Excess molar volumes

The physicochemical and thermodynamic properties of liquid mixtures have attracted much attention from both the theoretical and engineering applications point of view. Many engineering applications require quantitative data on the density of liquid mixtures. The density data of liquid mixtures are utilized to determine their excess molar volume, $V^E$. The $V^E$ data of liquid mixtures are required for the development of separation techniques and equipment, industrial applications in many engineering disciplines along with testing of theories/models of liquid mixtures. The $V^E$ can be determined directly by means of density measurements, dilatometer and continuous dilution methods which in turn are briefly described below:

1. **Density measurement method**

   This method involves the densities of pure liquids and their mixtures. The density data are measured either by conventional pycnometer or vibrating tube densimeter. In pycnometer measurements, serious errors arise due to the composition of liquid mixtures which are made outside the pycnometer. However, these errors are minimized by applying corrections for, (i) buoyancy; (ii) displacement of vapors of first component on the addition of second; and (iii) the density of the vapors in the space above the liquid. In the present studies, we have measured the density data using density and speed of sound analyzer (DSA-5000).

2. **Dilatometer method**

   Dilatometer method for measuring excess molar volumes, $V^E$ require fewer and less accurate weighing as compared to density method. In this method, liquids are kept separated by a mercury column and the level of liquid in dilatometer capillary before and after the mixing is measured by a cathetometer. The basic advantage of
this method is that the diameter of dilatometer capillary can be varied on the basis of magnitude of $V^E$ values. A minor drawback of the dilatometer method is that the pressure on the liquid before and after the mixing does not remain constant.

3. **Continuous dilution method**

In continuous dilution method, components of liquid mixtures are progressively mixed in a closed system, except for capillary, in which $V^E$ is measured by a change in mercury level. Further, only mild degassing of the liquids is required. Several researchers have\(^1\textdash{}^2^3\) have measured excess molar volumes of binary liquid mixtures using several types of pycnometer, vibrating tube densimeter and dilatometer and the same have been correlated with molecular interactions. Some of the momentous results on $V^E$ of binary mixtures (component molecules being ionic liquid or organic liquid) are discussed below:

The densities and viscosities for 1-n-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF\(_4\)] + acetonitrile or dichloromethane or 2-butanone or N,N-dimethylformamide binary mixtures have been measured as a function of composition at 298.15 K by Wang et al\(^2^4\). The excess molar volumes, $V^E$ (calculated using density data) are fitted to Redlich-Kister polynomial. It has been observed that the $V^E$ values for the studied mixtures are negative in all the ranges of compositions. The results have been discussed in terms of the ion-dipole interactions between the cations of the ionic liquid and the organic liquids. Zhang et al\(^2^5\) have measured densities and viscosities for 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF\(_4\)] + water binary mixture over the entire range of composition at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15) K. The measured data have been utilized to determine excess molar volumes, $V^E$, viscosity deviations, $\Delta\eta$. The results suggest that the densities and viscosities deviations are dependent strongly on water content. Further, it has been observed that increasing temperature causes density to decrease slightly. Heintz\(^2^6\) has reviewed on recent developments in thermodynamics and thermophysics of non-aqueous mixtures containing ionic liquids. Densities and viscosities for water + 1-butyl-3-methylimidazolium tetrafluoroborate [Emim][BF\(_4\)] mixture have been measured over the entire mole fraction range from (303.15 to 353.15) K using pycnometer andubbleohde capillary viscometer respectively by Zhou et al\(^2^7\). The measured data have been utilized to predict excess molar volumes, $V^E$, viscosity deviations, $\Delta\eta$ and fitted to Redlich-Kister equation to calculate binary
adjustable parameters and standard deviations. The $V^E$ data for studied mixtures are negative at all temperatures over whole mole fraction range.

Bhujraj and Deenadayalu\textsuperscript{28} have determined excess molar volumes, $V^E$ from densities measurements for 1-ethyl-3-methylimidazolium diethyleneglycol monomethylethersulphate [Emim] [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3$] or 1-butyl-3-methylimidazolium diethyleneglycol monomethylethersulphate [Bmim] [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3$] or 1-methyl-3-octylimidazolium diethylene glycol monomethylethersulphate [Mmim] [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3$] + methanol; [Emim] [$\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OSO}_3$] + water mixtures over entire composition at (298.15, 303.15, 313.15) K. The densities of the pure ionic liquids as well as those of their mixtures decrease with an increase in temperature and an increase in the size of the cation, and follow the order: [Emim] > [Bmim] > [Mmim]. The $V^E$ data have been discussed in terms of intermolecular interactions and packing effects. Densities, viscosities and electrical conductivities of 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF$_6$] + monoethanolamine or N,N-dimethylethanolamine mixtures have been measured as a function of composition from (288.15 to 323.15) K by Geng et al\textsuperscript{29}. The results indicate that the densities of both the binary mixtures decrease linearly with increasing temperature. Excess molar volumes, $V^E$ and viscosities deviations, $\Delta\eta$ have been obtained from experimental measurements and fitted to the Redlich-Kister equation to obtain adjustable parameters along with standard deviations. The results have been discussed in terms of molecular interactions existing in mixtures.

Mokhtarani et al\textsuperscript{30} have measured the densities and viscosities of 1-butylpyridium tetrafluoroborate or 1-octylpyridinium tetrafluoroborate + water binary mixtures at atmospheric pressure and temperatures from (283.15 to 348.15) K. From densities and viscosities data excess molar volumes, $V^E$ and viscosity deviations, $\Delta\eta$ have been estimated. While $V^E$ values are positive; $\Delta\eta$ values are negative over entire composition range. Thermodynamic parameters have been utilized to extract information about molecular interactions in mixtures. Densities of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] or 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF$_6$] + N-methyl-2-pyrroldinone (NMP) have been measured over the full range of composition at (298.15, 303.15, 308.15, 313.15) K and atmospheric pressure by Qi and Wang\textsuperscript{31}. Excess molar volumes, $V^E$ have been obtained from the experimental data and fitted to the fourth-order Redlich-Kister equation. The negative $V^E$ values indicate a more efficient
packing and/or attractive interactions in the mixed state. The experimental $V^E$ values have been used to test the applicability of the Prigogine-Flory-Patterson (PFP) theory. The PFP theory has shown good performance in predicting the $V^E$ values of [Bmim][PF$_6$] + NMP, but it has a certain deviation in predicting the $V^E$ of [Bmim][PF$_6$] + NMP mixture.

Zhou et al. have measured the densities for choline cyclohexane carboxylate or choline cyclopentane carboxylate + ethanol mixtures over the whole range of composition from (293.15 to 303.15) K. The $V^E$ values (derived from densities results) are negative over entire composition range. The $V^E$ values suggest that there is a clathrate formation among the constituent molecules in the mixtures. Densities and speeds of sound of pure styrene (STY), acetone (ACT) and dimethylsulphoxide (DMSO) and of their binary mixtures STY + ACT or DMSO have been measured as a function of composition range at (298.15, 303.15, 308.15, 308.15) K by Ali and Nabi. The excess molar volumes, $V^E$, excess intermolecular free lengths, $L^E$, deviations in isentropic compressibilities, $\Delta \kappa_s$, have been calculated from experimental data. The $V^E$ values have been estimated by using the Flory’s theory. It has been observed that theory fails to predict correctly the magnitude of $V^E$ values. Densities, viscosities, refractive indices and conductance measurements have been made for binary 1-methyl-3-pentylimidazolium hexafluorophosphate [Mip][PF$_6$] + polyethylene glycol (PEG) mixtures as a function of composition at temperatures (293.15 to 353.15) K by Wu et al. Experimental densities are utilized to calculate coefficient of isothermal expansion, $\alpha$, excess molar volumes, $V^E$. All the $V^E$ values within the tested range are negative, and continue to become increasingly negative with increasing temperature.

Alvarez et al. have measured densities and speeds of sound data for 2-hydroxy ethylammonium acetate [2-HEAA] + water or methanol or ethanol mixtures throughout entire composition range from the temperature of (288.15, 293.15, 303.15, 313.15, 323.15) K at atmospheric pressure. The experimental data have been employed to determine excess molar volumes, $V^E$, variations of the isentropic compressibility, $\Delta \kappa_s$, the apparent molar volume, $V_\phi$, isentropic apparent molar compressibility, $\phi_\kappa$, and thermal expansion coefficient, $\alpha$. The Peng-Robinson equation of state coupled with the Wong-Sandler mixing rule and COSMO-SAC
A model has been used to predict densities. Densities and refractive indices for the 2-Hydroxyethanaminium formate [HEF] or 2-Hydroxyethanaminium acetate [HEA] or 2-Hydroxyethanaminium propionate [HEP] or 2-Hydroxyethanaminium lactate [HEL] + methanol mixtures have been measured at the temperature range from (293.15 to 313.15) K and at atmospheric pressure by Kurnia et al\textsuperscript{36}. The excess molar volumes $V^E$, refractive index deviations, $\Delta n_D$ for these mixtures have been calculated from the observed data. The values of $V^E$ for the studied mixtures are negative for the entire mole fraction range and increase with temperature, whereas the values of $\Delta n_D$ are positive and also increase with temperature. Taib and Murugesan\textsuperscript{37} have measured densities and refractive indices of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] + water or monoethanolamine mixtures at temperature range (293.15 to 353.15) K and within the whole range of composition. The densities of mixtures decrease with increasing temperature. Excess molar volumes, $V^E$ have been deduced from the measured density data and fitted to Redlich-Kister equation. The magnitude of the excess volume increases with increasing temperatures which in turn might be due to attributed to the decreasing importance of hydrogen bonding effect with increasing temperature. Densities and viscosities of 1-hexyl-3-methylimidazolium tetrafluoroborate [C$_6$mim][BF$_4$] + 1-propanol binary mixtures have been measured over the whole composition range at atmospheric pressure and in the temperature range of 293.15 to 333.15 K by Kermanpour and Sharifi\textsuperscript{38}. The excess molar volumes, $V^E$, excess thermal expansion coefficients, $\alpha^E$ and isothermal coefficient of excess molar enthalpy, $\partial H^E / \partial p$ and excess viscosities, $\eta^E$ have been predicted from experimental values. The $V^E$ and $\eta^E$ are negative over the entire mole fraction range. The $V^E$ data have been analyzed in terms of Prigogine-Flory-Patterson theory. The results indicate good agreement between calculated and the experimental $V^E$ results at all temperatures. Zhu et al\textsuperscript{39} have measured densities and viscosities for 1-octyl-3-methylimidazolium tetrafluoroborate [C$_8$mim][BF$_4$]+ butanone or methyl acetate or ethyl acetate or propyl acetate or butyl acetate mixtures at 298.15K. The experimental data have been used to determine the excess molar volumes, $V^E$ and the viscosity deviations, $(\ln \eta)^E$. While $V^E$ are negative, those of $(\ln \eta)^E$ are positive in the whole concentration range. The results are discussed in terms of the ion-dipole interactions between cations of the ionic liquid and the organic molecules and the hydrogen bonding interactions between anions of the ionic liquid and the organic compounds.
Densities, speeds of sound and viscosities for tetramethyl ammonium hydroxide or tetraethyl ammonium hydroxide or tetrapropyl ammonium hydroxide or tetrabutyl ammonium hydroxide + N-methyl-2-pyrrolidone (NMP) mixtures have been measured over the full composition range as a function of temperature by Kavitha et al\textsuperscript{40}. Excess molar volumes, $V^E$, the deviations in isentropic compressibilities, $\Delta \kappa$, and viscosities, $\Delta \eta$ have been predicted using experimental data. The observed parameters have been discussed in terms of the ion-dipole, ion-pair interactions, and hydrogen bonding between ionic liquids and NMP molecules.

