SECTION-II

EXCESS MOLAR VOLUME, VISCOSITY AND ULTRASONIC VELOCITY
CHAPTER - 6

LITERATURE REVIEW
6. LITERATURE REVIEW

6.1 Critical Review

Excess Molar Volume

The excess properties of binary liquid mixtures are important from both theoretical and practical point of view, as they provide the insight to the actual behaviour of the molecules constituting the mixture. In principle, the interaction between the molecules present in the mixture can be established from the departure from ideal behaviour of the physical properties like excess molar volume, Gibbs free energy of activation of flow etc.

Viscosity

Viscosity is the property of fluids, which measures the resistance to flow offered by a fluid layer when another adjacent and parallel fluid layer tends to flow past the first layer. Newton deduced that the internal friction or viscosity would produce retarding forces proportional to the velocity gradient, \( \frac{du}{dx} \), normal to the direction of flow and to the area of contact, \( A \), between the moving sheets of liquid:

\[
\frac{f}{\eta} = A \frac{du}{dx}
\]


\( \alpha \)

or

\[
\frac{f}{\eta} = A \frac{du}{dx}
\]

where \( \eta \) is called the coefficient of viscosity. This law holds good for all homogeneous liquids. Viscosity is a dynamic, non-equilibrium property on a macro scale but it reflects the effect of molecular motions and interactions on micro-scale. The viscosity of liquids decreases considerably with the rise of temperature (roughly about 2% per degree).

According to hole theory [283], there are vacancies or holes in a liquid. The liquid molecules keep on moving continuously into these vacancies thus permitting relative motion to take place. A liquid molecule, therefore needs some activation energy to move into a hole. As the activation energy becomes increasingly available at increasing temperatures, a liquid can flow more easily at higher temperatures. The
coefficient of viscosity, thus, falls appreciably with rise in temperature, according to Andrade's equation:

\[ \mu = A e^{B/RT} \]  

(6.3)

where \( A, B \) are constants for a given liquid.

Moderate pressures do not affect viscosity of liquids below boiling point but at high pressure range, increase in viscosity has been noted. This is attributed to decrease in the number of holes as pressure is increased. Consequently, it becomes more difficult for liquid molecules to move around one another and hence it becomes more difficult for them to flow. More complex the molecular structure, more is the effect of pressure.

The viscosity of a fluid depends on the molecular size and on the magnitude of the intermolecular forces between the closely packed molecules. Non-polar organic liquids (e.g. Benzene) generally have low viscosity, whereas liquids in which direct bonding occurs (e.g. hydrogen bonds in Glycerol) have relatively high viscosities.

For the same class of liquids, the viscosity increases with the size and molar mass of the substance. The complex molecules and the molecules involving branching in the side-chains, in general, show higher viscosities.

The viscosity of any liquid gets affected to a large extent by the addition of additives, for e.g. the substances like sugar etc. which can interact more strongly with water, would tend to increase the viscosity of the medium, whereas, the salts which get ionized in the medium, tends to decrease the viscosity because of the disruption of the hydrogen bonds. The presence of the suspension and colloidal particles also increase the viscosity of the medium.

In a mixture, if the constituents strongly interact with each other, then the observed fluidity is less than the calculated value, i.e. a considerable increase of viscosity occurs in such a case. If the mixture involves a polar and a non-polar liquid such as Alcohol and Benzene, then the observed fluidities are higher than the predicted fluidities.

Numerous methods have been developed for the prediction and measurement of viscosity. The correlation between viscosity of liquid mixtures and that of pure
components is very complicated. No theory has been developed so far which can predict viscosity of liquid mixtures satisfactorily taking into account the deviations from the properties of ideal mixtures. This is because the effect of molecular structure is very large and even the small change in molecular structure can cause large changes in viscosity.

**Ultrasonic Velocity**

Numerous studies on the measurement of ultrasonic velocities and isentropic compressibilities of liquid mixtures have been carried out. It has been recognized that there exists a strong correlation between the magnitude of the ultrasonic velocity and the chemical structure of the molecules. Empirical relationships have been obtained relating these parameters and numerous attempts for prediction of properties, based on such relations, have been made. The physico-chemical behaviour of liquid mixtures can be well judged by the deviation from rectilinear behaviour of the ultrasonic velocities and the isentropic compressibilities.

The following is the **Critical Literature Review** regarding the systems studied:

Densities and viscosities for \( p \)-xyylene with cyclohexane, heptane, octane and \( n \)-methyl-2-pyrrolidone have been determined from (298.15 to 353.15) \( K \) and at atmospheric pressure by Yang et al. [441] using a vibrating-tube density meter and an Ubbelohde viscometer. The excess molar volumes and viscosity deviations have been fitted to the Redlich-Kister equation and the coefficients and estimates of the standard error values are given.

