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An over view for Thermophysical properties of ATP & PILs

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Abstract: The ionic liquids are liquid salts which have been reported to be as a liquid state compounds at temperatures below then 100°C or at normal room temperature because of poor alignment of their ions. The crystal lattice of ionic liquid is not stable due to the presence of one delocalized charge on one ion and one organic component. The formation of ionic liquid is studied in detail but it is found that pyridinium and methylimidazolium ionic liquids are the most stable ones. To understand their unique qualities, a thermophysical analysis of their mixture and pure form should be made. Due to low availability of data on ionic liquid, the thermophysical analysis is of vital importance. The present review will provide information about detailed properties of ionic liquids.

Ionic liquids

Ge, *et al.,* (2010) highlighted that ionic liquids are compounds gaining interest among researchers and industrialists due to their wide variety of applications. To understand their unique qualities, a thermophysical analysis of their mixture and pure form should be made. Due to low availability of data on ionic liquid, the thermophysical analysis was of vital importance. On the other hand, with the help of thermophysical models and latest data calculation methods, an ionic liquid can be studied to its full extent. Robert (1969) studied diverse thermodynamic properties of the hydrolysis of adenosine triphosphate. Seymour, *et al.,* (1981) studied the mechanism of the hydrolysis of Adenosine 5′-Triphosphate (ATP) and devised four primary pathways for the nonenzymatic hydrolysis of ATP. After these four pathways, two new pathways were also devised for the further hydrolysis of ATP. Representative values of pseudo 1st order rate constants were also identified. John (2006) suggested a direct molecular mechanism of energy transfer from chemical energy to mechanical energy in hydrolysis and phosphorylation reaction from adenosine triphosphate. Sarang and Sunil (2009) established a method of quantitative analysis of energy transfer from adenosine triphosphate. Terminal phosphorous-oxygen bond cleavage during ATP hydrolysis was identified by simulation of the event. Standard state Gibbs free energy and the elementary steps after the division of energy transfer process were predicted easily which were not clearly predictable before.

Yasuda, *et al*., (2013) reported the formation of protic ionic liquids by the neutralization of allylamines with trifluoromethanesulfonic acid. For the sake of high conductivity and good physiochemical properties of these protic ionic liquids, they were compared with a group of propylamines. It was found that the magnitude of the attractions in the interacting ion pairs and the directionality of the interactions for both allyl-ammonium based IL and propyl-ammonium based IL was the same. Allyldimethylammonium trifluoromethanesulfonate was the PIL reported till now in the results that has the highest ionic conductivity of 75 mS·cm–1 at 150 °C.

Excess enthalpy and related excess properties

Ficke, *et al.,* (2010) established excess enthalpy measurements of four ionic liquids (1-ethyl-3-methylimidazolium thiocyanate, 1-ethyl-3-methylimidazolium diethylphosphate, ethyl (tributyl) phosphonium diethylphosphate, and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate) in water mixture. They also measured heat capacities and densities of seven pure ionic liquids and compared their values with their previously calculated physical properties of phosphonium and imidazolium based ionic liquids. Miran, *et al.,* (2012) described the neutralization of 1,8-diazabicyclo-[5,4,0]-undec-7-ene with various Bronsted acids which led to the formation of protic ionic liquids. The physiochemical properties like thermal properties, density, conductivity, viscosity,

self-diffusion coefficient, vibrational stretching frequency, and [1]H-chemical shifts of the N–H bond were analyzed. Akbar, *et al*., (2012) demonstrated that the study of the preparation of a binary mixtures of 1-hexyl-3-methylimidazolium bis (trisfluoromethylsulfonyl) imide [hmim] with *N*-methyldiethanolamine. Density ρ, dynamic viscosity η and refractive index nD, of the binary mixtures were measured over a temperature range of 303.15 K to 323.15 K. Cumicheo, *et al.,* (2015) established the relation between ionic liquid and its absorption capacity in the light of water + LIBr and water + ammonia systems. The study due to less data was made on the system [Bmpyr] [dca] + H$_2$O. The properties of density, speed of sound, viscosity, and surface tension of [Bmpyr] [dca] + H$_2$O were made. Seven molar compositions were used from the temperature of 288.15 K and 333.15 K. The results showed a proper feasibility of the discussed mixture for the application of thermophysical properties of absorption and refrigeration. Kermanpour and Sharifi, (2014) analyzed the density, and viscosity of a binary mixture of [x11-propanol + x22-propanol] sideways with a ternary mixture of {x11-hexyl-3-methylimidazolium tetrafluoroborate + x21-propanol ([Hmim] [{BF4]) + x32-propanol}. The density and viscosity was measured over the complete composition range from 293.15 K to 333.15 K and on a pressure of 0.1 MPa. These viscosity deviations were found to be decreasing with increasing temperature. The ternary and binary excess molar volumes were linked with the Cibulka and Redlich–Kister equations.