Solanki et al\textsuperscript{41} have measured densities, speeds of sound of 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF$_4$] + pyridine or $\alpha$- or $\beta$- or $\gamma$-picoline mixtures at (293.15, 298.15, 303.15, 308.15) K and excess molar enthalpies, $H^E$ of the same set of mixtures at 298.15K over entire mole fraction range. From these results, excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa^E$ values have been predicted. The $V^E$, $H^E$ and $\kappa^E$ values for the investigated mixtures are negative over entire composition. The analysis of $V^E$ data in terms of Graph theory suggest that while 1-ethyl-3-methylimidazolium tetrafluoroborate is characterized by electrostatic forces of attraction and exist as monomer; pyridine or $\alpha$- or $\beta$- or $\gamma$-picoline exist as associated molecular entities. Further, binary mixtures are characterized by interactions between nitrogen and fluorine atom of 1-ethyl-3-methylimidazolium tetrafluoroborate with nitrogen and carbon atoms of pyridine and isomeric picolines to form 1:1 molecular complex. The $V^E$, $H^E$ and $\kappa^E$ values predicted by Graph theory compare well with experimental values. The IR studies also lend additional support to this view point. Matkowska and Hofman\textsuperscript{42} measured densities of pure 1-butyl-3-methylimidazolium methylsulphate [C$_4$ mim][MeSO$_4$] and its mixture with methanol over the temperature (283.15 to 333.15) K and pressure ranges (0.1-35) MPa. The experimental densities for pure ionic liquid and alcohol have been correlated by the Tait equation. Excess molar volumes, $V^E$ have been obtained directly from experimental values, while isobaric expansivities, Isothermal compressibilities and related excess properties have been calculated from the correlation equation. Densities, refractive indices of ethylammonium acetate (N$_2$Ac) or propylammonium acetate (N$_3$ Ac) + water binary mixtures have been measured as a function composition at 298.15 K under atmospheric pressure by Hou et al\textsuperscript{43}. The excess molar...
volumes, $V^E$, apparent molar volumes, $V_i$, partial molar volumes, $\bar{V}_m$, and excess partial molar volumes, $\bar{V}_m^E$ of the binary mixtures have been calculated from the density data. The intermolecular interactions and structural effects have been analyzed on the basis of the measured and the derived properties.

Govinda et al.\textsuperscript{4} have measured densities, speeds of sound and viscosities for triethylammonium acetate [Et$_3$nh][CH$_3$COO] (TEAA) or triethylammonium dihydrogen phosphate [Et$_3$nh][H$_2$PO$_4$] (TEAP) or triethylammonium hydrogen sulfate [Et$_3$nh][HSO$_4$] (TEAS) + dimethylsulfoxide (DMSO) mixtures over whole range of composition at temperatures (298.15, 303.15, 308.15) K under atmospheric pressure. The excess molar volumes, $V^E$, the deviations in isentropic compressibilities, $\Delta\kappa_i$ and viscosities, $\Delta\eta$ have been calculated using experimental data. The obtained $V^E$, $\Delta\kappa_i$ and $\Delta\eta$ values have been correlated by using the Redlich–Kister polynomial equation.

Densities (293.15 to 343.15) K and viscosities (293.15 to 353.15) K of N-methyldiethanolamine (MDEA) or diethanolamine (DEA) + 1-butyl-3-methylimidazolium acetate [Bmim][acetate] mixtures have been measured over the whole range of mole fraction by Haghtalab and Shojaeian\textsuperscript{45}. From the results, excess molar volumes, $V^E$, coefficients of thermal expansions, $\alpha$, viscosities deviations, $\Delta\eta$, molar activation entropy, $\Delta S$, molar activation enthalpy, $\Delta H$ and molar activation Gibbs free energy, $\Delta G$ have been calculated. In the binary mixture of the MDEA + [Bmim][acetate], the density of the mixture reduces with decreasing concentration of the ionic liquid and for the DEA + [Bmim][acetate] mixture the density of the blend enhances to reduce the concentration of the ionic liquid. Moreover, the $V^E$ values show a positive deviation from ideality for the both binary mixtures. Vranes et al.\textsuperscript{46} have measured densities of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Bmim][NTf$_2$] + propylene carbonate (PC) over the whole composition range in the temperature range at 293.15 to 323.15 K with 5 K interval and atmospheric pressure. The excess molar volumes, $V^E$ values are positive only in the PC rich-region ($x_i \leq 0.07$). Negative values of $V^E$ in composition range $x_i > 0.07$ indicate significant interactions between [Bmim][NTf$_2$] and PC which is a consequence of hydrogen bonding. Densities for 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] + 1,4-dioxane; 1-ethyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] + 1,4-dioxane or ethylene glycol (EG) mixtures have been measured as a function of composition at 293.15, 298.15, 303.15, 313.15,
323.15, 333.15, 343.15, 353.15 K and atmospheric pressure (101 ± 2 kPa) by Ciocirlan et al. The excess molar volumes, $V^E$ have been calculated by using the measured experimental data. It has been observed that $V^E$ values are positive for the mixtures with EG and negative for both mixtures with 1,4-dioxane at all investigated temperature over whole composition range. The PFP theory has a good performance in predicting the $V^E$ of the studied binary mixtures, better for 1,4-dioxane mixtures.

The highest quality of density and excess molar volumes data of multi component liquid mixtures are required for improving the interaction parameters of the predictive models which in turn are used in process simulation packages. However, such data for ternary mixtures reported in literature in comparison to binary mixtures are limited. Some of the significant work reported on thermodynamic properties of ternary mixtures (components being ionic or organic liquids) are described below:

Nikam and Kharat et al. have measured densities and viscosities of N, N-dimethylformamide (DMF) + benzene + chlorobenzene and their corresponding binary mixtures DMF + benzene or chlorobenzene; benzene + chlorobenzene as a function of composition at (298.15, 303.15, 308.15, 313.15) K. From these data, excess molar volumes, $V^E$ and viscosity deviations, $\Delta \eta$ have been calculated. The $V^E$ and $\Delta \eta$ of the investigated ternary mixtures are negative. Several empirical equations have been used to calculate the $V^E$ and $\Delta \eta$ of ternary mixtures. Densities of trifluoroethanol + 1-propanol or 2-propanol; acetone or methanol or ethanol or 1-propanol or 2-propanol + water binary and trifluoroethanol + methanol or ethanol or 1-propanol or 2-propanol or acetone + water ternary mixtures have been measured at 298.15 K and the pressure 101 kPa have been measured by Atik et al. Excess molar volumes, $V^E$ have been computed from experimental data. The maxima in $V^E$ values of trifluoroethanol ternary mixtures changes with the polarity of the solutes, and vary between 1.082 and -1.472 cm$^3$ mol$^{-1}$. The $V^E$ values of ternary mixtures have been fitted and predicted by many empirical expressions using data for the corresponding binary mixtures. The measured and calculated values of all mixtures are in good accordance, and are theoretically and statistically satisfying. Sharma and Kumar measured excess molar volumes, $V^E$ of 1, 3-dioxolane or 1, 4-dioxane + water + formamide or di-methylformamide ternary mixtures dilatometerically over the entire composition range at 308.15 K. The resulting data have been analyzed in terms of Graph; Sanchez & Lacombe; and Flory theories. It is observed that $V^E$ values
predicted by the Graph theory compare well with their corresponding experimental values. However, $V^E$ values predicted by Sanchez & Lacombe as well as Flory theory are of same sign and order.

Densities of ethanol + water + 1-hexyl-3-methylimidazolium chloride [C$_6$ mim][Cl] ternary and ethanol or water + [C$_6$ mim][Cl] binary mixtures have been measured at 298.15 K and atmospheric pressure by Gomez et al$^{68}$. The $V^E$ values (determined from densities data) for present ternary mixtures are negative over the whole composition range. The negative $V^E$ values of ethanol or water + [C$_6$ mim][Cl] suggest that relatively few ethanol or water molecules fit into the free volume between the relatively large ions of [C$_6$ mim][Cl]. Deenadayalu et al$^{69}$ have measured densities for 1-ethyl-3-methylimidazolium diethylenglycol monomethylether sulphate [Emim][CH$_3$(OCH$_2$CH$_2$)$_2$OSO$_3$] + methanol + water ternary mixture over entire composition range at (298.15, 303.15, 313.15) K under atmospheric pressure. Excess molar volumes, $V^E$ have been evaluated from density measurements. The $V^E$ values have been found to be negative at (298.15 and 303.15) K. However, the $V^E$ values at 313.15 K become positive at higher mole fraction of ionic liquid and at a corresponding decrease in mole fraction of water. The $V^E$ data have been analyzed in term of Graph theory. It has been observed that $V^E$ values evaluated by Graph theory compare well with experimental data.

Gonzalez et al$^{70}$ have measured densities and viscosities of 1-butyl-3-methylimidazolium methylsulphate [Bmim][MeSO$_4$] + ethanol + water ternary at 298.15 K and its [Bmim][MeSO$_4$] + ethanol or water binary mixtures over the whole composition range at (298.15, 313.15, 328.15) K and 0.1 MPa. Excess molar volumes, $V^E$, and viscosity deviations, $\Delta \eta$ for the binary and ternary mixtures have been calculated from experimental results. The $V^E$ data for binary and ternary mixtures have been fitted to Redlich–Kister and Cibulka equation respectively to determine the fitting parameters and the root-mean-square deviations. The geometrical solution model has been employed to predict the $V^E$ data. Calvar et al$^{71}$ have measured densities, viscosities and refractive indices of ternary ethanol or 1-propanol + water + 1-ethyl-3-methylpyridinium ethylsulfate [Empy][ESO$_4$] mixtures at 298.15 K and atmospheric pressure. Excess molar volume, $V^E$, refractive index deviations, $\Delta n_D$ and viscosity deviations, $\Delta \eta$ have been calculated from experimental data and fitted to equations proposed by Cibulka and Singh et al. The
Cibulka equation gives the smaller deviations for the studied thermodynamic properties in both mixtures.

The densities and viscosities have been measured for methyl acetate + methanol + 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₈mim][NTf₂] ternary and its binaries at 298.15 K by Andreatta et al.⁷². From these data, excess molar volumes, \( V^E \) and viscosity changes of mixing, \( \Delta \eta \) have been estimated and well fitted with Redlick-Kister polynomials to determine the fitting parameters and the root mean square deviations. The \( V^E \) values for binary and ternary mixtures are negative over entire composition range. The negative \( V^E \) values for the studied binary mixtures are attributed to a more efficient packing and attractive interactions in mixed state as compared to pure state. Densities and viscosities for ethyl acetate or ethanol + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₄mim][NTf₂ ] binary and ethyl acetate + ethanol + [C₄mim][NTf₂] ternary mixtures have also been measured over entire mole fraction range at 298.15 K and atmospheric pressure by Andreatta et al.⁷³. Experimental data have been used to evaluate excess molar volumes, \( V^E \), viscosity changes of mixing, \( \Delta \eta \). The \( V^E \) values for ternary mixture are negative over the entire range of homogenous mixtures. The results have also been compared with experimental data for ethyl acetate + ethanol + 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide.

Kim et al.⁷⁴ have measured densities of dimethyl carbonate (DMC) + methanol or 1-ethyl-3-methylimidazolium ethyl sulfate [Emise] or 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄]; methanol + [Emise] or [Bmim][BF₄] binary and DMC + methanol + [Emise] or [Bmim][BF₄] ternary mixtures at 298.15 K. The observed data have been used to evaluate excess molar volumes, \( V^E \). The \( V^E \) values for all the investigated mixtures show negative deviation from ideal behavior over whole composition range. The magnitude of negativity of \( V^E \) for the binary mixtures follows the order: methanol + [Emise] > methanol + [Bmim][BF₄] > DMC + [Emise] > DMC + [Bmim][BF₄] > DMC + methanol. It has been observed that negativity of \( V^E \) values increases with addition of ionic liquids to the DMC + methanol mixture. Densities of ternary water + 1,2-ethanediol or 1,2-propanediol or 1,3-propanediol or 1,2-butanediol + 1-butyl-3-methylimidazolium bromide[Bmim][Br] and their water or 1,2-ethanediol or 1,2-propanediol or 1,3-propanediol or 1,2-butanediol + [Bmim][Br]; water + 1,2-ethanediol or 1,2-propanediol or 1,3-propanediol or 1,2-butanediol sub-binaries have been measured at
298.15 K by Rodrigues and Francesconi\textsuperscript{75}. The observed data have been utilized to determine excess molar volumes, $V^E$. The $V^E$ values are negative over the whole composition range for all studied mixtures. For binary and ternary mixtures, the magnitude of the minimum of the excess molar volume follows the sequence: 1,2-ethanediol < 1,3-propanediol < 1,2-butanediol < 1,2-propanediol.

