

Thermal decomposition behavior of [dema]CF_3COO and its binary systems also have been investigated by DTA measurements. DTA curves of [dema]CF_3COO and their binary mixtures have been carried out at a heating rate of 10°C min^{-1} under constant nitrogen atmosphere. Above figures show the DTA profile of [dema]CF_3COO and its binary systems

within the temperature range 30 to 550°C. All DTA curves give sharp endothermic peak. When the mole fraction of [dema]CF_3COO are X_{PIL}= 0.25, 0.35, 0.50, 0.65, 0.75 and 0.85 a broad endothermic peak was observed. Which indicate the strong interaction between [dema]CF_3COO and alcohols in the binary systems. From the above figures shows that thermal stability changed with alkyl chain length of the alcohol as well as mole fraction of [dema]CF_3COO.

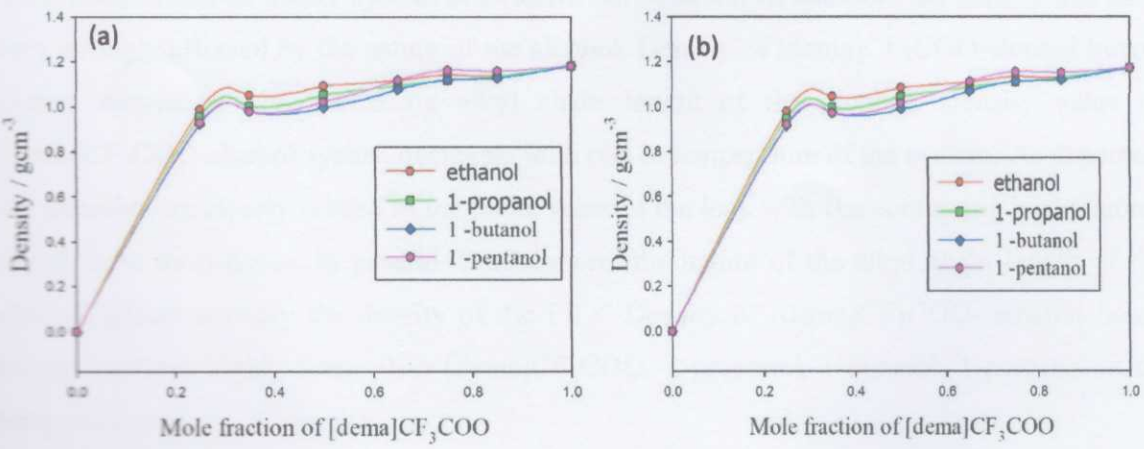
3.4 Densities of [dema]CF_3COO and Its Binary Mixtures with Alcohol

The densities of PIL and its binary mixtures with alcohol at different mole fractions were measured at 10°C temperature intervals from 30 to 70°C.

3.4.1 Densities as a Function of the Mole Fraction of [dema]CF_3COO

The density of pure [dema]CF_3COO and their binary mixtures with alcohol with mole fraction of PIL, X= 0.00, 0.25, 0.35, 0.50, 0.65, 0.75, 0.85 and 1.00 were measured at 10°C temperature intervals from 30 to 70°C.

Figure 3.7 shows density as a function of [dema]CF_3COO mole fraction and its binary system at different temperature. It shows that at all temperatures the [dema]CF_3COO densities of their binary mixtures with alcohol increase non-linearly with the increasing mole fraction of [dema]CF_3COO. Generally, density of the [dema]CF_3COO decreases with alkyl chain length of the alcohol but when alcohol carbon number more than four density of the binary mixtures don't follow this trend. The decrease is more pronounced in alcohol-rich mixtures than in PIL-rich mixtures.