Coquelet, *et al*., (2009) examined the measurement of densities of pure hexamethyleneimine and of its aqueous solutions from 273.16 to 363.15 K and from 283.15 to 353.15 K on an atmospheric pressure by the help of an Anton Paar digital vibrating tube densimeter. Dauber *et al*. for pure hexamethyleneimine and Bettin and Spieweck standards for pure water were used to correlate data with the experimental data. Therefore, reliability of recently measured data was established through those standards. For the hydrophobic interfaces, it was found that the Redlich–Kister equation showed incorrect data behavior mainly at low concentrations. Thermodynamic properties like thermal expansion coefficients for the pure hexamethyleneimine and excess thermal expansion coefficient of the binary mixture were measured over the complete mole fraction range from the temperature of 283.15 to 298.15 K.

Sharma, *et al.,* (2013) reported that according to the composition status of the given ionic liquids, the thermodynamic properties of densities, speed of sound, heat capacities of pure 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-methyl

pyrrolidin-2-one, pyrrolidin-2-one, pyridine and ternary mixtures of 1-ethyl-3-methylimidazolium tetrafluoroborate (1) + 1-methyl pyrrolidin-2-one or pyrrolidin-2-one (2) + pyridine (3) and their binary mixtures of 1-methyl pyrrolidin-2-one or pyrrolidin-2-one (2) + pyridine (3) were measured at the given temperatures of 293.15 K, 298.15 K, 303.15 K, and 308.15 K at atmospheric pressure. The volumetric properties of excess molar volumes and excess isentropic compressibilities were calculated from the density and speed of sound properties measured. Graph theory was employed to calculate the thermodynamic properties of the binary and ternary mixtures. The results obtained showed promising values of the excess molar volumes and excess isentropic compressibilities for the binary and ternary mixtures under study.

Equipment design by thermophysical properties

França, *et al., (2009)* analyzed the effect of thermophysical properties of ionic liquids on the design of some latest industrial process and heat transfer equipment. Alkylmethylimidazolium liquids, with (BF4) and (PF6) anion's thermodynamic data base was used to find further data on the same ionic liquids used in the study. They established from the results that the errors in thermophysical properties of ionic liquids will make the process equipment design costly or undesignable. The heat storage capacity of the ionic liquids was also measured and analyzed. It was found that these ionic liquids can also replace currently used silicon based heat transfer fluids. The results showed that to avoid over dimensioned equipment design with low efficient operation and increased capital cost, selection of experimental data must be made carefully. Furthermore they recommended to revise the methods of thermophysical analysis of ionic liquids and establish references to experimental data with low uncertainty so that errors in experimental data could be avoided.

Contribution models for thermophysical properties

Coutinho, *et al., (2010)* highlighted that predictive group contribution models were developed after the thermophysical property analysis of ionic liquids of various groups and classifications. Thermophysical properties that were analyzed are density, viscosity, and surface tension, speed of sound, refractive index, heat capacity, electrical conductivity, thermal conductivity, isobaric expansivity, and isothermal compressibility. Results identified that the predicted models have accuracy similar to that of the experimental data. These models can predict values for new ionic liquids and can classify new groups of cations and anions based on the availability of new data from these predicted models. Alya and Chérif (2009) proposed a modified form of Lipmann's "group transfer potential" by the partitioning of gas phase