Andreatta et al\textsuperscript{76} have measured densities and viscosities of ternary isopropyl acetate + isopropanol + 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonylimide [C$_4$mim][NTf$_2$] and isopropyl acetate or isopropanol + [C$_4$mim][NTf$_2$] binary mixtures at 298.15 K under atmospheric pressure. The excess molar volumes, $V^E$ and viscosity changes of mixing, $\Delta\eta$ (derived from the observed data) have been fitted to the Redlich-Kister equation to determine adjustable parameters with standard deviation. The $V^E$ values for isopropyl acetate + [C$_4$mim][NTf$_2$] binary mixtures show an S-shaped dependence on composition. Further, $V^E$ values for isopropanol + [C$_4$mim][NTf$_2$] binary mixtures and isopropyl acetate + isopropanol + [C$_4$mim][NTf$_2$] are negative over the entire range of composition. N. Deenadayalu et al\textsuperscript{77} measured densities of the ternary 1-butyl-3-methylimidazolium methyl sulfate [Bmim][MeSO$_4$] + methanol or ethanol or 1-propanol or nitromethane mixtures at 298.15 K. The experimental results have been utilized to determine excess molar volumes, $V^E$. The $V^E$ values are negative over all mole fraction range of [Bmim][MeSO$_4$] and increase with increasing mole fraction of [Bmim][MeSO$_4$]. The negative $V^E$ values suggest that the ion-dipole interactions as well as the packing effects among the alcohol, nitromethane and the [Bmim][MeSO$_4$] dominate over the dissociation of intermolecular hydrogen bonds in the alcohol and nitromethane.

The densities for methyl trioctylammonium bis(trifluoromethylsulfonylimide [Moa][Tf$_2$N] + 2-propanol or 1-butanol or 2-butanol; 1-butanol or 2-butanol + ethyl acetate binary and [Moa][Tf$_2$N] + 2-propanol or 1-butanol or 2-butanol + ethyl acetate ternary mixtures have been measured at (298.15, 303.15, and 313.15) K by Bahadur et al\textsuperscript{78}. The experimental data have been utilized to compute excess molar volumes, $V^E$ for various binary and ternary mixtures and the same have been fitted to Redlich–Kister and Cibulka equations respectively. The results have been interpreted in terms of alcohol chain length and it has been observed that $V^E$ values increase with chain length increase and decrease slightly with temperature. Virial-Based Mixing Rules have also been used to correlate the binary $V^E$ data with $V^E$ data of ternary mixtures.
Navarro et al.\textsuperscript{79} have measured densities of the water or 2-propanol + 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF₄] binary and 2-propanol + [Bmim][BF₄] ternary mixtures at 298.15 K. The measured data have been employed to determine excess molar volumes, $V^E$. While $V^E$ data for water + [Bmim][BF₄] are negative; those for 2-propanol + [Bmim][BF₄] are positive over entire mole fraction range. The sign and magnitude of $V^E$ values for ternary mixture is dictated by the relative proportion of components in mixtures. Lee and Park\textsuperscript{80} measured densities of di-isopropyl ether (DIPE) + 1-propanol or trihexyltetradecylphosphonium bis(2,4,4-trimethylpentyl)phosphinate [P₆6₆, 1₄][TMPP]; Tert-amyl methyl ether (TAME) + methanol or [P₆6₆, 1₄][TMPP]; methanol or 1-propanol + [P₆6₆, 1₄][TMPP] binary and DIPE + 1-propanol + [P₆6₆, 1₄][TMPP]; TAME + methanol + [P₆6₆, 1₄][TMPP] ternary mixtures at 298.15 K. Excess molar volumes, $V^E$ for studied mixtures have been calculated from the measured densities of pure liquids and mixtures. The $V^E$ values for all binary mixtures show negative deviations from ideal behavior. This may be caused mainly by the strong association and the attractive interaction of the alkanol and the ethers. These negative values indicate that alcohol tends to fill the interstices of the [P₆6₆, 1₄][TMPP]. The binary $V^E$ have been correlated with four- or five-parameter Redlich-Kister equation. The ternary mixtures indicate negative values for $V^E$ over all of the composition range.

Excess molar volumes $V^E$, and viscosity deviations, $\Delta \eta$, of the $N,N$-dimethylacetamide + $N$-methylformamide + propane-1,2-diol ternary and its binary $N,N$-dimethylacetamide + $N$-methylformamide or propane-1,2-diol; $N$-methylformamide + propane-1,2-diol mixtures have been obtained from the experimental densities and viscosities measurements at temperatures (293.15, 303.15, 313.15, 323.15, 333.15) K by Zarei et al.\textsuperscript{81} Negative trend have been observed for the $V^E$ values of the binary mixtures in the whole composition range except for $N$-methylformamide + propane-1,2-diol mixture in the $N$-methylformamide rich region. Also, negative $V^E$ values have been observed for the ternary mixture except a few mole fractions in accordance with their binary mixtures. The results have been explained based on the strength of specific interaction, size and shape of molecules. Bahadur and Deenadayalu\textsuperscript{82} have measured densities of 1-butyl-3-methylimidazolium methyl sulphate [Bmim][MeSO₄] + nitromethane + methanol or ethanol or 1-propanol ternary mixtures at 303.15, 308.15, 313.15 K. The excess molar volumes, $V^E$ have been calculated from the experimental densities at each temperature and are negative.
for all mole fractions of the ionic liquid. The minimum $V^E$ increase with an increase in temperature for the [Bmim][MeSO$_4$] + nitromethane + methanol or ethanol mixture and decrease for the [Bmim][MeSO$_4$] + nitromethane + 1-propanol mixture. The results have been interpreted in terms of the alcohol chain length and the intermolecular interactions. Densities, speeds of sound and heat capacities of pure 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF$_4$], aniline (A), N-methylaniline (MA), 2-methylaniline (2MA) and [Emim][BF$_4$] + 2MA + A or MA ternary and their 2MA + A or MA binary mixtures have been measured as a function of composition by Sharma et al$^{83}$ at (293.15, 298.15, 303.15, 308.15) K and atmospheric pressure. The measured data have been employed to determine excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa_S^E$ of the investigated mixtures. The $V^E$ and $\kappa_S^E$ data of the binary as well as ternary mixtures have been calculated by utilizing the topology of the constituents of mixtures (Graph theory). It has been observed that Graph theory successfully describes well the $V^E$ and $\kappa_S^E$ data of the studied binary as well as ternary ionic liquid mixtures.

Kermanpour et al$^{84}$ have measured densities and viscosities of pure 1-hexyl-3-methylimidazoliumtetrafluoroborate [Hmim][BF$_4$], 2-methyl-2-propanol and propylamine, along with binary [Hmim][BF$_4$] + 2-methyl-2-propanol; [Hmim][BF$_4$] + propylamine and 2-methyl-2-propanol + propylamine and ternary mixture of [Hmim][BF$_4$] + 2-methyl-2-propanol + propylamine at 298.15 K. Excess molar volumes, $V^E$ and viscosities deviations, $\Delta \eta$ have been determined from experimental data. The obtained $V^E$ and $\Delta \eta$ of all of the binary and ternary mixtures are negative over the entire composition range. For all of the binary mixtures, the $V^E$ have been correlated by applying Redlich–Kister equation and Prigogine–Flory–Patterson (PFP) theory, while the $\Delta \eta$ have been correlated using McAllister, Hind, and Nissan equations. Densities have been measured for ethanol (EtOH) + dimethylformamide (DMF) + tetrahydrofuran (THF) ternary and EtOH + DMF or THF; DMF + THF binary mixtures by Gianni et al$^{85}$ at 298.15 K. Excess molar volumes, $V^E$ and excess molar Gibbs energies, $G^E$ have been obtained from measured data. Negative $V^E$ are displayed by the binaries involving DMF, whereas EtOH + THF shows an S-shaped curve with very small $V^E$ values. The $V^E$ of the ternary system are negative nearly over the whole composition domain suggesting a more ordered structure in mixtures, namely that EtOH–DMF association prevails on EtOH and
DMF self-association. Taib et al\textsuperscript{86} have measured densities of 1-butyl-3-methylimidazolium tetrafluoroborate + monoethanolamine + water ternary mixtures at temperature range from (303.15 to 353.15) K. The measured data have been correlated as a function of concentration and temperature. Excess molar volumes, \( V^E \) have been deduced from the experimental data. The results have been interpreted in terms of molecular interactions operating among the constituent molecules. Mato et al\textsuperscript{87} have measured densities and excess molar enthalpies, \( H^E \) for the ternary 1,3-dichlorobenzene + benzene + 1-chlorohexane mixture at 298.15 K and atmospheric pressure using a vibrating-tube densimeter and Calvet microcalorimeter respectively. Excess molar volumes, \( V^E \) have been determined from the densities of the pure liquids and mixtures. Smooth representations have been presented and used to construct constant contours of \( V^E \) and \( H^E \) on Roozeboom diagrams. Several empirical expressions have been suggested for predicting excess properties of ternary mixtures from the experimental binary data. Densities of ethanol (EtOH) + dimethylformamide (DMF) + cyclohexane (CyH) ternary and DMF + CyH; EtOH + CyH or DMF binary mixtures have been measured at 298.15 K by Gianni et al\textsuperscript{88}. The \( V^E \) values (obtained from experimental data) are largely positive for DMF + CyH and EtOH + CyH mixtures, while slightly negative for EtOH + DMF mixture. The \( V^E \) values of the ternary mixtures are always positive except in a narrow strip in the proximity of the binary EtOH + DMF. The \( V^E \) data of the present mixtures have been qualitatively explained with a net destruction in the mixing process of hydrogen bonding in EtOH and of dipolar interactions in DMF.

**Speeds of Sound, isentropic compressibilities and excess isentropic compressibilities**

The speed of sound and its related properties like isentropic compressibilities and excess isentropic compressibilities have been extensively used to study physiochemical behavior and molecular interactions in a variety of liquid mixtures. The study of speed of sound data of liquid mixtures is important not only to design and control chemical processes in industries but also from the theoretical point of view to predict the properties and characteristic of ionic liquids or organic liquids or liquid mixtures. Researchers\textsuperscript{89-102} have, therefore, extensively measured speed of sound data of liquid mixtures to extract information regarding molecular interactions and also to
test various theories/models. Few of the significant results on speed of sound data and its derived properties for liquid mixtures are described below:

Ali et al\textsuperscript{103} have measured speeds of sound and densities of formamide (FA) + 1-butanol or 2-methyl-1-propanol or 2-methyl-2-propanol mixtures over the whole composition range at 308.15 K. From experimental data, the deviations in isentropic compressibilities, $\Delta\kappa_s$ and excess molar volumes, $V^E$ have been determined. The $\Delta\kappa_s$ and $V^E$ values are negative for all studied mixtures over full range of composition. The extent of negative deviations in $\Delta\kappa_s$ and $V^E$ indicate that the strength of interaction between FA and alcohol molecules follows the order: 1-butanol $<$ 2-methyl-1-propanol $<$ 2-methyl-2-propanol. The $V^E$ data have also been analyzed in terms of Prigogine-Flory-Patterson theory and is quite successful in predicting the trend of the dependence of $V^E$ on composition for the investigated mixtures.