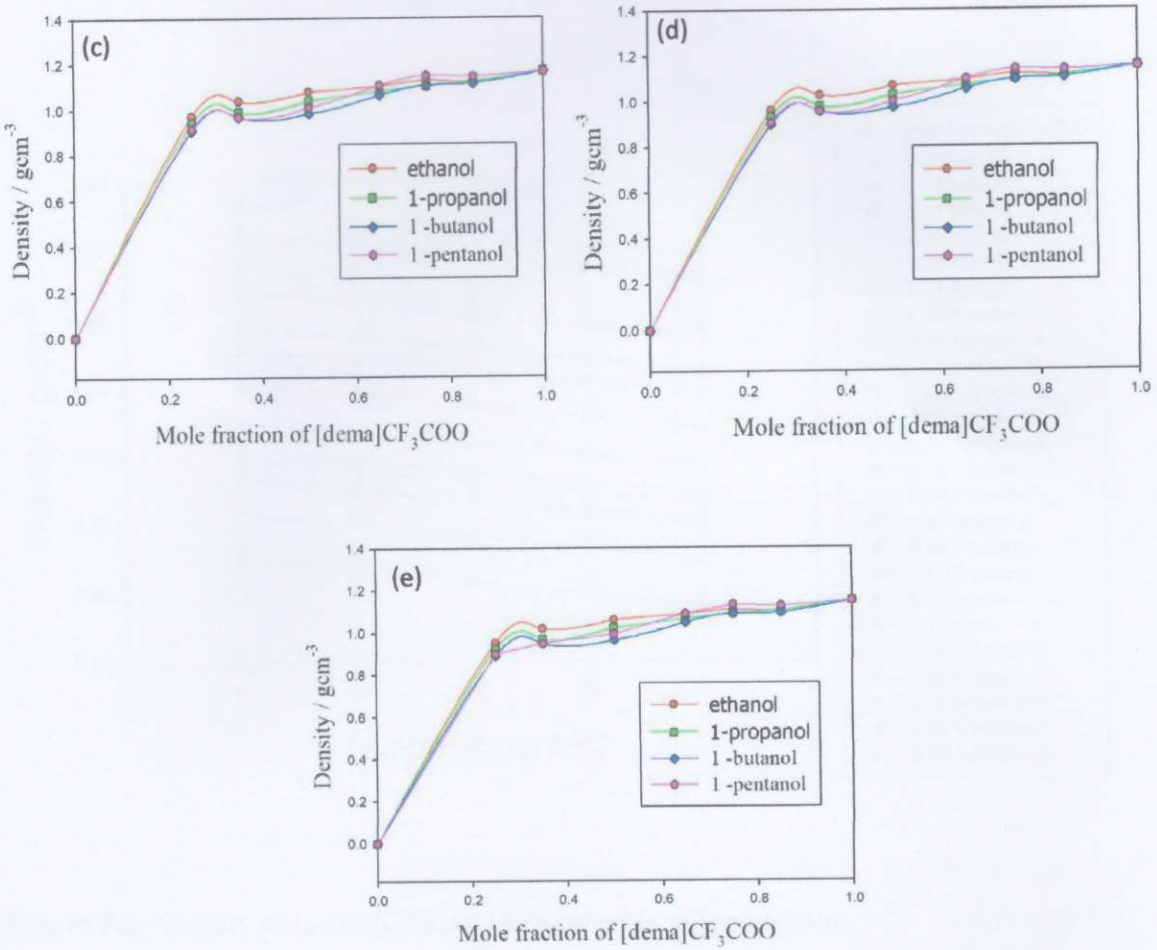


Figure 3.7: Density as a function of mole fraction of [dema]CF_3COO at (a) 30°C (b) 40°C (c) 50°C (d) 60°C and (e)70°C.

3.4.2 Densities as Function of Temperature

Figures 3.7 (a), 3.7(b), 3.7(c), 3.7(d) and 3.7(e) show density as a function of [dema]CF_3COO mole fraction and its binary system at different temperature. In addition, the density of PIL is very strongly affected by the nature of the alcohol. Density of [dema]CF_3COO-alcohol binary system decreases with increasing alkyl chain length of the alcohol. Density value of [dema]CF_3COO-alcohol system decreases with rise in temperature of the system. As expected, the densities are closely related to the molar mass of the ions with ILs containing heavy atoms found to be most dense, in general. Furthermore, the nature of the alkyl chain length of the alcohol affects strongly the density of the PILs. Density of [dema]CF_3COO- ethanol based binary mixtures highly dense than [dema]CF_3COO- 1-propanol, 1-butanol, 1-pentanol at all temperatures.