electronic energy of methyl triphosphate which is a group of adenosine triphosphate into atomic and group contributions which is in accordance with the quantum theory of atoms in molecules. It is found that due to complexation with magnesium the transfer potential of the terminal phosphate group in ATP is reduced from +241.7 to +73.1 kcal/mol. Changes in the energy of reaction and regions in ATP where there were great change in electronic energy on hydrolysis were identified. Nelyubina, *et al.,* (2016) highlighted the volume-based forecast of melting points and other thermophysical properties of ionic liquids by the help of empirical relations. Ionic volumes by Bader's partitioning of electron densities with the help of X-ray diffraction were calculated. 1-tetradecyl-3-methylimidazolium salt's volume with various different anion types were observed to be correlating linearly with melting points. Thus, larger anions showed lower-melting ionic liquids. The stability of 1-alkyl-3-methylimidazolium ionic liquid cations showing undeviating correlations of ionic volumes with the existence of LC mesophase were discovered. That showed that balanced design of ionic liquid cations is possible by the use of appropriate size of ions. Neves, *et al., (2013)* observed the importance of ionic liquids and stated that in the recent years, ionic liquids with cyano-functionalized anions have showed applications for the electrochemical and separation process. In the light of the bright future of the ionic liquids a study for the densities, viscosities and refractive indices of imidazolium-based ionic liquids with cyano-based anions was conducted at 0.1 MPa within a wide temperature range from 278 to 363 K. It was found that by the increase in the cyano groups the densities were decreased irrespective of the cation used. The decrease in the refractive index was reported in the given order of: $(SCN)- > (N (CN)2)- \approx (C (CN)3)- > (B (CN)4)-$. The viscosity values showed no specific trend. The viscosity values showed the following decreasing order as: $(SCN)- > (B (CN)4)- > (N (CN)2)- > (C (CN)3)-$. On the other hand the isobaric thermal expansion coefficient, molar refraction, the free volume, and the viscosity energy barrier of all compounds were calculated from the trial data. In the end models for the prediction of the ionic liquid properties were estimated by group contribution models.

Taherifard and Raeissi, (2016) examined the development of a group contribution method for estimating and predicting densities of ionic liquids at certain temperatures and pressures. A comprehensive database was made with the help of literature data for a huge diversity of ionic liquids consisting of 25850 data points. Pressure ranges were set from 0.10–300 MPa and temperature ranges were set from 217.58–473.15 K. It was found that the model was easy to

understand and implement. The information of the chemical structure of ionic liquid was needed to use the model and after practical usage of the model a decent accuracy of 0.95% was established. Therefore, it was concluded in the results that this group contribution model can be used easily for estimating the densities of the ionic liquid when experimental density data is not present. Kermanioryani, *et al.,* (2016) analyzed the preparation and characterization of three new imidazolium-based ionic liquids containing aromatic group in the cation combined with bis (trifluoromethylsulfonyl) imide anion. Density, viscosity, thermal decomposition, glass transition, and heat capacity were the measured thermophysical properties at numerous temperatures and atmospheric pressures. Physicochemical properties that were molar volume and crystal lattice potential energy were also established from the measured density data. Density and viscosity of ionic liquids were reported to be projected by the group contribution method formulated by the Gardas and Coutinho models.

2.5 Thermophysical properties of imidazolium, non-imidazolium based ILs and uncommon ILs

Nawshad, *et al.,* (2012) reported the formulation and characterization of dual functionalized imidazolium based ionic liquids via H NMR, FTIR, and elemental analysis. Viscosity density and refractive indices were computed for a temperature range of (293.15 to 353.15 K) and (293.15 to 333.15 K). Effect of functionalized side chains on thermophysical properties was also studied. Furthermore, thermal expansion coefficient was calculated with the help of density and thermal trend of these ionic liquids was studied by the help of thermogravimetric analyzer and differential scanning calorimeter. Sun, *et al.,* (2012) studied the formation of a group of butylsulfate-based ionic liquids by combining butylsulfate anions with different cations and studied their thermal property, electrochemical window, density, viscosity, and ionic conductivity. Voltammetric measurements showed good electrochemical stability of the butylsulfate based ionic liquids and also showed a very small increase in cathodic stability. Due to the difference of ion size taken in account the adjusted Walden plot showed a decrease in deviations between ionic liquid and ideal KCL line as compared to general Walden plot. Fernandez, *et al.,* (2007) highlighted the use of differential scanning calorimetry for the determination of glass-transition, heat capacity, crystallization and melting temperature of 1-ethyl-3-methylimidazolium ethylsulfate ([Emim] [EtSO4]) and 1-butyl-3-methylimidazolium methylsulfate ([Bmim] [MeSO4]) ionic liquids. The thermal stabilities of these ILs were determined by thermogravimetric analysis. Isothermal TGA experiments were proposed to find thermal

stability of ionic liquids due to effect of heating rate over decomposition temperatures. Results showed the glass transition temperature of 1-ethyl-3-methylimidazolium ethylsulfate to be −78.4 °C and 1-butyl-3-methylimidazolium methylsulfate to be −91.9 °C. The melting temperature of 1-butyl-3-methylimidazolium methylsulfate was reported to be −4.1 °C. The values of heat capacity was found to be increasing linearly with temperature.