Mehta et al\textsuperscript{104} have measured speeds of sound and densities for pyrrolidin-2-one + o- or m- or p-xylene or ethylbenzene binary mixtures have been measured over the entire range of composition at 303.15 K. Excess molar volumes, $V^E$ and isentropic compressibility deviations, $\Delta\kappa_s$ values have been determined from experimental data and fitted to the fourth order Redlich-Kister equation. The $V^E$ and $\Delta\kappa_s$ values are negative over whole composition range. The $V^E$ values for MeCN mixtures are more negative than MeOH mixtures. However, the $\Delta\kappa_s$ values in MeOH are more than MeCN mixtures. The results have been interpreted in terms of ion-dipole interactions and structural factors of the ionic liquids and organic liquids.

Speeds of sound and densities for binary 1-butylimidazolium hexafluorophosphate [Bmim][PF$_6$] or 1-butylimidazolium tetrafluoroborate [Bmim][BF$_4$] + methanol or acetonitrile mixtures have also been measured as
function of composition under atmospheric pressure at (298.15, 303.15, 308.15, 313.15, 318.15) K by Moattar and Shekaari\textsuperscript{106}. The data have been used to calculate excess molar volume, $V^E$, isentropic compressibility, $\kappa_s$ and excess isentropic compressibility, $\kappa_s^E$. The $V^E$ and $\kappa_s^E$ data have been described well by of Prigogine-Flory-Patterson theory. Gonzalez et al\textsuperscript{107} have measured speeds of sound and densities of 1-ethyl-3-methylimidazolium ethyl sulfate [Emise] with methanol or 1-propanol or 2-propanol mixtures at (298.15, 313.15, 328.15) K and 0.1MPa over the entire range of composition. Excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa_s^E$ have been computed from measured results. The negative $V^E$ values indicate ion-dipole interactions and packing between alcohols and ionic liquid in mixed state.

Speeds of sound and densities of 1-methyl-3-octylimidazolium hexafluorophosphate [Omm][PF$_6$] + hexane or heptane or 2-propanol binary mixtures have been measured at (298.15, 298.15, 303.15) K by Pereiro and Rodriguez\textsuperscript{108}. The experimental data have been utilized to predict excess molar volumes, $V^E$, isentropic compressibilities, $\kappa_s$ and deviations in isentropic compressibilities, $\Delta\kappa_s$. The analysis of $V^E$ and $\Delta\kappa_s$ suggest that interactions between [Omm][PF$_6$] and hexane or heptane or 2-propanol mixtures components are stronger as compared to their pure components.

Speeds of sound and densities for 1-propyl-3-methylimidazolium bromide [C$_3$mim][Br] + acetonitrile (MeCN) or dimethylformamide (DMF) or dimethylsulphoxide (DMSO) binary mixtures have been measured in the dilute concentration region at (288.15, 293.15, 298.15, 303.15, 308.15) K by Sadeghi et al\textsuperscript{109}. From experimental data, isentropic compressibilities, $\kappa_s$, excess molar volumes, $V^E$ and isentropic compressibilities deviations, $\Delta\kappa_s$ have been determined. The $V^E$ and $\Delta\kappa_s$ data are negative and become more negative as the temperature or concentration of ionic liquid increases. The magnitude of $V^E$ and $\Delta\kappa_s$ values follows the order: [C$_3$mim][Br] + DMSO > [C$_3$mim][Br] + DMF > [C$_3$mim][Br] + MeCN, which indicates stronger ion-dipole interactions and packing effects in MeCN mixtures as compared to DMF and DMSO mixtures. Yadav et al\textsuperscript{110} measured speeds of sound, $u$, excess molar volumes, $V^E$ and excess molar enthalpies, $H^E$ of pyrrolidin-2-one (2-Py) + ethanol or propan-1-ol or propan-2-ol or butan-1-ol mixtures at 308.15 K over entire composition range. Excess isentropic compressibilities, $\kappa_s^E$ have been predicted from $u$ data. The $\kappa_s^E$ values for 2-Py + ethanol or propan-1-ol or propan-2-ol are negative.
over entire composition range and sign of $\kappa_s^E$ for 2-Py + butan-1-ol mixture is dictated by relative proportion of 2-Py. The $V^E$ data for studied mixtures are negative; $H^E$ data are positive over whole range of composition. The various excess thermodynamic properties have been analyzed in term of Graph theory. It has been observed that $V^E$, $\kappa_s^E$ and $H^E$ values calculated by Graph theory compare well with their experimental values. Mardones et al.\textsuperscript{111} have measured speeds of sound and densities for 1-butylpyridinium tetrafluoroborate [Bpy][BF$_4$] + methanol or ethanol mixtures at (293.15, 303.15, 313.15, 323.15) K. The experimental values are employed to determine excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa_s^E$. A detailed analysis and interpretation of results have been carried out in structural and energetic terms using thermodynamic excess functions.

Speeds of sound and densities of N, N-dimethylformamide (DMF) + diethylammonium acetate ([Et$_2$NH][CH$_3$COO], DEAA) or triethylammonium acetate ([Et$_3$NH][CH$_3$COO], TEAA) or triethylammonium dihydrogen phosphate ([Et$_3$NH][H$_2$PO$_4$], TEAP) or triethylammonium sulfate ([Et$_3$NH][HSO$_4$], TEAS) or 1-benzyl-3-methylimidazolium chloride ([Bmim][Cl]) have been measured over the whole composition range at 298.15 K under atmospheric pressure by Attri et al.\textsuperscript{112}. Excess molar volumes, $V^E$ and deviations in isentropic compressibilities, $\Delta \kappa_s$ have been predicted using these properties as a function of the concentration of ionic liquid (IL). The measured and the derived properties have been discussed in terms of the ion–dipole, ion-pair interactions, and hydrogen bonding between ILs and DMF molecules and their structural factors. Pal and Kumar\textsuperscript{113} measured speeds of sound and densities for 1-butyl-3-methylimidazolium hexafluorophosphate [Bmim][PF$_6$] + ethylene glycol monoethyl ether [EGMEE] or diethylene glycol monoethyl ether [Di-EGMEE] or triethylene glycol monoethyl ether [Tri-EGMEE] as a function of composition at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K. Experimental data have been utilized to estimate excess molar volumes, $V^E$ and isentropic compressibilities deviation, $\Delta \kappa_s$. The $V^E$ values are negative and become more negative with the addition of an –OC$_2$H$_4$ group at the middle of EGMEE and are in order: EGMEE > Di-EGMEE > Tri-EGMEE. The $\Delta \kappa_s$ values are also negative for all mixtures over the whole composition range and become more negative in the order: Tri-EGMEE > Di-EGMEE > EGMEE.
Speeds of sound and densities for 2-hydroxy ethylammonium acetate (2-HEAA) + water or methanol or ethanol mixtures throughout the concentration range at (288.15 to 323.15) K and atmospheric pressure have been measured by Alvarez et al.\textsuperscript{114} The excess molar volumes, $V^E$, variations of the isentropic compressibilities, $\Delta \kappa_s$, the apparent molar volumes, $\phi_v$, isentropic apparent molar compressibilities, $\phi_{s}^{\kappa}$ and thermal expansion coefficients, $\alpha$ have been obtained from the experimental data. The $V^E$ values are negative over the whole composition range. The NMR and X-ray Scattering studies suggest the presence of micelles form due to ion pair interactions above a critical concentration of ionic liquid in the mixtures. Vercher et al.\textsuperscript{115} measured speeds of sound and densities of 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [Emim][Triflate] + 2-propanol or tetrahydrofuran mixtures over entire range of composition at (278.15, 288.15, 298.15, 308.15, 318.15, 328.15) K and pressure (101±2) kPa. From these experimental data, excess molar volumes, $V^E$, excess speeds of sound, $u^E$, isentropic compressibilities, $\kappa_s$ and excess isentropic compressibilities, $\kappa_s^E$ have been calculated. The density and speed of sound of all the mixtures increases with increase in mole fraction of [Emim][Triflate] and decreases with increasing temperature, $T$, while $\kappa_s$ decreases with $x_i$ and increases with temperature. The $V^E$ and $\kappa_s^E$ data have also been analyzed in terms of Prigogine-Flory-Patterson theory.

Speeds of sound and densities for methanol or ethanol or 1-propanol or 2-propanol or acetone or acetonitrile or dichloromethane + 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide [Hmim][NTf$_2$] binary mixtures have been measured over whole composition range at (288.15, 293.15, 298.15, 313.15, 328.15) K and 0.1MPa by Gonzalez et al.\textsuperscript{116} Excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa_s^E$ have been calculated from the experimental results. A sinusoidal of behavior $V^E$ is observed for methanol or ethanol or 1-propanol or 2-propanol + [Hmim][NTf$_2$] mixtures. However, $V^E$ values are negative in the whole composition range for acetone or acetonitrile or dichloromethane + [Hmim][NTf$_2$] mixtures. The $V^E$ values for the binary mixtures containing protic POCs (alcohols) are closer to ideality than those obtained for the mixtures containing aprotic POCs (acetone, acetonitrile, dichloromethane). For all studied mixtures $\kappa_s^E$
values are negative over entire range of composition and suggest that these mixtures are less compressible than the corresponding ideal mixtures due to a closer approach of unlike molecules and stronger interactions between components of mixtures. Pal et al\textsuperscript{117} have measured speeds of sound and densities for 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF\textsubscript{4}] + ethylene glycol monoethyl ether [EGMEE] or diethylene glycol monoethyl ether [Di-EGMEE] or triethylene glycol monoethyl ether [Tri-EGMEE] mixtures over the complete range of composition at (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K. The results have been utilized to calculate excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa^E_s$. The $V^E$ and $\kappa^E_s$ values are negative for all mixtures and decrease in sequence: EGMME < di-EGMME < tri-EGMME. The $V^E$ and $\kappa^E_s$ values decreases with an increase in temperature. Further, the more negative $V^E$ and $\kappa^E_s$ values suggest that the interactions between the unlike molecules are strong and increase with the introduction of the $–\text{OC}_2\text{H}_4$ group in the alkoxyethanol.

Speeds of sound and densities for 1-butyl-3-methylpyridium tetrafluoroborate [B\textsubscript{3}mpy][BF\textsubscript{4}] or 1-butyl-4-methylpyridium tetrafluoroborate [B\textsubscript{4}mpy][BF\textsubscript{4}] + methanol or ethanol mixtures have been measured as a function of composition at (298.15, 303.15, 313.15, 323.15) K by Mardones et al\textsuperscript{118}. The $V^E$ and $\kappa^E_s$ values (calculated from the measured data) are negative and minima are shifted toward rich composition in alkanol. Kavitha et al\textsuperscript{119} have measured speeds of sound and densities of trimethylammonium acetate [((CH\textsubscript{3})\textsubscript{3}NH)[CH\textsubscript{3}COO] (TMAA) or trimethylammonium hydrogen sulphate [((CH\textsubscript{3})\textsubscript{3}NH)[HSO\textsubscript{4}] (TMAS) or trimethylammonium dihydrogen phosphate [((CH\textsubscript{3})\textsubscript{3}NH)[H\textsubscript{2}PO\textsubscript{4}] (TMAP) or triethylammonium dihydrogen phosphate [((CH\textsubscript{3}CH\textsubscript{2})\textsubscript{3}NH)[H\textsubscript{2}PO\textsubscript{4}] (TEAP) + N-methyl-2-pyrrolidone (NMP) mixtures over entire concentration range and at (298.15, 303.15, 308.15, 313.15, 318.15) K under ambient pressure. Excess molar volumes, $V^E$ and isentropic compressibility deviations, $\Delta\kappa_s$ have been obtained for from experimental data. A qualitative analysis of molecular interactions between ionic liquids and NMP is discussed in terms of the ion-dipole, ion-pair interactions, and hydrogen bonding. Gonzalez et al\textsuperscript{120} measured speeds of sound and densities for 1-propanol or 2-propanol or 1-butanol + 1-butyl-1-methylpyrrolidinium dicyanamide [Bmpyr][DCA] mixtures over the whole composition range at (298.15, 313.15,
Experimental data have been employed to determine excess molar volumes, \( V^E \) and excess isentropic compressibilities, \( \kappa_S^E \). The excess properties have been fitted to Redlich-Kister equation to compute adjustable parameters and standard deviations. The negative \( V^E \) and \( \kappa_S^E \) values have been attributed to strong interaction between the alcohols and [Bmpyr][DCA].