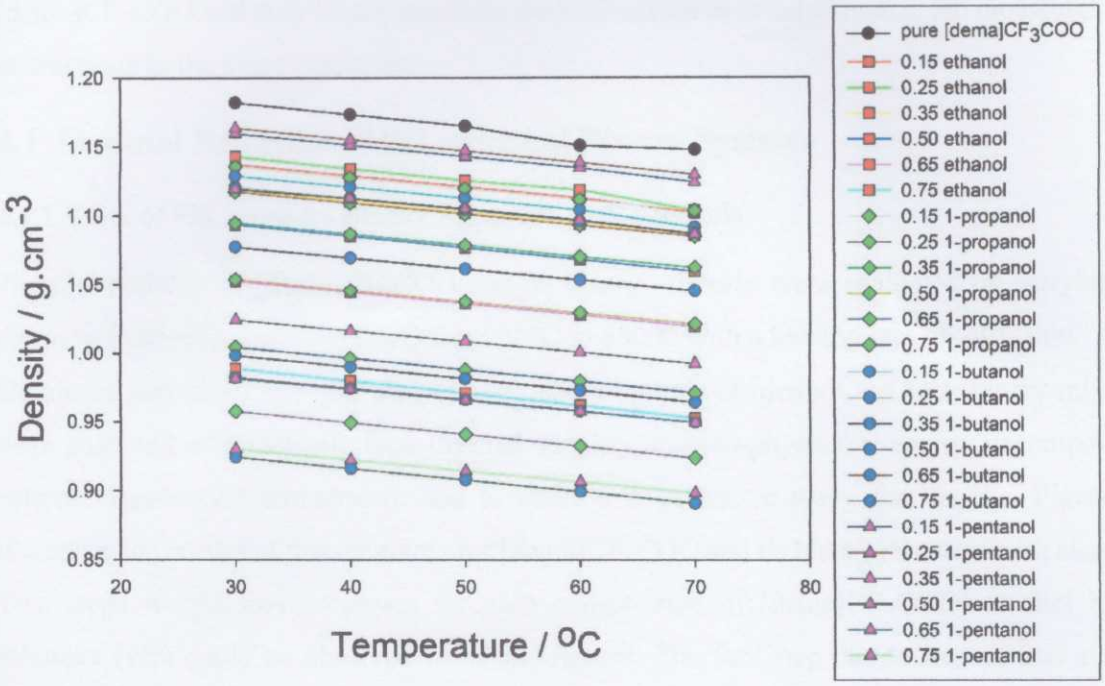


Figure 3.8: Density of [dema]CF_3COO as a function of temperature.

4.0 Discussion

Excess properties, spectroscopic analyses, ionic nature, conductivity, molar concentration of [dema]CF_3COO and their binary mixtures were discussed in detail to realize the molecular level interactions in the binary systems.

4.1 Thermal Behavior of PIL-Alcohol Binary Systems

4.1.1 TGA of PILs and its Binary Mixtures with Alcohols

Thermal stability of [dema]CF_3COO and its binary mixtures were evaluated by carrying out thermogravimetric analysis (TGA) from 30°C to 550°C with a heating rate of 10°C min^{-1} using aluminium pan under nitrogen atmosphere. Thermograms of [dema]CF_3COO- binary mixtures were analyzed to investigate their thermal stability, thermo-physical property, decomposition pattern, degradation temperature and to make a comparative study for the ILs. Figure 3.5 illustrates the curves of thermograms for [dema]CF_3COO and its binary mixtures with alcohols. Two steps weight loss processes for each composition of [dema]CF_3COO- alcohol binary mixtures (v/v) could be observed from this figures. The first step due to loss of free alcohol present in the PILs[66]. The temperature corresponding to evaporation of ethanol, 1- propanol, 1-butanol and 1- pentanol could be observed in the range 80 to 110°C and varies with alcohol content in the binary mixture. The TGA curve remains steady with further increase in temperature and a sharp fall is observed in the temperature range of 200- 280°C. The stability of the system is markedly affected by its composition. The thermal stability of the [dema]CF_3COO- alcohol changed with increasing alkyl chain length of the alcohol as well as mole fraction of the PIL.

4.2 Excess molar volume of [dema]CF_3COO and its binary mixtures with alcohols

Excess thermodynamic properties, which depend on the composition and temperature, are of great importance in understanding the nature of molecular aggregation that exists in the binary mixtures. The excess molar volume, V_m^E is the deviation of molar volume from the ideal additive behavior for binary mixtures. Excess molar volume for all systems were derived using density of corresponding systems. Figure 4.1. depicts the excess molar volume, V_m^E change of [dema]CF_3COO–alcohol binary system over the whole composition at different temperatures along with the fitting to Redlich-Kister equation.[34]

The equation is as follows:

$$V_m^E = x_2(1-x_2)\sum_{i=0}^{n} A_i(2x_2-1)^i$$

where, A_i is the fitting coefficient and x_2 is the mole fraction of [dema]CF_3COO. Figure 4.1.1 shows that for binary mixtures of [dema]CF_3COO and ethanol the excess molar volumes were positive for the mole fraction range 0.50 to 1.00, on the other, [dema]CF_3COO and its binary mixtures with ethanol shows negative deviation at the mole fraction range 0.00 to 0.50.