Chhotaray, *et al*., (2014) analyzed an atom economization process which was used to synthesize lactam based ionic liquids from lactam which is caprolactam or butyrolactam by the use of bronsted acid such as formic acid, acetic acid or hexanoic acid. The thermophysical parameter like density, speed of sound and viscosity were measured at atmospheric pressure and for the temperature range of T = (293.15 to 333.15) K. Then the experimental density and viscosity values were fitted with linear and Vogel–Tamman–Fulcher equations. It was found that the fitting values were below experimental error values. Thermodynamic properties like thermal expansion (α) and isentropic compressibility (β_s) were calculated from the speed of sound values and experimental density values. Lattice potential energy (U_{POT}) and the standard entropy (S^0) was calculated to understand the ionic interaction strength between the ions and to estimate the disorder within the fluids. Arrhenius equation was used to discuss the low values of viscosity by the help of activation energy calculations. In the end alkyl chain length effect on the anion, geometry of the cation and temperature has been studied for the properties discussed. Gonfa, *et al.,* (2015) highlighted the study of the preparation and measurement of the thermophysical properties of new cyano-based ionic liquids with thiocyanate anion and nitrile, ally, benzyl, and hydroxyl functionalized imidazolium cations. Density, viscosity, and refractive index values of the stated ionic liquids were dignified over several temperature ranges. Molecular volume, standard molar entropy, lattice energy, and thermal expansion coefficient of the ionic liquids were established from the values of density. The thermal stabilities and the special effects of functionalized imidazolium side chains on the thermophysical properties of the ionic liquids were inspected.

Tao, *et al.,* (2014) demonstrated the study of a sequence of imidazolium-based ionic liquids with varying functionalities from aliphatic to aromatic groups and a fixed anion, bis{[trifluoromethane]sulfonyl}amide. Structure–property associations were explored about the substituent effects on the imidazolium cation among n-alkyl versus cycloalkyl and aromatic versus aliphatic groups. Density, thermal transition temperatures, and decomposition temperatures were the thermophysical properties

measured. The densities values produced were in the order of n-alkyl < cycloalkyl < aromatic. All ionic liquids in the study showed a considerable weight loss at 300 °C. Shah, *et al., (2015)* examined over a diverse temperature range the thermophysical properties of imidazolium-based phenolate ionic liquids. Various alkyl groups such as ethyl, butyl, hexyl, octyl, and decyl were trussed to the 1-methylimidazolium cation to study the outcome of alkyl chain length on thermophysical properties. Density, viscosity, refractive index, heat capacity, and surface tension were calculated. The molecular volume, standard molar entropy, lattice energy, surface entropy, and surface enthalpy of the ionic liquids were estimated at 303.15 K from the measured values of density and surface tension.

Murray, *et al.,* (2013) demonstrated the study of the correlations of various models with the thermophysical properties of three lipidic ionic liquids i.e. 1-oleyl-3-methylimidazolium bistriflimide, 1-elaidyl-3-methylimidazolium bistriflimide, and 1-linoleyl-3-methyl-imidazolium bistriflimide which were measured from the temperature range of 273 K to 353 K. Molar volume and volume expansivity were also calculated. The results showed lower densities for longer chains and higher viscosities for shorter chains. Melting point was also estimated which showed difference in the melting point of three compounds but it has very less influence on the thermodynamic properties of the liquid phase. Ghanem, *et al.,* (2015) emphasized on the preparation of a sequence of new ionic liquids based on 1-octyl-3-methylimidazolium with glycinate, alaninate, serinate, prolinate, and asparaginate anions. The density, viscosity, surface tension, and heat capacity values of these new ionic liquids were dignified at several temperatures and atmospheric pressures. By using empirical methods thermal expansion coefficient values, molecular volume, standard molar entropy, and lattice energy values were also calculated. In the end, anion effect on the considered properties were studied more in different ways.

Yan, *et al.,* (2015) established a study the thermophysical properties at atmospheric pressure from 288.15 K to 318.15 K of the density, refractive index, and viscosity of the ionic liquids (Cnmim) Cl (Cnmim = 1-alkyl-3-methylimidazolium; n = 2, 4, 6, 8 for ethyl, butyl, hexyl, and binary system of octyl) + N, N-dimethylformamide. From the experimental data the molar excess Gibbs energy, excess molar volume, and apparent molar volume were calculated. The refractive index and viscosity deviations from the ideal behavior had been found and well fitted to the Redlich–Kister equation. The results obtained showed that DMF can successfully modify the physicochemical properties of 1-alkyl-3-