Speeds of sound and densities of binary 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF_4] + aniline (A) or N-methylaniline (MA) or 2-methylaniline (2MA) mixtures at 293.15, 298.15, 303.15, 308.15 and excess molar enthalpies, \( H^E \) of same set of mixtures at 298.15 K have been measured over entire mole fraction range by Sharma and Solanki\(^{121}\). Excess molar volumes, \( V^E \) and excess isentropic compressibilities, \( \kappa_S^E \) have been calculated by utilizing the measured experimental data. The Graph theory has been applied to predict (i) state of components of mixture in pure and mixed state; (ii) nature and extent of mixtures existing in the mixtures; and (iii) \( V^E, \kappa_S^E \) and \( H^E \) values. The analysis of \( V^E \) data in terms of Graph theory suggests that [Emim][BF_4] is characterized by electrostatic forces of attraction and exists as monomer, whereas A, MA, 2MA exists as associated molecular entities. Further, these mixtures are characterized by interactions between nitrogen and fluorine atoms of [Emim][BF_4] with nitrogen and hydrogen atoms of A or MA or 2MA to form 1:1 molecular complex. The IR studies also support this view point. Results indicate that \( V^E, \kappa_S^E \) and \( H^E \) values obtained by Graph theory are in good agreement with experimental data. Speeds of sound and densities have been measured for the binary ethanol or 1-propanol or 2-propanol + 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonylimide) [Bmpyr][NTf_2] or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonylimide) [Bmpyr][NTf_2] mixtures by Gonzalez et al\(^{122}\) over entire range of composition at (298.15, 303.15, 308.15) K and atmospheric pressure. The observed data have been used to determine the corresponding excess isentropic compressibilities, \( \kappa_S^E \) and excess molar volumes, \( V^E \). The \( V^E \) values change from negative to positive as the alcohol’s alkyl-chain length increases, while \( \kappa_S^E \) values are negative over whole composition range. The shapes of the \( V^E \) and \( \kappa_S^E \) curves for the mixtures containing [Bmpyr][NTf_2] and [Bmpyr][NTf_2] are quite similar showing that nature of the cation does not seem to have a large effect on the values of these excess
properties. Yameeka et al. measured speeds of sound, excess molar volumes, $V^E$ and excess molar enthalpies, $H^E$ for 1-methyl pyrrolidin-2-one (NMP) + water or propan-1-ol or propan-1-ol mixtures over entire range of composition at 308.15 K using interferometer, dilatometer and 2-drop micro calorimeter respectively. Speeds of sound have been used to calculate excess isentropic compressibilities, $\kappa_S^E$. The $V^E$ and $\kappa_S^E$ values for these mixtures suggest that water or propan-1-ol gives relatively more closed packed structure as compared to propan-2-ol in NMP. The observed $V^E$, $\kappa_S^E$ and $H^E$ values have been analyzed in terms of (i) Graph and (ii) Prigogine-Flory-Patterson theories. Results indicate that $V^E$, $\kappa_S^E$ and $H^E$ values predicted by Graph theory compare well with their corresponding experimental values. Speeds of sound and densities of 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide [Pmpyr][NTf$_2$] + methanol or ethanol or 1-propanol mixtures have been measured over whole composition range at (298.15, 303.15 and 308.15) K by Gonzalez et al. Excess molar volumes, $V^E$ and excess isentropic compressibilities, $\kappa_S^E$ have been determined from experimental data. The $V^E$ shows sinusoidal behavior while $\kappa_S^E$ values are negative over the entire range of composition. The $V^E$ and $\kappa_S^E$ values become more negative when the temperature increases. Chaudhary et al. have measured speeds of sound and densities of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF$_4$] + water mixtures over the whole composition range at different temperatures (293.15 - 323.15) K with 5 K interval. The excess isentropic compressibilities, $\kappa_S^E$ and excess molar volumes, $V^E$ values (derived from experimental data) are positive over entire composition range at all studied temperatures. The positive $\kappa_S^E$ values suggest the disruption of ion-pair interactions of [Bmim][BF$_4$] and the hydrogen-bonding network of water. The NMR and IR studies confirm the disruption of ion pair interactions of [Bmim][BF$_4$] and the hydrogen-bonded network of water in the aqueous mixture of [Bmim][BF$_4$]. Speeds of sound and densities for 1-hexyl-3-methylimidazolium tetrafluoroborate [C$_6$mim][BF$_4$] or 1-octyl-3-methylimidazolium tetrafluoroborate [C$_8$mim][BF$_4$] + butylamine (BA) or octylamine (OA) mixtures have been measured by over entire mole fraction at 298.15, 308.15, 318.15 K Malek et al. Excess isentropic compressibilities, $\kappa_S^E$ and excess molar volumes, $V^E$ have been determined from experimental data. The $\kappa_S^E$ and $V^E$ of
the binary mixtures are negative over range of composition and decreases with increasing temperature, except \( V^E \) for the \([\text{C}_8\text{mim}][\text{BF}_4] + \text{OA}\) and \([\text{C}_6\text{mim}][\text{BF}_4] + \text{OA}\) mixtures, which changes the sign from negative to positive at higher composition of the ILs. The Prigogine-Flory-Patterson (PFP) theory has been applied to interpret the \( V^E \) data.

Limited data on speeds of sound data and its derived properties for ternary mixtures have been reported in the literature\(^{127-138}\). Speeds of sound of the benzene + acetone + chloroform ternary and the binary benzene + acetone + chloroform and acetone + chloroform mixtures have been measured at 298.15 K and atmospheric pressure by Savaroglu and Aral\(^{139}\). Isentropic compressibilities, \( \kappa_s \), deviations in speeds of sound, \( \Delta u \) and isentropic compressibilities, \( \Delta \kappa_s \) for both the binary and ternary mixtures have been calculated from experimental data. The speed of sound \( u \) and \( \kappa_s \) values have been compared with calculated values from Free Length Theory (FLT), Collision Factor Theory (CFT), Nomoto's relation (NR), Junjie's relation (JR) and Van Deal's Ideal Mixing relation (IMR). The \( \Delta u \) and \( \Delta \kappa_s \) data have been fitted to the Redlich-Kister equation in the case of binary mixtures, while the equation of Cibulka has been used to fit the values related to the ternary mixture. Savaroglu and Aral\(^{140}\) have also measured speeds of sound and densities of 2-propanol + acetone + cyclohexane ternary and the corresponding binaries 2-propanol + acetone or acetone + cyclohexane; acetone + cyclohexane at 298.15, 313.15 K. The isentropic compressibilities, \( \kappa_s \), speed of sound deviations, \( \Delta u \) and changes of isentropic compressibilities, \( \Delta \kappa_s \) have been evaluated from experimental data. The speed of sound and \( \kappa_s \) values have been compared with calculated values from free length theory (FLT), collision factor theory (CFT), Namoto’s relation (NR), Van Deal’s ideal mixing relation (IMR) and Junjie’s relation (JR). Speeds of sound of pyrrolidin-2-one + N-methyl pyrrolidin-2-one + water ternary and its sub-binary mixtures have been measured at 298.15 K by Alcalde et al\(^{141}\). From these experimental data, excess isentropic compressibilities, \( \kappa^E \) and excess internal pressure, \( \pi^E \) have been evaluated and the same have been analyzed in terms structural effects and ternary interactions. The investigated properties support the formation of strong hydrogen bond between water and the cyclic amides. The observed weakening of hydrogen bond in the ternary
mixtures compared with the binary constituents reveals that no significance ternary net interactions are present in the mixture.

Calvar et al\textsuperscript{142} measured speeds of sound and densities of the ternary ethanol + water + 1-butyl-3-methylimidazolium chloride [C\textsubscript{4}mim][Cl] and its binaries ethanol or water + [C\textsubscript{4}mim][Cl] over complete composition range at 298.15K and 0.1 MPa. Isentropic compressibilities, $\kappa_s$ have been calculated (using Laplace equation) from measured data. The $\kappa_s$ data for the studied ternary mixture are positive over entire composition range. Calvar et al\textsuperscript{143} have also measured speeds of sound and densities of ternary ethanol + water + 1-octyl-3-methylimidazolium chloride [C\textsubscript{8}mim][Cl] or 1-ethyl-3-methylimidazolium ethylsulfate [Emise] mixtures 298.15 K and atmospheric pressure. Experimental values have been utilized to calculate excess molar volumes, $V^E$, isentropic compressibilities, $\kappa_s$, molar isentropic compressibilities, $\kappa_{s_m}$, isentropic compressibilities deviations, $\Delta\kappa_s$ and excess isentropic compressibilities, $\kappa_s^E$. The derived excess properties have been fitted to Cibulka and Singh et al equations. Speeds of sound and excess molar volumes, $V^E$ of $\alpha$-toluidine (OT) + toluene + $\alpha$- or p-xylene ternary mixtures and speeds of sound of OT + toluene or $\alpha$- or p-xylene binary mixtures have been measured as a function of composition at 308.15 K by Dimple et al\textsuperscript{144}. Speeds of sound data have been utilized to evaluate excess isentropic compressibilities, $\kappa_s^E$ for binary and ternary mixtures. The $\kappa_s^E$ and $V^E$ data have been fitted to the Redlich-Kister equation to calculate ternary adjustable parameters and standard deviations. The $\kappa_s^E$ and $V^E$ values for OT + toluene + $\alpha$-xylene ternary mixtures are positive over the entire composition range. However, for OT + toluene + p-xylene ternary mixture $\kappa_s^E$ and $V^E$ values change sign from positive to negative with an increase in mole fraction of OT. Flory theory for binary mixtures has been extended to predict $\kappa_s^E$ and $V^E$ for the studied ternary mixtures. It has been observed that theory correctly predicts the sign of $V^E$ values for OT + toluene + $\alpha$-xylene and $\kappa_s^E$ values for OT + toluene + p-xylene ternary mixtures.

Davila et al\textsuperscript{145} have measured densities, speeds of sound and heat capacities, for 2-pyrrolidone (PYR) + methanol (M); N-methyl-2-pyrrolidone (NMP) + M; N-cyclohexyl-2-pyrrolidone (CHP) + M; PYR + NMP; PYR + CHP; NMP + CHP binary and PYR + NMP + M; PYR + CHP + M; CHP + NMP + M ternary mixtures at 298.15 K and 0.1 MPa. Excess molar volumes, isentropic compressibilities, excess
isentropic compressibilities, and excess heat capacities have been evaluated from the
experimental data. The results suggest formation of hydrogen bonding and dipolar
interactions between cyclic amides and methanol which become weaker on the
addition of third component. Further, ternary mixtures show strong deviation from
ideality because of the existence of strong hetero association competing with homo
association through hydrogen bonding. Speeds of sound and excess molar volumes,
$V^E$ of 2-pyrrolidinone (2-Py) + benzene + toluene or o- or p- xylene ternary mixtures
have been measured as a function of composition at 308.15 K by Yadav et al\textsuperscript{146}. The
speed of sound data have been used to determine excess isentropic compressibilities,
$\kappa^E_s$. The $V^E$ and $\kappa^E_s$ values for the investigated binary mixtures are negative over
entire range of mole fractions. More negative $V^E$ and $\kappa^E_s$ values for 2-Py + benzene +
toluene mixtures than those for 2-Py + benzene + o- or p-xylene mixtures suggest that
toluene gives relatively more packed structure as compared to o- or p-xylene in 2-
Py:benzene molecular entity. Syamala et al\textsuperscript{147} measured speeds of sound and
viscosities of dimethylsulphoxide + 1,2-dichlorobenzene + 1-propanol or 1-butanol or
1-pentanol or 1-hexanol or 1-heptanol or 1-octanol mixtures at 303.15 K. Isentropic
compressibilities, $\kappa_s$, deviation in viscosities, $\Delta\eta$ have been determined from
experimental data. The various parameters have been discussed to explain the nature
of intermolecular interactions. Speeds of sound and excess molar volumes, $V^E$ of 2-
pyrrolidin-2-one + toluene + o- or p-xylene mixtures have been measured by Yadav et
al\textsuperscript{148} by using dilatometer and interferometer over the whole composition range at
308.15 K. The $V^E$ and $\kappa^E_s$ values (determined from speed of sound data) have been
fitted to Redlich-Kister equation to predict ternary adjustable parameters and standard
deviations. The $V^E$ and $\kappa^E_s$ data have been analyzed in terms of Flory; and Sanchez &
Lacombe theories. The Flory theory correctly predicts the sign of $V^E$ and $\kappa^E_s$ values.