Figure 4.1 shows that for binary mixtures of [dema]CF_3COO and 1- propanol the excess molar volumes were positive, for binary mixtures of [dema]CF_3COO and 1-butanol the excess molar volumes were positive for whole mole fraction range. Figure 4.1.1 also shows that for binary mixtures of [dema]CF_3COO and ethanol the excess molar volumes were positive for the mole fraction range 0.00 to 0.50, on the other, [dema]CF_3COO and its binary mixtures with ethanol shows negative deviation at the mole fraction range 0.50 to 1.00.

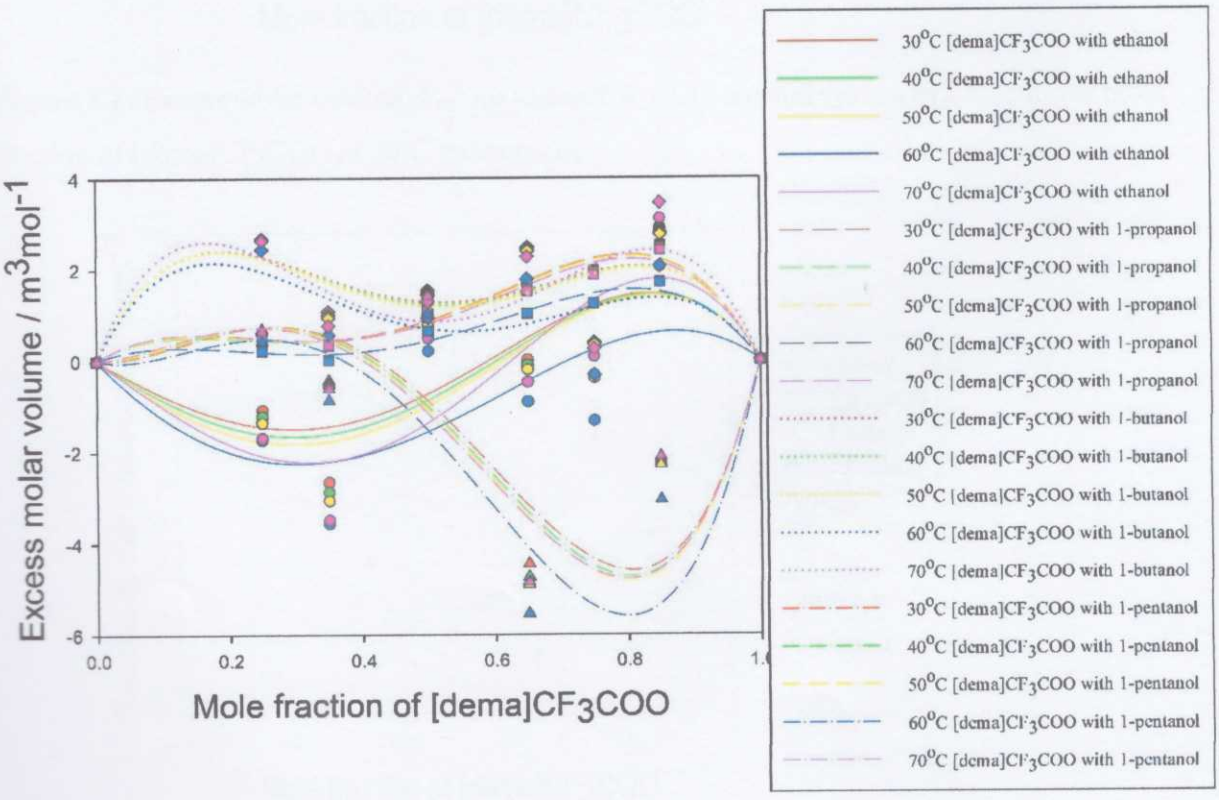


Figure 4.1: Excess molar volume, V_m^E for [dema]CF_3COO-alcohol system as a function of mole fraction of [dema]CF_3COO at different temperatures.

Figures (4.2, 4.3, 4.4, 4.5 and 4.6) show excess molar volume, V_m^E as a function of [dema]CF_3COO mole fraction and its binary system at constant temperature.