methylimidazolium ionic liquid according to its physiochemical property structure. Pinto, *et al.,* (2013) highlighted the importance of the ionic liquids for CO_2 capturing and reported the study of two blends of equally miscible ionic liquids that were 1-ethyl-3-methylimidazolium bis [trifluoromethanesulfonyl] imide + 1-ethyl-3-methylimidazolium ethylsulfate and 1-ethyl-3-methylimidazolium bis [trifluoromethanesulfonyl] imide + 1-butyl-3-ethylimidazolium ethylsulfate. The ability of carbon capturing at various composition ratios of these blends at 16 bar pressure and 298.2 K temperature was measured. Thermal phase-transition temperatures and thermophysical properties of density, viscosity, and surface tension at different temperatures and pressures were found. The NRTL (Non-Random Two-Liquid) model was used to correlate absorption data which was noted successful for determination of the levels of CO_2 absorption in the ionic liquid blends. Kurnia, *et al.,* (2011) discussed the measurement from temperature range of 293.15 K to 343.15 K, the thermophysical properties of density and surface tension of the ionic liquids 1-(2-aminoethyl)-3-methylimidazolium tetrafluoroborate, and 1-(3-aminopropyl)-3-methylimidazolium tetrafluoroborate. Other thermodynamic properties including volumetric properties like coefficient of thermal expansion, molecular volume, standard molar entropy, and lattice energy were estimated by the help of using investigational density data. On the other hand, surface tension was used to measure enthalpy and entropy. The molar enthalpy vaporization of the ionic liquid was calculated using the Kabo *et al* method at 298.15K. The thermal expansion coefficient was calculated which showed great amount of similarity between experimental data. Zaitsau, *et al.,* (2016) analyzed a group of imidazolium-based ionic liquids with PF6– anions which were well-thought-out to be low-cost solvents in various separation processes but on the other hand, reveal limited thermal stabilities. Measurement of vaporization thermodynamics through commonly used methods have failed. The study involved at n = 2, 4, 6, 8, and 10 and from the temperature range 403–461 K, a quartz-crystal microbalance technique to find out the absolute vapor pressures for the (Cnmim) (PF6) family. By the help of reduced total reflection-infrared spectroscopy, we determined absence of decomposition of ILs in experimental circumstances. Through enthalpy and entropy studies of the liquid and gas phases the reliability of the experimental results within the homologous series was proven.

Nazet, *et al.,* (2017) reported the study as a function of temperature, the transport property data of electrical conductivity and dynamic viscosity for non-imidazolium ionic liquids namely, [Et3S] [TFSI],

[Et2MeS] [TFSI], [BuPy] [TFSI], [N8881] [TFA], and [P14] [DCA]. At a diverse temperature range of 238.15 K to 468.15 K the electrical conductivity was calculated. On the other hand, dynamic viscosity was measured from the temperature range of 278.15 to 408.15 K. The data was fitted in the Vogel–Fulcher–Tammann equation. The results discussed from the temperature range of (278.15 to 363.15) K and (283.15 to 343.15) the densities, except for [N8881] [TFA] and refractive indices, of the above mentioned ionic liquids. The density and refractive indices values showed a linear change in temperature. The ionic liquid [P14] [DCA] was reported to be unstable. Ullah, *et al.,* (2015) highlighted the preparation of 1-hydrogen-3-methyl imidazolium hydrogen sulphate. 1-methylimidazole (0.01 moles) was charged in two neck flask connected with condenser. The apparatus was mounted on hotplate with magnetic stirrer. Equal moles (0.01 moles) were poured in the two neck flask contained 1-methylimidazole (0.01 moles). The addition was dropwise and the apparatus was cooled with magnetic stirring. The mixture was stirred for 6 hours at room temperature and was cooled for 30 minutes. The impurities were removed in a rotary evaporator by pouring the viscous liquid in it under low pressure for six hours (51). The structure of ionic liquid was found using the NMR Bruker Avance (500 MHz). The H NMR data is given as: 1H NMR spectroscopy (Bruker, 500 MHz, DMSO-*d*6) δ = 3.86 (s, 3H), 5.72 (s, 1H), 7.59 (s, 1H), 7.66 (s, 1H), 8.98 (s, 1H). The 1 H-3-methylimidazolium acetate was manufactured using the procedure stated by Qian *et al* (2012). 1-methylimidazole (0.01 moles) was defused in two neck flask with acetic acid under cooling. The stirring of the sample was employed for 6 hours under cooling at room temperature. NMR Bruker Avance (500 MHz) was used to classify the structure of the ionic liquid after the evaporation of the viscous liquid in a rotary evaporator. 1H NMR spectroscopy (Bruker, 500 MHz, DMSO-d6); δ: 7.60 (s, 1H, C2-H), 7.12 (s, 1H, C4-H), 6.90 (s, 1H, C5-H), 4.35 (s, 1H, N2-H), 3.65 (s, 3H, N3-CH3), 1.92 (s, 3H, CH3COO)