Chhikara et al\textsuperscript{149} measured speeds of sound, densities and excess molar
volumes, $V^E$ for 1-methyl pyrrolidin-2-one + benzene or methyl benzene or
cyclohexane + proan-2-ol mixtures over entire composition range at 308.15 and
atmospheric pressure. The resulting data have been utilized to evaluate excess isentropic compressibilities, $\kappa^E_s$ of the investigated ternary mixtures. The $V^E$ and $\kappa^E_s$
data have been analyzed in terms of Graph theory. Experimental $V^E$ and $\kappa^E_s$ values are
in good agreement with the values determined from Graph theory. Speeds of sound, densities and viscosities have been measured for tetrahydrofuran + methanol + benzene or toluene or chlorobenzene or nitrobenzene or anisole or cyclohexane or cyclohexanone mixtures at 298.15 K by Pradhan and Roy\textsuperscript{150}. From the experimental values, excess isentropic compressibilities, $\kappa^e_S$, excess molar volumes, $V^e$, viscosities deviations, $\Delta \eta$ and Gibb's free energy of activation, $\Delta G^E$ have also been calculated. The results have been discussed and interpreted in terms of molecular package and specific interactions predominated by hydrogen bonding. Sastry et al\textsuperscript{151} have measured speeds of sound and densities for ternary methyl methacrylate (MMA) + 1-butanol or 1-pentanol or 1-heptanol + benzene or toluene or p-xylene or ethylbenzene or cyclohexane mixtures across the mole fraction range at 298.15 and 308.15 K. The experimental data have been utilized to determine excess isentropic compressibilities, $\kappa^e_S$ and excess molar volumes, $V^e$ and the same have been compared with the values calculated using similar data for the binary pairs through Redlich-Kister, Tsao and Smith, and Kohler equations. As compared to others, the Redlich-Kister equation predict the $\kappa^e_S$ and $V^e$ adequately.

Blanco et al\textsuperscript{152} measured speeds of sound and densities of ternary N-methyl-2-pyrrolidinone (NMP) + water + ethanol mixture over the entire mole fraction range at (293.15, 303.15, 313.15, 323.15) K. Excess molar volumes, $V^e$, isentropic compressibilities, $\kappa_S$ and excess isentropic compressibilities, $\kappa^e_S$ have been determined by utilizing the experimental data. The density and speed of sound values increase when the NMP and water concentration increases in the mixtures. The negative $V^e$ and $\kappa^e_S$ values suggests hydrogen bonding among the constituents molecules. Speeds of sound and densities of N-methyl-2-pyrrolidinone (NMP) + ethanolamine (MEA) + water ternary mixture have also been measured at the different values of temperature (293.15, 303.15, 313.15, 323.15) K and $10^5$ Pa by Blanco et al\textsuperscript{153}. From the experimental data, isentropic compressibilities, $\kappa_S$, isentropic compressibilities deviations, $\Delta \kappa_S$, excess isentropic compressibilities, $\kappa^e_S$ and excess molar volumes, $V^e$ have been computed. Negative $V^e$ values suggest that the present ternary mixture show a more compact structure than in pure state, mainly due to the hydrogen bonding between NMP and water molecules. Roy et al\textsuperscript{154} have measured speeds of sound and densities for the tetrahydrofuran (THF) + 1,3-dioxolane + formic
acid or acetic acid or propionic acid or butyric acid ternary and THF or 1,3-dioxolne + formic acid or acetic acid or propionic acid or butyric acid; THF + 1,3-dioxolne binary mixtures at 298.15 K under atmospheric pressure. Deviations in isentropic compressibilities, \( \Delta \kappa_s \) and excess molar volumes, \( V^E \) have been calculated from the measured experimental data. The derived properties of the binary and ternary mixtures have been fitted to Redlich-Kister and Cibulka equations, respectively. Speeds of sound and densities have been measured for the ternary morpholine + cyclohexanone + isoamyl alcohol mixture at 308.15 and 318.15 K by Venis and Kumar\textsuperscript{155}. Using experimental data, isentropic compressibilities, \( \kappa_s \) and excess molar volumes, \( V^E \) have been computed. The deviations of the liquid mixture from ideality have been explained based on the molecular interactions between unlike molecules. Hooda et al\textsuperscript{156} have measured speeds of sound and densities of ternary o-toluidine (OT) + tetrahydropyran (THP) + pyridine (Py) or benzene or toluene mixtures over entire mole fraction of OT and THP at 298.15, 303.15 and 308.15 K. The excess isentropic compressibilities, \( \kappa_s^E \) and excess molar volumes, \( V^E \) values are negative for all the mixtures over entire composition range. The \( \kappa_s^E \) and \( V^E \) values have been analyzed in terms of Graph theory. It has been observed that Graph theory correctly predicts the sign as well as magnitude of \( \kappa_s^E \) and \( V^E \) values of the investigated mixtures. Speeds of sound, \( u \) and densities, \( \rho \) of monoethanolamine (MEA) + water + N-ethyl-2-pyrrolidone (NEP) for NEP mass fraction lower than 0.3 have been measured by Abuin et al\textsuperscript{157} at (293.15, 303.15, 313.15, 323.15) K and atmospheric pressure. Isentropic compressibilities, \( \kappa_s^E \) and excess molar volumes, \( V^E \) have been calculated from \( u \) and \( \rho \) values. The \( V^E \) shows almost entirely negative values which indicate a deviation with regard to ideality and also a possible interaction between different molecules.

Sharma et al\textsuperscript{158} have measured speeds of sound and densities of 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF\textsubscript{4}] + 2-methylaniline (2MA) + pyridine or \( \alpha \)- or \( \beta \)- or \( \gamma \)-picoline ternary mixtures at 293.15, 298.15, 303.15, 308.15 K. The measured data have been employed to determine excess isentropic compressibilities, \( \kappa_s^E \) and excess molar volumes, \( V^E \). The \( \kappa_s^E \) and \( V^E \) have been fitted to Redlich-Kister equation to calculate ternary adjustable parameters and standard
deviations. The $\kappa^E_S$ and $V^E$ have been analyzed in terms of Graph and Prigogine-Flory-Patterson theories. It has been observed that Graph theory describes well $\kappa^E_S$ and $V^E$ data of the studied ternary ionic liquid mixtures. However, PFP theory correctly predicts the sign of $\kappa^E_S$ and $V^E$ data of the studied mixtures. Speeds of sound and densities of 1-methylpyrrolidin-2-one (NMP) + pyrrolidin-2-one (2-Py) + $o$- or $m$- or $p$-chlorotoluene ternary and NMP + 2-Py; NMP or 2-Py (i) + $o$- or $m$- or $p$-chlorotoluene (j) binary mixtures have been measured at 293.15, 298.15, 303.15, 308.15 K and atmospheric pressure by Sharma et al\textsuperscript{159}. From the experimental data, excess isentropic compressibilities, $\kappa^E_S$ and excess molar volumes, $V^E$, of binary and ternary mixtures have been computed. Excess properties of the various binary and ternary mixtures have been related to Redlich-Kister equation and the binary and ternary parameters along with corresponding standard deviations have been calculated. The results have also been analyzed in terms of Graph theory. It has been observed that $\kappa^E_S$ and $V^E$ values predicted by Graph theory compare well with their experimental values. The IR studies also lend support to the proposed molecular entities and interactions in mixtures.

**Excess molar enthalpies**

The excess molar enthalpy, $H^E$ of liquid mixtures is an important basic property used in chemical engineering designs. The $H^E$ data of liquid mixtures are utilized in understanding the interactions and structure of liquid mixtures in addition to the development of industrial processes. The measurements, correlations and the theoretical calculations of the excess molar enthalpy are the subject of active research\textsuperscript{160-177}. Some significant results are discussed below:

Comelli et al\textsuperscript{178} have measured excess molar enthalpies, $H^E$ of dimethyl sulphoxide (DMSO) + ethylene glycol (EG) or propylene glycol (PPG) or diethylene glycol (DEG) or tetraethylene glycol (TEG) or tetraethylene glycol (TETG) or poly(ethylene glycol)-200 (PEG-200) or poly(ethylene glycol)-300 (PEG-300) or poly(ethylene glycol)-400 (PEG-400) or poly(ethylene glycol)-600 (PEG-600) mixtures as a function of composition at 308.15 K and atmospheric pressure. The $H^E$ values for all investigated mixtures are negative over whole mole fraction range and at equimolar composition vary in order: PPG $>$ EG; DEG $>$ TEG $>$ TETG; PEG-200 $>$ PEG-300 $>$ PEG-400 $>$ PEG-600. The dependence of $H^E$ values on mixture
composition is qualitatively discussed in terms of molecular interactions. Rebelo et al\textsuperscript{179} have measured excess molar enthalpies, heat capacities and excess molar volumes (derived from densities data) of 1-butyl-3-methylimidazolium tetrafluoroborate [C\textsubscript{4}mim][BF\textsubscript{4}] + water mixture over whole composition range as a function of composition from (278.15 to 333.15) K at atmospheric pressure. The $H^E$ and $V^E$ values are positive over entire composition. The large positive $H^E$ suggest that water reduces the strong electrostatic attractions between the ions and/or that the hydrogen bonding water-anion is energetically weak and does not superimpose some loss of water-water and anion-cation hydrogen bond upon mixing. Excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ of 1,4-dioxane + propan-1-ol or + propan-2-ol or + butan-1-ol or butan-2-ol binary mixtures have been measured at 308.15 K by Sharma and Kumar\textsuperscript{180}. The $V^E$ and $H^E$ data have been analyzed in terms of the Graph, Flory and Lacombe & Sanchez theories. The $H^E$ and $V^E$ values predicted by Graph theory are in agreement with experimental values. Minamihonoki et al\textsuperscript{181} have measured excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ of nonafluorobutylmethylether (FBME) + 2-propanone or 2-butanone or 3-pentanone binary mixtures at 298.15 K. The $H^E$ and $V^E$ values are positive over whole range of concentrations for all the mixtures and for an equimolar mixture follows order: 2-propanone > 3-pentanone > 2-butanone; 3-pentanone > 2-butanone = 2-propanone respectively.