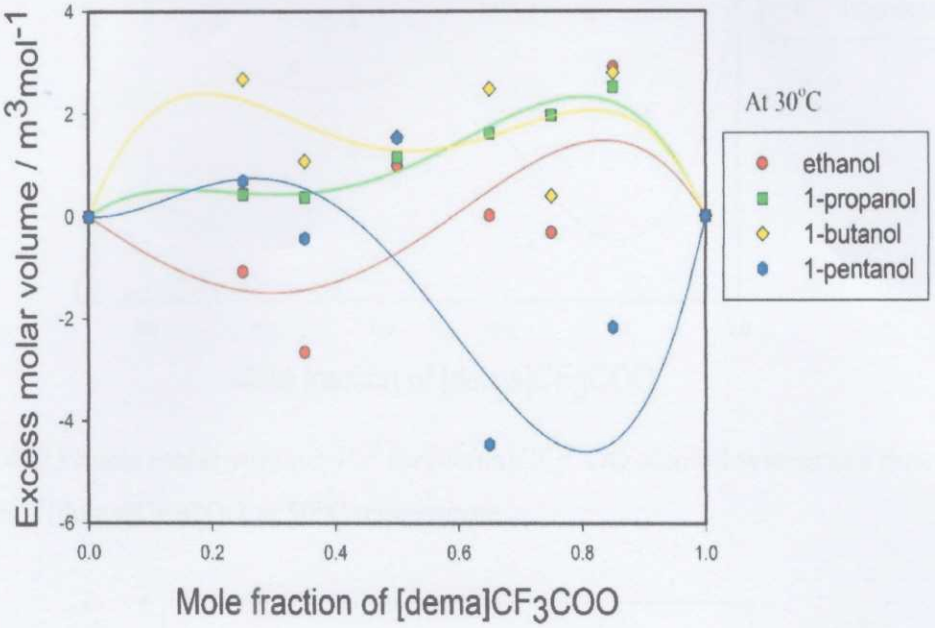


Figure 4.2: Excess molar volume, V_m^E for [dema]CF_3COO-alcohol system as a function of mole fraction of [dema]CF_3COO at 30°C temperature.

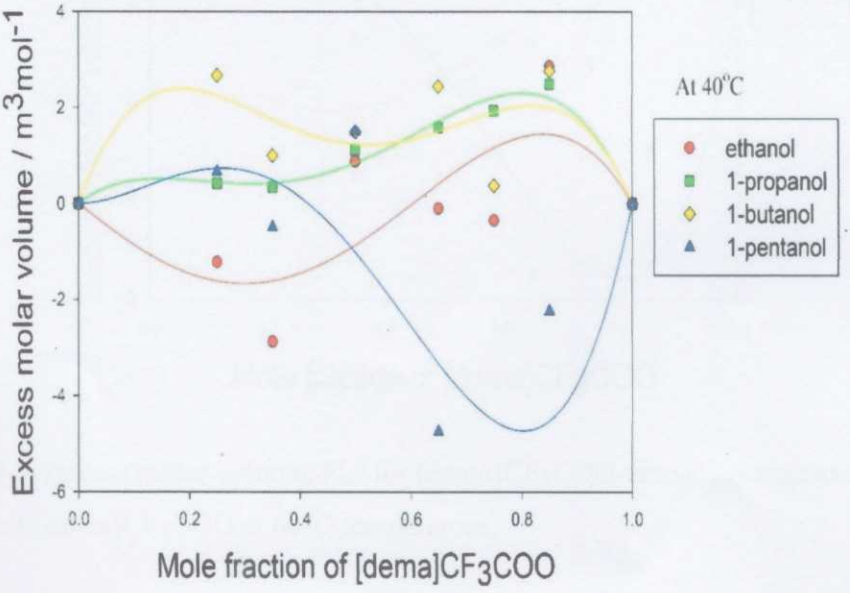


Figure 4.3: Excess molar volume, V_m^E for [dema]CF_3COO-alcohol system as a function of mole fraction of [dema]CF_3COO at 40°C temperature.