Thermophysical properties of phenolate ionic liquids

Syed, *et al.,* (2015) reported the study of thermophysical properties of imidazolium based phenolate ionic liquids over a variety of temperature range. Ethyl, butyl, hexyl, octyl, and decyl groups were reduced to 1-methylimidazolium cation to study the alkyl chain length effect on thermophysical properties. Thermal stability of these ionic liquids were studied using a thermogravimetric analyzer. Moreover, the molecular volume, standard molar entropy, lattice energy, surface entropy, and surface enthalpy were calculated with the help of density and surface tension values at 303.15 K temperature.

Lethesh, *et al.,* (2014) reported the study of the preparation of 12 ionic liquids based on 1,8-diazobicyclo [5.4.0] undec-7-ene (DBU) cation with anions of chloride, bromide, and thiocyanate. The density and viscosity from a temperature range of 293.15 K to 373.15 K were noted at atmospheric pressure and their effect on temperature was also studied. The thermal expansion values were calculated by the values of density. The entropy and enthalpy were reported from the values of surface tension at 303.15 K. The thermal properties of these ionic liquids were calculated by the help of thermogravimetric analysis.

2.7 Thermophysical properties of acetate-based ionic liquids

Hugo, *et al.*, (2012) stated that acetate based ionic liquids have great potential towards carbon dioxide capturing and bio mass reduction and hence thermophysical properties of acetate based ionic liquids are studied. Five protic and aprotic ionic liquids were studied and their density, viscosity, refractive index and surface tension values were identified. Ionic liquids used are N, N-dimethyl-N-ethylammonium acetate, 1-ethylimidazolium acetate, 1-ethyl-3-methylimidazolium acetate, 1-butyl-3-methylimidazolium acetate, and 1-butyl-1-methylpyrrolidinium acetate. Isobaric thermal expansion coefficient, the surface entropy and enthalpy, and the critical temperature were estimated due to temperature dependency of the measured thermophysical properties. Zubier, *et al.,* (2016) examined the study at a wide temperature range for the decomposition temperature, glass transition temperature, density, and viscosity of imidazolium-based ionic liquids combined with the tricyanomethanide anion and the bis [trifluoromethylsulfonyl] imide anion. The thermal stability was improved by the addition of hydroxyl functionalization in the cation's alkyl chain. It was also noted that other functionalization had no significant effect on the thermal stability. The increase in the density and a decrease in the viscosity was reported for the ether group for all ionic liquids. The hydroxyl group enhanced both properties of density and viscosity. The effect on CO_2 solubility was not noted by the presence of the ether groups. On the other hand hydroxyl group greatly decreases CO_2 solubility. The electrolyte perturbed-chain statistical associated fluid theory equation of state was used which showed promising results for the CO_2 solubility for ionic liquids and the Henry's law constant. Filipe*, et al*., (2015) described the effect on the Ionicity of 1-ethyl-3-methylimidazolium acetate by the addition of inorganic salts. Solubility of these inorganic salts on the basis of ammonium and sodium cations in the ionic liquid were determined experimentally at room temperature. Viscosity, density, conductivity, and refractive index values were calculated for different concentrations of inorganic salt in the ionic liquid and ionicity was determined. It was found in results that ammonium based inorganic salts on addition can increase the ionicity of the ionic liquid and form high ionicity ionic liquid.

Holbrey, *et al*., (2002) demonstrated the preparation of highly economical ionic liquids containing methyl and ethyl sulfate anions by reacting 1-alkylimidazoles with dimethyl sulfate and diethyl sulfate. The prepared ionic liquids were 1,3-dialkylimidazolium alkyl sulfate and 1,2,3-trialkylimidazolium alkyl sulfate. It was found that 1,3-Dialkylimidazolium salts containing at least one non-methyl N-alkyl substituent were liquid at or below room temperature and the other three salts were crystalline at room temperature and therefore, X ray structure of single crystal of 1,3-dimethylimidazolium methyl sulfate was determined which showed the structural bonding of the salt in detail. It was stated in the results that the salts can be used as alternatives for halide salts in the preparation of 1-butyl-3-methylimidazolium hexafluorophosphate via meta-thesis reaction. Results also showed that the salts were stable, water soluble, chloride-free and displayed an electrochemical window of more than 4V. Castro, *et al.,* (2010) reported that nanomaterials and common solvents have thermophysical properties which can modernize present use of heat transfer fluids and heat storage cycles. The improvements in thermal conductivity derived from the presence of additional mechanisms of heat transfer in contrast with the base solvent was studied. They found that Ionic liquids under manipulation contain thermo-physical properties which justify the replacement of several chemical processes. The performance of these nano-fluids with ionic liquids proposes that nanocluster formation and preferred paths for heat transfer and storage are present and can cause the observed phenomena, however, they admitted that the existing theories cannot yet explain the results achieved.