Nebig et al\textsuperscript{182} measured excess molar enthalpies, $H^E$ and vapour liquid equilibria, (VLE) data for hexane or ethanol or 1-propanol + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [Emim][BTI]; hexane or benzene or toluene or methylcyclohexane or acetone or butanone or octane or nonane or octane + 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [Bmim][BTI]; hexane or water or 1-octene or toluene or benzene or ethanol or acetone or butanone or 3-pentanone + 1-hexyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [Hmim][BTI]; hexane or 1-octyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide [Omim][BTI] mixtures covering the temperature range from 323.15 to 413.15 K. The measured data have been analyzed in terms of modified UNIFAC (Dortmund) model. The results show that modified UNIFAC (Dortmund) model can be applied successfully also for mixtures with ionic liquids. Excess enthalpies, $H^E$ and heat capacities of water + 1-ethyl-3-methylimidazolium ethylsulfate [Emim][EtSO\textsubscript{4}] or 1-ethyl-3-methylimidazolium
trifluoromethanesulfonate [Emim][OTf] or 1-ethyl-3-methylimidazolium trifluoroacetate [Emim][TFA] mixtures have been measured over entire composition and wide temperature range from (283.15 to 348.15) K by Ficke et al\textsuperscript{183}. The $H^E$ data are exothermic for water + [Emim][EtSO\(_4\)] or [Emim][TFA] mixtures. The negative values of $H^E$ suggest that the water/IL interactions are stronger than the corresponding IL/IL; water/water interactions. The $H^E$ is endothermic for the water + [Emim][OTf] mixture. Further, $H^E$ values for all mixture increase with increasing temperature.

Miaja et al\textsuperscript{184} measured excess molar enthalpies, $H^E$ for 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF\(_4\)] or 1-hexyl-3-methylimidazolium tetrafluoroborate [Hmim][BF\(_4\)] or 1-butyl-3-methylpyridinium tetrafluoroborate [Bmpyr][BF\(_4\)] or 1-ethyl-3-methylimidazolium ethylsulfate [Emim][EtSO\(_4\)] or 1-butyl-3-methylimidazolium methylsulfate [Bmim][MetSO\(_4\)] or 1-ethyl-3-methylimidazolium trifluoromethanesulfonate [Emim][triflate] or 1-butyl-3-methylimidazolium trifluoromethanesulfonate [Bmim][triflate] + nitromethane mixtures at 303.15 K and densities and heat capacities of same set of mixtures at (293.15, 298.15, 303.15, 308.15, 313.15, 318.15) K. The experimental data have been used to calculate excess molar volumes, $V^E$ and excess heat capacities, $C^E_p$. It has been observed that excess properties are properly reproduced by ERAS model. Excess molar enthalpies, $H^E$ and densities for 1-butyl-2-methylpyridinium tetrafluoroborate [B\(_2\)mpy][BF\(_4\)] + water or methanol or ethanol or propan-1-ol or butan-1-ol mixtures have been measured at 298.15, 318.15 K by Navas et al\textsuperscript{185}. The observed density data have been employed to determine $V^E$. The quantam chemical method COSMO-RS has been applied to predict excess properties of these mixtures and results show significant contribution of hydrogen bond interactions in the behavior of the mixtures. Ficke and Brennecke\textsuperscript{186} measured excess molar enthalpies, $H^E$ of 1-(2-hydroxyethyl)-3-methylimidazolium trifluoroacetate [OHemim][TFA] or 1-ethyl-3-methylimidazolium hydrogensulfate [Emim][HSO\(_4\)] or 1-ethyl-3-methylimidazolium methyl sulfate [Emim][MeSO\(_4\)] or 1-ethyl-3-methylimidazolium methanesulfonate [Emim][MeSO\(_3\)] + water mixtures as a function of composition at (313.15 to 348.15) K. The combination of experimental thermodynamic measurements of $H^E$ and theoretical calculations of the atomic charges provides excellent insight into the molecular interactions of ionic liquids with water. Densities of 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF\(_4\)] or 1-ethyl-3-methylimidazolium
tetrafluoroborate [Emim][BF₄] + 2,2,2-trifluoroethanol (TFE) mixtures at (283.15, 293.15, 303.15, 313.15, 323.15, 333.15) K and (293.15 to 333.15) K and excess molar enthalpies, $H^E$ for the same set of mixtures at 293.15, 333.15 K and 0.1MPa have been measured by Curras et al.¹⁸⁷ Excess molar volumes, $V^E$ have been calculated from the experimental values. The $H^E$ values are positive for both the mixtures. However, $V^E$ values are positive in the case of [Emim][BF₄] + TFE between (283 and 323) K and slightly negative at 333 K, whereas negative for [C₁C₂im][BF₄] + TFE mixture in the (293 to 333) K temperature range. The results have been discussed in terms of molecular interactions.

Excess molar enthalpies, $H^E$ of 1-ethyl-3-methylimidazolium dimethylphosphate [Emim][DMP] + water or ethanol or methanol mixtures have been measured over entire mole fraction range at 298.15 K by Ren et al.¹⁸⁸ The results indicate that the mixing processes of [Emim][DMP] with water or ethanol or methanol are exothermal, and for an equimolar mixture vary in the order: ethanol > methanol > water. Porcedda et al.¹⁸⁹ have measured excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ of ethylammonium nitrate (EAN) or propylammonium nitrate (PAN) + water mixtures over entire composition at 298.15 K and atmospheric pressure. While $H^E$ values are positive; $V^E$ are negative over entire composition range. The analysis of $H^E$ data suggest that as the hydrophobic/hydrophilic ratio increases, along with the alkyl chain in the ionic liquids, the specific interactions among ionic liquid and water molecules becomes less important. Excess enthalpies, $H^E$ and excess molar volumes, $V^E$ (calculated from densities values) of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₁C₂Im][NTf₂] or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₁C₄Im][NTf₂] or 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₁C₆Im][NTf₂] or 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₁C₈Im][NTf₂] or 1-decyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C₁C₁₀Im][NTf₂] + methanol mixtures have been measured at 298.15 K by Deng et al.¹⁹⁰ The $H^E$ values are positive for all studied mixtures and for the case of methanol do not vary monotonously with the length of the alkyl side-chain of the cation on the ionic liquid increasing from [C₁C₂Im][NTf₂] to [C₁C₆Im][NTf₂] and then decreasing from [C₁C₈Im][NTf₂]. Faneite et al.¹⁹¹ have measured excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ (derived from densities data) of binary propan-1-ol or butan-1-ol or pentan-1-ol + 2,2,4-trimethylpentane mixtures over whole composition range at 298.15K and ambient
pressure. Wilson and Non Random Two Liquids (NRTL) models have been applied for $H^E$ correlation. The behavior of the thermo physical properties has been analyzed in terms of the length of the alkanol chain and the balance between positive and negative deviations of the ideality.

Krolikowska et al\textsuperscript{192} measured excess molar enthalpies, $H^E$ and heat capacities of N-hexylisoquinolinium thiocyanate [HiQuin][SCN] + water mixtures at (298.15, 303.15, 308.15) K and ambient pressure. The $H^E$ data for the present mixtures are exothermic. The negative $H^E$ values suggest that attractive interaction between IL and water are stronger than those pertaining to IL-IL and water-water pairs. The $H^E$ values of the investigated mixtures have also been described in terms of UNIQUAC model.

Laavi et al\textsuperscript{193} have measured excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ of methyl isobutyl ketone (MIBK) + 2-butanol (t-BuOH) or tert-pentanol (t-PnOH) or 2-ethyl-1-hexanol (2-EH) binary mixtures at 298.15 K. The experimental data have been used for the optimization of Wilson and Redlich-Kister equation parameters. The $H^E$ values are positive in the entire mole fraction range for all of the studied binary mixtures. The $V^E$ values are positive except for MIBK + t-PnOH. For MIBK + 2-BuOH the $V^E$ values are the highest and for MIBK + 2-EH the values are smallest indicating more ideal behavior. Excess molar enthalpies, $H^E$ of binary 1-nonanol or 1-decanol + acetonitrile mixtures have been measured as a function of composition at atmospheric pressure and (298.15, 303.15, and 308.15) K by Viola and Francesconi\textsuperscript{194}. The $H^E$ values are positive for both mixtures over the whole composition range, and increase with temperature and with alkanol chain length. The experimental data have been analyzed in terms of (ERAS-Model). Agreement between theoretical and experimental values is satisfactory.

Paduszynski et al\textsuperscript{195} have measured excess molar enthalpies, $H^E$ of 1-butyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imide [C\textsubscript{4}C\textsubscript{1}Pip][NTf\textsubscript{2}] or 1-hexyl-1-methylpiperidinium bis[(trifluoromethyl)sulfonyl]imide [C\textsubscript{6}C\textsubscript{1}Pip][NTf\textsubscript{2}] + ethanol or 1-propanol mixtures at 298.15 K and atmospheric pressure. Experimental data have been modeled in terms of perturbed-chain statistical associating fluid theory (PC-SAFT). The results indicate that calculated values are in agreement with experimental values.

Excess molar enthalpies, $H^E$ and heat capacities for N-octylisoquinolinium thiocyanate [C\textsubscript{8}iQuin][SCN] + water mixtures have been measured for different IL mole fractions at wide range of temperature and ambient pressure by Krolikowska et al\textsuperscript{196}. The $H^E$ values exhibit the S-shaped behavior. The $H^E$ values at high IL
concentrations become more negative as temperature increases and $H^E$ values at low IL concentration increases with temperature. The heat capacity values increases slightly with increasing temperature at the same mole faction. The $H^E$ data have been analyzed in terms of universal quasichemical (UNIQUAC) activity coefficient model. Kurnia and Coutinho have reviewed the excess molar enthalpies, $H^E$ of the binary mixtures containing ionic liquid (IL) and molecular solvents, taking into account the various structural features of both the IL and molecular solvent. Further, the capability of the conductor-like screening model (COSMO-RS) has also been used to predict the $H^E$ data and a good agreement between experimental $H^E$ and COSMO-RS prediction has been obtained. Excess molar enthalpies, $H^E (298.15, 308.15) \text{ K}$ and excess molar volumes, $V^E (308.15 \text{ K})$ for formamide + 1-propanol or 2-propanol mixtures have been measured over the entire range of composition by Rani and Maken. The $H^E$ and $V^E$ data have been utilized to study the thermodynamics of molecular interactions in terms of Prigogine–Flory–Patterson theory and Treszczanowicz–Benson association model with a Flory contribution term. Domanska et al have measured excess molar enthalpies, $H^E$ of pyrrole + benzene or pyridine or cyclohexane or 1-propanol or 1-butanol or 1-pentanol mixtures at 298.15 K. The $H^E$ is positive for pyrrole + benzene or cyclohexane mixtures, which is a result of breaking hydrogen bonding between molecules of pyrrole. The $H^E$ for pyrrole + pyridine mixture is negative, which is coming from the stronger interaction between molecules of pyrrole and pyridine. The $H^E$ is positive for all alcohols and increases with an increasing of the alcohol chain length. The $H^E$ data have also been analyzed in terms of Mod. UNIFAC (DO) and DISQUAC models. Excess molar enthalpies, $H^E$ for 1-methyl-3-octylimidazolium tetrafluoroborate [Omim][BF$_4$] + ethanol or 1-propanol or 2-propanol or 1-butanol or 1-pentanol mixtures have been measured over full composition range at 298.15 K by Fan et al. The $H^E$ values are positive for all the studied mixtures and for an equimolar composition follows the order: (a) 1-propanol > 1-butanol > 1-pentanol in the whole composition range; (b) 2-propanol > 1-propanol in the whole composition range; (c) ethanol > other alcohols at the low composition range of [Omim][BF$_4$], while ethanol < 1-propanol < 2-propanol at the high composition range of [Omim][BF$_4$]. The $H^E$ data have also been tested in terms of UNIQUAC model. Machanova et al have measured excess molar enthalpies, $H^E$ at 303.15 K and Excess molar volumes, $V^E$ (obtained from density data) of N-alkyltriethylammonium bis(trifluoromethylsulfonyl)imide [$N_{R,222}$][Tf$_2$N] (R=6, 8 or 12) +
methanol mixtures within the temperature interval (283.15-338.15) K and atmospheric pressure. The $H^E$ values of the mixtures are positive over the whole composition range and increase slightly with the length of the alkyl side-chain of the cation on the ionic liquid. The $V^E$ values increase with the increase of the alkyl-chain length of the ammonium cation of the ionic liquid and decrease with temperature. The $H^E$ and $V^E$ values have been analyzed in terms of ERAS model.