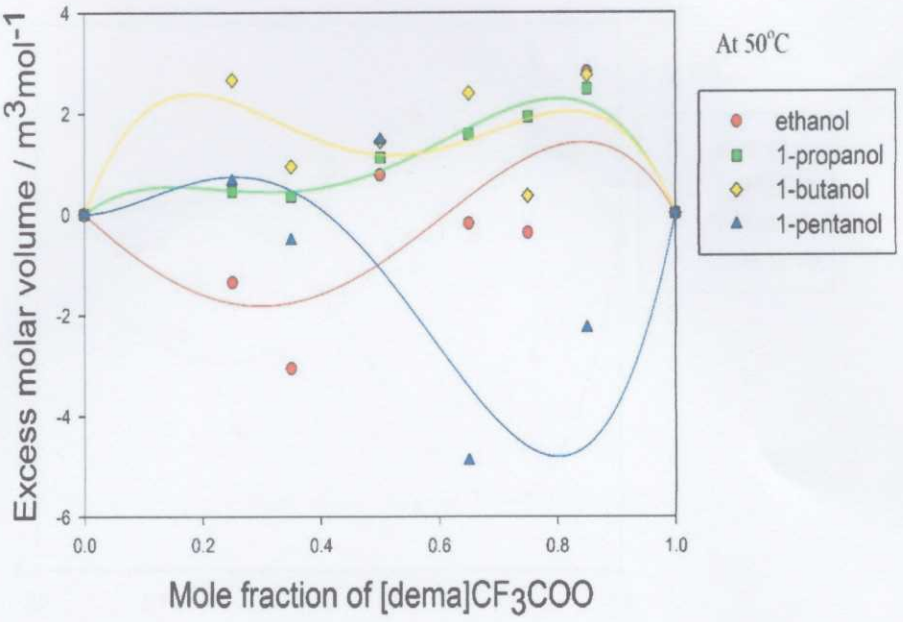


Figure 4.4: Excess molar volume, V_m^E for [dema]CF_3COO-alcohol system as a function of mole fraction of [dema]CF_3COO at 50°C temperature.

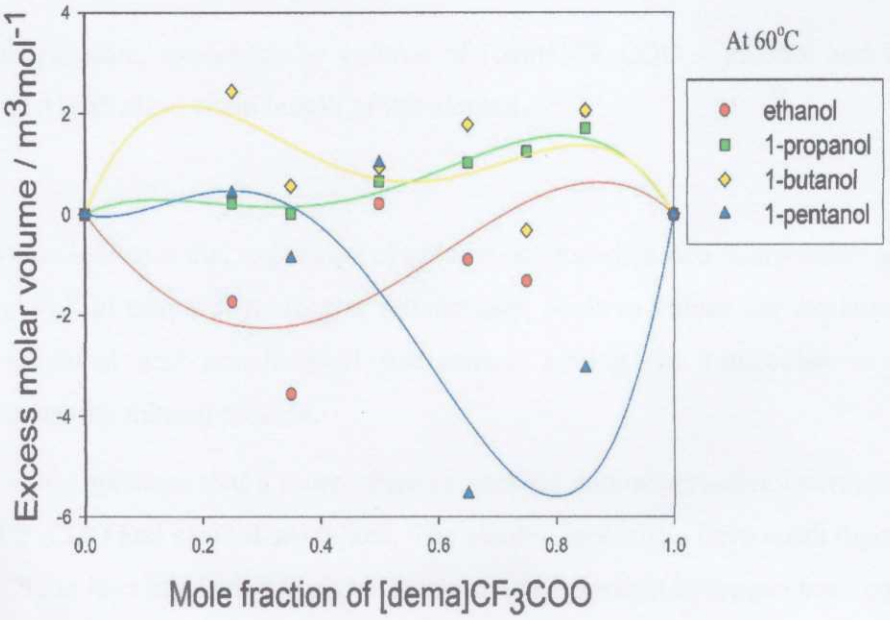


Figure 4.5: Excess molar volume, V_m^E for [dema]CF_3COO-alcohol system as a function of mole fraction of [dema]CF_3COO at 60°C temperature.

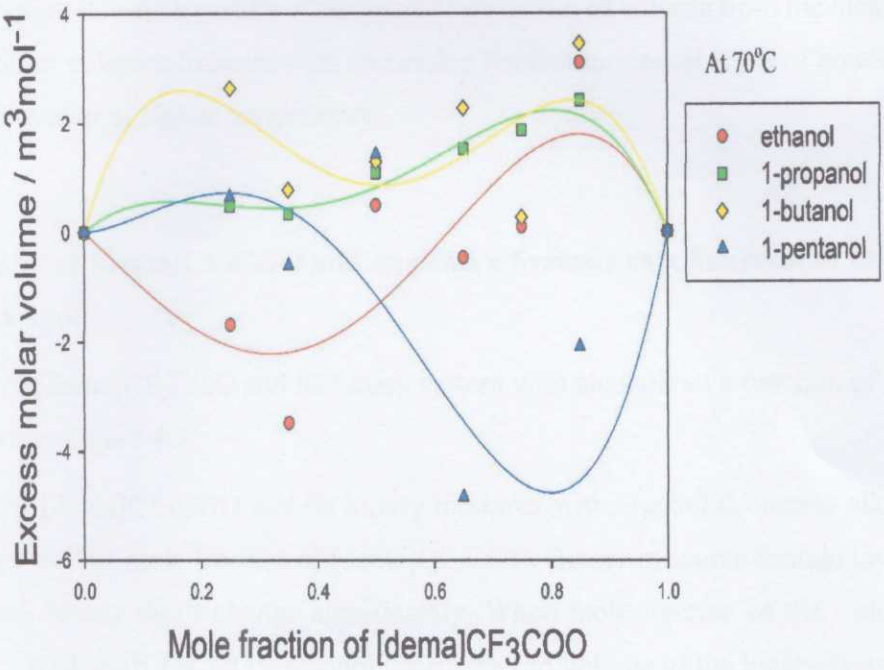


Figure 4.6: Excess molar volume, V_m^E for [dema]CF_3COO-alcohol system as a function of mole fraction of [dema]CF_3COO at 70°C temperature.