2.8 Conformational isomerism & configurational properties in ILs

Johannes and Cory (2010) highlighted the conformational isomerism study of 1-hexyl-3-methylimidazolium hydrogen sulfate by the help of density functional theory calculations and experimentations involving infrared absorption and Raman scattering spectroscopy. The Trans conformer for hydrogen sulfate anion was found to be good isomer in the ionic liquid. Three low energy conformations were also found for 1-hexyl-3-methlimidazolium cation that differ only in hexyl chain orientation. The IR and Raman spectroscope data was compiled and its vibrational frequency

comparison showed good relation among three conformations. Thus showed the presence of three conformations in the ionic liquid. They also indicated possible proton transfer from cation to anion from sulfuric acid vibration data. Modes appearing around 2000 cm^{-1} in the IR spectrum supported the phenomenon stated earlier. Anwar and Riyazuddeen, (2017) described the study of densities, speeds of sound and dynamic viscosities of pure ionic liquid namely 1-ethyl-3-methylimidazolium ethylsulfate. The binary and ternary mixtures of solvents of 1-butanol and methanol were measured at a temperature range from 298.15 K to 323.15 K with a temperature difference of 5 K and at a pressure of 0.1 MPa. The apparatus used was Anton Paar vibrating tube density and sound velocity meter DSA 5000M and Lovis microviscometer 2000M. The properties of excess molar volumes, isentropic compressibilities, molar isentropic compressibilities, excess molar isentropic compressibility and viscosity deviations were calculated at the same temperature from the investigational data. Pressure for [EMIM] [ES] + 1-butanol/methanol binary system was also determined. The Redlich-Kister equation was used to find excess molar volume and viscosity changes for the examined binary/ternary systems by fitting values to the equation. The differences in excess molar volume values and changes in viscosity values along with variations in composition and temperature were concluded in the results in the light of configurational effects on the mixing of ILs and solvents in reference to hydrogen bonding and ion–dipole interactions. Shekaari, *et al.,* (2015) highlighted the importance of solvation properties of aspirin according to pharmaceutical point of view in non-aqueous ionic liquid solutions. The thermodynamic properties of aspirin in acetonitrile solutions are effected by ionic liquid presence and was studied in detail. Densities, viscosities, speeds of sound, and refractive indices for aspirin system, 1-butyl-3-methylimidazolium bromide, and acetonitrile was measured at temperature from 288.15 K to 318.15 K at atmospheric pressure. The standard partial molar volumes, apparent molar isentropic compressibility, molar refractions, and viscosity B coefficients were calculated from the measured thermophysical properties. It was showed in the results that the ionic liquid acts as a structure-maker in the considered solutions by the help of calculated Hepler's constant $(\partial 2V\phi 0/\partial 2T)$ P and the transfer volumes $\Delta tV\phi 0$ showed ion–polar and polar–polar interactions as leading interfaces between aspirin and ionic liquid.

2.9 Physiochemical properties of ammonium-based ILs and role of alkyl chain length on ILs

Reddicherla, *et al.,* (2014) examined the density, ultrasonic sound velocity, refractive index and viscocity of ammonium based ionic liquids. The study comprised of diethylammonium acetate, triethylammonium acetate, diethylammonium hydrogen sulfate, triethylammonium hydrogen sulfate, trimethylammonium acetate, and trimethylammonium hydrogen sulfate ionic liquids in water and values were reported over a wide composition range at 25 °C temperature under atmospheric pressure. The deviations in isentropic compressibility, excess molar volume, deviations in refractive indices and viscosity deviations were calculated experimentally and were correlated by Redlich-Kister polynomial equation. Negative values were found for excess molar volume and isentropic compressibility factor but positive values were reported for refractive indices deviations and viscosity deviations. The result was discussed qualitatively in the form of ion dipole, ion pair interactions and hydrogen bonding between water and ionic liquid. Moreover, HyperChem 7 software was used to identify hydrogen bonding between ionic liquid and water via molecular modeling. Machanová, *et al.,* (2012) analyzed from the temperature range of 293.15 K to 363.15 K the property of density, rheology, and conductivity of a homologous sequence of ammonium-based ionic liquids N-alkyl-triethylammonium bis [(trifluoromethyl) sulfonyl] imide. The study told the effect of the cation structure which was calculated for individually studied properties. That study proved a decrease of the density and conductivity values. Whereas for the alkyl chain length on the ammonium cation, the viscosity values were found to be decreased. It was found that the ionic liquids under study were Newtonian and non-Arrhenius. It was also analyzed that how water effects the viscosity of the ionic liquids by the addition of water till both liquids got saturated at 293.15 K. The results showed by pure ionic liquid viscosity comparison with the water mixed solution disclosed an intense decrease in viscosity of ionic liquids which was noted to be up to 3 times. In the end molar volumes and thermal expansion coefficients by the help of calculated density data were tabulated as a function of temperature and of cationic configuration. On the basis of these calculated volumetric properties, Jacquemin's group contribution model had been used and verified for alkylammonium-based ionic liquids within the range of a relatively good uncertainty which was close to 0.1 %.