Multicomponent liquid mixtures frequently appear in chemical processes. However, $H^E$ data reported by researchers for these mixtures are quite few. Kuus et al. have measured excess molar enthalpies, $H^E$ of toluene + p-xylene + 1,2-dichloroethane ternary and toluene + 1,2-dichloroethane binary mixtures at 298.15 K. The observed data have been fitted to Redlich-Kister equation to determine binary and ternary adjustable parameters and standard deviations. The $H^E$ values of binary mixtures are wave-shaped, negative at lower mole fraction of 1,2-dichloroethane, and positive at higher mole fraction of 1,2-dichloroethane. The ternary $H^E$ values exhibit two regions of endothermic mixing: a narrow region in the vicinity of binary mixture toluene + p-xylene, and a bigger one at mole fractions of 1,2-dichloroethane higher than 0.58. A region of exothermic mixing exhibits between these two endothermic regions. Excess molar enthalpies, $H^E$ of methanol or ethanol + 2-propanol + 1,4-dioxane ternary mixture at 298.15 K and ambient pressure have been measured by Bhuiyan and Tamura. The experimental results have been correlated with a polynomial equation and used to construct constant excess enthalpy contours. The results have been compared with those calculated from a UNIQUAC associated solution model. Kwaterski et al. have measured excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ of ethanol or 1-butanol + triethylamine (TEA) + n-hexane ternary mixture and their binaries ethanol or 1-butanol + n-hexane or TEA; TEA + n-hexane at 298.15 K. The $H^E$ data are exothermic for the ethanol or 1-butanol + TEA mixtures and endothermic for ethanol or 1-butanol + n-hexane; TEA + n-hexane mixtures over whole composition range. However, $H^E$ values for ternary mixtures are mostly negative within entire composition range. The $H^E$ data have been analyzed in terms of ERAS model for describing both thermodynamic excess properties of ternary mixtures. Excess molar enthalpies, $H^E$ of the ternary tert-butyl methyl ether (MTBE) + ethanol + hexane and binary MTBE + ethanol or hexane; ethanol + hexane mixtures have been measured at 298.15 K and atmospheric pressure by Mato et al. The $H^E$ values of binary and ternary mixtures are positive over the entire range of
composition. Positive $H^E$ values suggest the predominance of the breaking of previous interactions over the formation of new interactions during the mixing process.

Excess molar enthalpies, $H^E$ for binary $p$-xylene + octane or diethyl carbonate; octane + diethyl carbonate and the ternary $p$-xylene + octane + diethyl carbonate mixtures have been measured at 298.15 K under atmospheric pressure by Verdes et al. The $H^E$ values are positive for the binary and ternary mixtures over the entire composition range. The maximum values of $H^E$ is due to the contribution of the binary mixture {octane + diethyl carbonate}, where the predominant effect is the destruction of the dipolar order of the diethyl during mixing. Shukla et al have measured excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ of toluene+cyclohexane + carbon; benzene + cyclohexane + toluene; carbon tetrachloride + benzene + cyclohexane tetrachloride ternary and their binary mixtures at 298.15 K. The $H^E$ and $V^E$ data have been analyzed in terms of Prigogine-Flory-Patterson and Bertrand-Acree-Bruchfield theories. The results obtained from these theories are very much comparable and are in good agreement with experimental data. Excess molar enthalpies, $H^E$ of $2$-methoxy-$2$-methylpropane (MTBE) + $1$-propanol + nonane ternary and $1$-propanol + nonane binary mixtures have been measured at 298.15 K and 0.1 MPa by Mato et al. The $H^E$ values of binary and ternary mixtures are positive over whole composition range. The ternary $H^E$ values increase as the chain length of the alkane increases. The group contribution model of the UNIFAC model has also been used to estimate ternary $H^E$ values. Aguilar et al have measured excess molar enthalpies, $H^E$ of dibutyl ether (DBE) + $1$-butanol + benzene ternary and its sub-binaries DBE + benzene or $1$-butanol; benzene + $1$-butanol at 298.15, 313.15 K and atmospheric pressure. All the investigated binary and ternary mixtures show endothermic character. The experimental data have been tested in terms of NTRL and UNIQUAC models. The values of the standard deviation indicate good agreement between the experimental results and those calculated from the models. Excess molar enthalpies, $H^E$ for the ternary cyclohexane + tetrahydropyran + piperidine and binary cyclohexane + tetrahydropyran or piperidine; tetrahydropyran + piperidine mixtures have been measured at 308.15 K and atmospheric pressure by Belaribi et al. The experimental binary and ternary results have been correlated using Redlich-Kister and Cibulka equations respectively to obtained binary and ternary adjustable parameters.
Excess molar enthalpies, $H^E$ for the ternary dibutyl ether (DBE) + 2,2,4-trimethylpentane (TMP) + 1-butanol and binary DBE + TMP or 1-butanol; TMP + 1-butanol mixtures at 298.15 K have been measured by Aguilar et al.$^{224}$ The $H^E$ values are positive for all the investigated mixtures. The $H^E$ data have been correlated well with the NRTL and UNIQUAC models and polynomials equations. Hasan and Peng$^{225}$ measured excess molar enthalpies, $H^E$ of dibutyl ether (DBE) or dipropyl ether (DPE) + 2,2-dimethylbutane + 2,3-dimethylbutane ternary mixtures at 298.15 K and 0.1MPa. A smooth representation of the results has been described and the constant-enthalpy contours for ternary mixtures are displayed on the respective Roozeboom diagrams. The $H^E$ values computed by Liebermann–Fried model are in agreement with experimental results. Excess molar enthalpies, $H^E$ of 1-hexene + tetrahydrofuran + 2,2-dimethylbutane or 2,3-dimethylbutane ternary mixtures have also been measured at 298.15 K by Hasan and Peng$^{226}$. It is shown that good estimates of the $H^E$ of the ternary mixtures have been obtained from the Liebermann–Fried model by using the physical properties of the components and the parameters determined from their binary mixtures. Liu et al.$^{227}$ have measured excess molar enthalpies, $H^E$ for ternary tributylphosphate (TBP) + water + methanol or ethanol and binary water + TBP mixtures at 298.15 K and atmospheric pressure using a TAM Air isothermal calorimeter. The $H^E$ values for the ternary mixtures are dictated by the relative proportion of components in mixtures. Excess molar enthalpies, $H^E$ and excess molar volumes, $V^E$ have been measured for the ternary dodecane + ethyl pentanoate + ethyl ethanoate and corresponding binaries dodecane + ethyl pentanoate or ethyl ethanoate; ethyl pentanoate + ethyl ethanoate binaries at 298.15 K by Perez et al.$^{228}$. The application of the UNIFAC group contribution model to estimate the $H^E$ yields acceptable results for the binary (with the exception of ester–ester) and ternary mixtures.

Dossoki$^{229}$ has measured excess molar enthalpies, $H^E$ for methanol + ethanol + oxane or 1,4-dioxane ternary and methanol + ethanol or oxane or 1, 4-dioxane; ethanol + oxane or 1, 4-dioxane binary mixtures at 298.15 K and atmospheric pressure. The experimental results have been correlated with a polynomial equation to estimate the coefficients. The experimental results have also been explained in terms of UNIQUAC associated solution model. Excess molar enthalpies, $H^E$ for the ternary 2-methoxy-2-methyl-propane (MTBE) + ethanol + nonane and the binary ethanol + nonane mixtures have been measured at 298.15 K.
and atmospheric pressure by Mato et al\textsuperscript{230}. The $H^E$ values for the binary and ternary mixtures are positive over the whole range of composition. The analysis of $H^E$ data suggest that the positive $H^E$ contributions to the breaking of interactions present in the pure liquids are energetically more important than the negative contribution, which is a specific interaction between unlike molecules. Zhang et al\textsuperscript{231} have measured excess molar enthalpies, $H^E$ of ternary 1-butyl-3-methylimidazolium dibutylphosphate [Bmim][DBP] + methanol or ethanol + water and binary [Bmim][DBP] + methanol or ethanol or water mixtures at 298.15 K and atmospheric pressure. The $H^E$ values for both ternary and binary mixtures are negative over the entire range of composition.

The $H^E$ of the ternary mixtures have also been predicted based on the binary interaction parameters. Excess molar enthalpies, $H^E$ of 1-ethyl-3-methylimidazolium tetrafluoroborate [Emim][BF$_4$] + 2-methylaniline (2MA) + pyridine (Py) or α- or β- or γ-picoline ternary mixtures have been measured over an entire mole fraction at 298.15 K by Sharma et al\textsuperscript{232}. The Redlich–Kister equation parameters have been fitted to measured data. The topology of the constituents of the mixtures (Graph theory) has been utilized to predict $H^E$ values of the investigated mixtures. The $H^E$ values determined by Graph theory compare well with their corresponding experimental values. The agreement between measured $H^E$ values and the values determined from Graph theory suggest that while [Emim][BF$_4$] exist as monomer; 2MA or Py or α- or β- or γ-picoline exist as associated molecular entities. Excess molar enthalpies, $H^E$ of 2-methoxy-2-methylpropane + 1-propanol + heptane ternary and 1-propanol + heptane binary mixtures have been measured at 298.15 K by Mato et al\textsuperscript{233}. The $H^E$ values are positive for both binary and ternary mixtures over the whole composition range. Aguilar et al\textsuperscript{234} have measured excess molar enthalpies, $H^E$ of ternary dibutyl ether (DBE) + 1-hexene + 1-butanol and DBE + 1-hexene or cyclohexane or 2,2,4-trimethylpentane + 1-butanol mixtures at 298.15 and 313.15 K. The $H^E$ values for all the studied mixtures are positive. For all the ternary mixtures, the endothermic effect is enhanced by the increase of the temperature. Excess enthalpies, $H^E$ of 1-ethyl-3-methylimidazolium dimethylphosphate [Emim][DMP] + water + methanol or ethanol ternary and [Emim][DMP] + water or methanol or ethanol binary mixtures have been measured at 298.15 K and under normal atmospheric pressure by Zhang et al\textsuperscript{235}. The binary interaction parameters in the NRTL and UNIQUAC models have been obtained and have been obtained and utilized to predict $H^E$ of ternary mixtures. The average relative deviations between experimental and calculated $H^E$ values for the
ternary mixtures are 1.86 - 7.89 %. Alonso et al\textsuperscript{236} have measured excess molar enthalpies, $H^E$ for 1-propanol + N,N,N-triethylamine (TEA) + 2-butanone mixture at 298.15 K. The data are interpreted in terms of different interactional contributions to $H^E$. From the results, it is concluded that 1-propanol and TEA molecules can participate in interactions between unlike molecules, and that 2-butanone is mainly a breaker of interactions between like molecules. The DISQUAC model has been utilized to predict $H^E$ of the investigated ternary mixture. Large differences between experimental values and theoretical results show the existence of ternary interactions. Excess molar enthalpies, $H^E$ for the ternary 1,2-dichloropropane (1,2-DCP) + 2-pentanol + 3-pentanol and their sub-binaries 1,2-DCP + 2-pentanol or 3-pentanol; 2-pentanol + 3-pentanol have been measured over the whole range of composition at 298.15 K by Kim\textsuperscript{237}. The $H^E$ values of all the mixtures are positive throughout the mole fraction range, except for the binary mixture 2-pentanol + 3-pentanol. The $H^E$ data for binary and ternary data have been fitted to Redlich-Kister equation, Cibulka and the Morris equations respectively. The experimental results have been qualitatively discussed in terms of molecular interactions.
References:

231. X. Zhang, R. Chang and Z. Zhao, Huagong Xuebao/CIESC J., 64, 1520, 2013.