At constant temperature, excess molar volume of [dema]CF_3COO – alcohol and its binary mixtures changed with alkyl chain length of the alcohol.

The positive value indicates that expansion of volume occurs when two components are mixed. In interpreting V_m^E in terms of molecular interactions, positive values are explained by the breaking of chemical and nonchemical interactions among the molecules in the pure components during the mixing process.

The negative value indicates that a more efficient packing and/or attractive interaction occurs when [dema]CF_3COO and alcohol are mixed. The alcohol molecules have weak dipole–dipole interactions and the ions of [dema]CF_3COO are associated through hydrogen bonding. Mixing of alcohol with PIL induces a mutual dissociation of dipole–dipole association in alcohol and breaking of H-bonding in PIL comprising ions and subsequent formation of new H-bonding leading to a contraction in volume, thus resulting into negative V_m^E.

It can be assumed that there is a breakdown of the mode of association in pure bulk IL and pure alcohol by the formation of hydrogen bonds between the two components in the mixture. This hydrogen bonding interaction is weaker than the bonding interactions between cations and

anions in pure IL which results in the positive deviation of volume from the ideal behavior. The excess molar volumes increase with increasing temperature as all types of bonding interactions becomes weaker at higher temperatures.

4.3 Density of [dema]CF_3COO and its Binary Systems as a Function of Carbon Number of the Alcohol

Density of [dema]CF_3COO and its binary system with alcohols as a function of carbon number are shown in Figure 4.7.

Density of [dema]CF_3COO and its binary mixtures with alcohol decreases alkyl chain of the alcohol as well as mole fraction of [dema]CF_3COO. Binary mixtures contain low mole fraction of alcohol density don't change significantly. When mole fraction of the alcohol increases aggregation [dema]CF_3COO – alcohol decreases and volume of the binary system increases so that density of the binary system decreases with alkyl chain length of the alcohol.

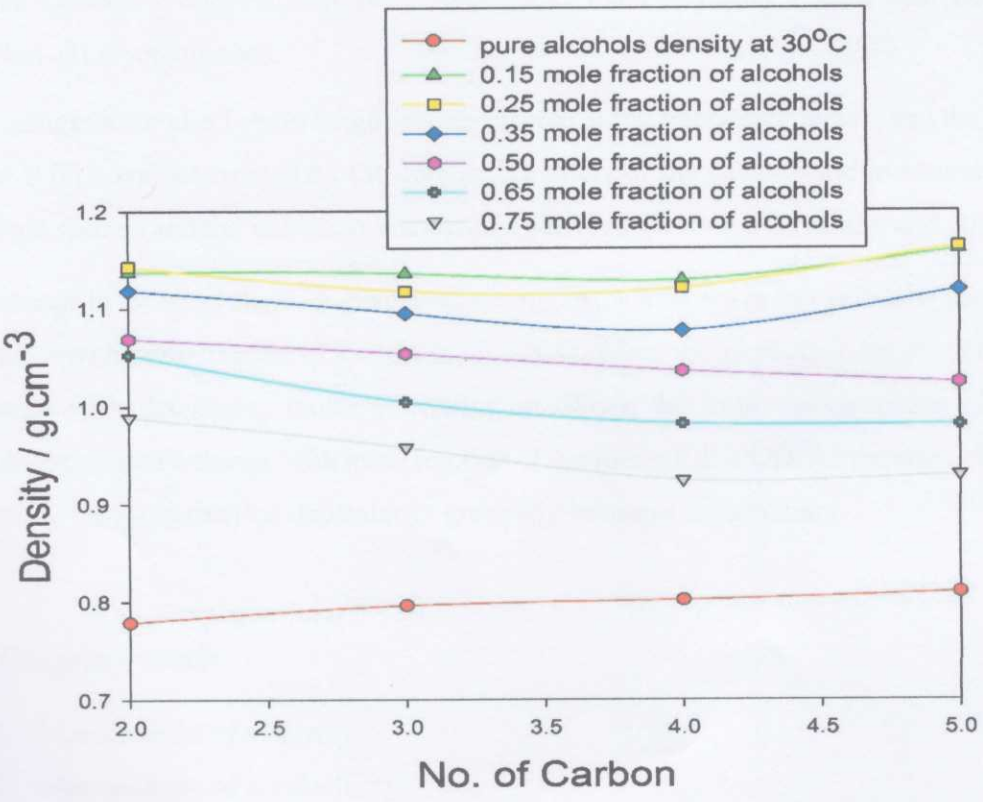


Figure 4.7: Density of [dema]CF_3COO binary systems as a function of carbon number of the alcohol.