Seoane, *et al.,* (2012) studied the density, speed of sound, refractive index, and viscosity of the commercial ionic liquids 1-ethyl-3-methylpyridinium bis (trifluoromethylsulfonyl) imide, 1-propyl-3-methylpyridinium bis (trifluoromethylsulfonyl) imide, 1-butyl-3-methylpyridinium bis (trifluoromethylsulfonyl) imide, 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)

imide, 1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide, 1-butyl-1-methylpyrrolidinium bis (trifluoromethylsulfonyl) imide, 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate, 1-hexyl-3-methylimidazolium trifluoromethanesulfonate, 1-butyl-3-methylimidazolium dicyanamide, and 1-hexyl-3-methylimidazolium dicyanamide. The Arrhenius-like law, Vogel–Fulcher–Tamman, a modified VFT, Litovitz, and fluidity equations were used to fit to a linear equation the values of viscosity and density, speed of sound, and refractive index data. Thermal expansion coefficient values were calculated from density values. Effect of temperature on the role of the alky chain length of the cation was also studied. In the end a comparison of the experimental and literature data was made. Shekaari, *et al.,* (2011) studied numerous thermophysical property measurement at 298.15 K like densities, viscosity, electrical conductivity and refractive index of two ionic liquids namely 1-pentyl-3-methylimidazolium bromide and 1-propyl-3-methylimidazolium bromide in the existence of N, N′-bis (2-pyridylmethylidene)-1,2-diiminoethane Schiff base in N, N-dimethylformamide solutions. Standard partial molar volumes, partial molar volumes of transfer, ion association constants, limiting molar conductivities, viscosity B-coefficients, and molar refractions were calculated from the above mentioned thermophysical properties measured. With increasing BPIE concentration, the above parameters decreased. On the other hand, these parameters showed an increase with increase in the alkyl chain length of ionic liquids. It has been stated in the results that between the BPIE Schiff base and the ionic liquid there was an increase in the nonpolar–nonpolar interactions. Shekaari and Kazempour, (2012) highlighted the ionic liquid structure effect on the thermophysical properties of aqueous d-xylose solutions. Thermophysical properties like density and viscosity were dignified at 298.15 K for ternary solutions which contained d-xylose and an ionic liquid [1-hexyl-3-methylimidazolium bromide, 1-octyl-3-methylimidazolium bromide, and 1-decyl-3-methylimidazoliume bromide ([DMIm Br)] in aqueous solution. By using the Jones–Dole equation vital thermophysical properties comprising standard partial molar volumes and viscosity B-coefficients were calculated. By using Feakin's transition state theory we calculated free energy of activation per mole of solvent and solute. In the results it was concluded that all the parameters increase with increasing concentration and the alkyl chain length of the imidazolium ring of the ionic liquids.

Shekaari, *et al*., (2012) examined the ternary mixtures of N, N-salicylidenephenylenediamine Schiff base (Salophen) + ionic liquid + N, N-dimethylformamide according to their density and viscosity measured at atmospheric pressure and 298.15 K temperature. The ionic liquids used in the study were: 1-propyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium bromide, 1-pentyl-3-methylimidazolium bromide, and 1-hexyl-3-methylimidazolium bromide. The standard partial molar volumes, transfer partial molar volumes, and viscosity B-coefficients for the inspected mixtures were calculated from density and viscosity data. Decreasing trend in the calculated volumetric and viscometric constraints was reported to be caused by an increase in concentration and alkyl chain length of ionic liquid. It was stated in the results that these measured constraints were used to infer the effect of ionic liquids on the non-aqueous solutions of Salophen Schiff base and solute–solvent interfaces occurring between the numerous mechanisms.

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