4.4 Molar Concentration of [dema]CF_3COO and its Binary Mixtures as a Function of Carbon Number of the Alcohols

Molar concentration of [dema]CF_3COO and its binary system with alcohols as a function of carbon number are shown in Figure 4.8.

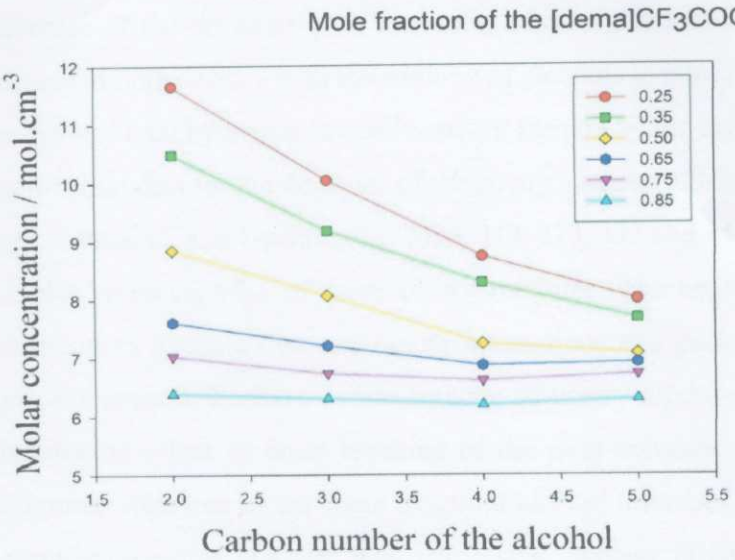


Figure 4.8: Molar concentration of [dema]CF_3COO and its binary system with alcohols as a function of carbon number.

The change in the alkyl chain length causes change in the interactive forces, and the properties of the RTILs are determined by the cumulative effect of the electrostatic interaction between the ionic species and the induction interactions between the ions, aggregates, and clusters [21].

The change in the alkyl chain length causes change in the interactive forces. Molar concentration decreases with mole fraction of the [dema]CF_3COO. When the alkyl chain length of the alcohol increases with decreasing molar concentration. When the ionic concentration high, molar concentration don't change with mole fraction of the [dema]CF_3COO. As the alkyl chain length increases, the mole fraction dependency gradually becomes insignificant.

4.5 Ongoing work

1. Measurement of viscosity
2. Measurement of conductivity
3. Calculation of ionicity using Walden rule

Conclusion

Transport properties such as density, viscosity and ionic conductivity of [dema]CF_3COO with added alcohols with varying alkyl chain length have been investigated. As expected, the densities of the [dema]CF_3COO and its binary mixtures decrease with increasing temperature. Additionally, a decrease of the densities with increasing alkyl chain length of the alcohol is observed. The decrease of both density with the addition of alcohols in pure PIL arises from the disruption of three-dimensional hydrogen bonded network formed by the cations and anions in pure PIL. The experimental data for the densities of the binary systems of [dema]CF_3COO with ethanol, 1- propanol, 1-butanol, and 1-pentanol at (303, 313, 323, 333,and 343) K were fitted to calculate excess molar volumes, V^E_m, of these binary mixtures. The negative excess molar volumes for these mixtures indicate that ion–dipole interactions and packing between ionic liquids and alcohols are present. Positive excess volume of binary mixtures are the result of intermolecular dissociation effect or bond breaking of the pure solvents. The excess molar volume in these mixtures increases as the chain length of alcohol increases. The properties of [dema]CF_3COO show progressive changes with successive increase in amount of alcohols. Thermal stability of [dema]CF_3COO also changes in a certain manner with increasing alcohols content. As the alkyl chain increase, thermal stability of PIL changes. It can be inferred from the analysis of density, viscosity and (FT-IR) ATR spectrum that [dema]CF_3COO interacts strongly with alcohols and hydrogen bonding is prominent for PIL- alcohols binary systems.

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