The viscosities, densities and speeds of sound of binary mixtures of 4-methylpentan-2-one with \( o \)-xylene, \( m \)-xylene, \( p \)-xylene and isopropylbenzene have been determined at 298.15 \( K \) over the whole composition range by Singh et al. [362]. Excess volume, excess compressibility and deviations in viscosity were calculated.

Densities and viscosities for binary mixtures of 1-pentanol with benzene, chlorobenzene, bromobenzene, iodobenzene, nitrobenzene, aniline, toluene and \( p \)-xylene have been measured over the whole composition range at 293.15 \( K \) by Tsierekzos et al. [401]. The excess volumes and the viscosity deviations were calculated and the results were fitted to a Redlich-Kister type polynomial relation.
Densities for binary mixtures of 2-propanol or 2-methyl-2-propanol or acetone or 2-butanone + o-xylene, + m-xylene, + p-xylene have been determined at 298.15 K by Ouyang et al. [278, 279] and excess molar volumes have been derived. Surface tension of these binary mixtures has been measured at 298.15 K by the pendant drop method and the values of the surface tension deviation for these mixtures were also calculated.

Densities for binary mixtures of isopropyl ether + o-xylene, + m-xylene and + p-xylene have been determined at 298.15 K and excess molar volumes have been derived by Ouyang et al. [277]. Surface tensions for binary mixtures of isopropyl ether + o-xylene, + m-xylene and + p-xylene and methyl tert-butyl ether + o-xylene, + m-xylene and + p-xylene have been measured at 298.15 K by the pendant-drop method and the values of the surface tension deviation for these mixtures were also calculated.

Experimental data on density and viscosity at 303.15 and 323.15 K are presented for the binary mixtures of sulfolane + benzene, toluene, ethylbenzene, p-xylene, o-xylene and m-xylene by Yang et al. [440]. From these data, excess molar volumes and deviations in viscosity have been calculated. The computed quantities have been fitted to the Redlich-Kister equation to derive the coefficients and estimate the standard error values.

Densities, viscosities and refractive indices at 298.15, 303.15 and 308.15 K and speed of sound values at 298.15 K have been presented for the binary mixtures of ethyl chloroacetate or cyclohexanone + benzene, + toluene, + p-xylene, + mesitylene and + methoxybenzene by Aralaguppi et al. [11, 12]. From the results of density, viscosity and refractive index, the excess molar volume, deviations in viscosity, molar refractivity, speed of sound and isentropic compressibility have been calculated. These results have been correlated by a polynomial Redlich-Kister equation to derive the coefficients and standard errors.

Densities, viscosities, refractive indices and surface tensions for 4-methyl-2-pentanone + ethyl benzoate mixtures have been measured over the whole composition range at 283.15, 293.15 and 303.15 K by Tsierkezos et al. [400]. The excess volumes, the viscosity deviations and the excess refraction were calculated and
show negative values. The results were fitted to a Redlich-Kister type polynomial relation and the corresponding parameters have been derived.

The excess volumes for 1-butanol or 2-butanol or 2-methylpropan-1-ol or 2-methylpropan-2-ol + α-xylene or m-xylene or p-xylene at 308.15 K have been measured over the whole range of composition by Bhardwaj et al. [28].

Densities, relative permittivities and refractive indices of propylene carbonate + p-xylene mixtures at (15, 20, 25, 30 and 35) °C have been measured by Konti et al. [168]. Excess molar volumes as well as deviations in relative permittivity and molar refraction were calculated and were found to be negative.

Prasad et al. [299] have reported the density and viscosity of the binary mixture formed by p-xylene with methanol, n-propanol and n-butanol at 303.15, 313.15 and 323.15 K. The representation of the data by common mixing rules is also studied.

Gupta and Singh [111, 112] have reported the densities and viscosities of binary mixtures of methyl ethanoate or n-n-dimethylformamide with benzene, toluene and α-, m- & p- xylenes at 298.15 K. Excess volumes have been calculated. The molecular interactions between the components were discussed and the results were used to justify the validity of some viscosity models.

The densities, viscosities and ultrasonic velocities of 3-pentanone with ethylbenzene and α-xylene have been determined at 293.15, 303.15 and 313.15 K over the entire compositional range by Katyal et al. [164]. Excess volume, excess compressibility and deviations in viscosity were calculated.

Timmermann’s [394] four volumes contain a large quantity of information on physical properties of mixtures from papers published and at least 54 different equations have been proposed to describe the viscosity of liquid mixture that have been compiled by Irving.

The densities and viscosities of binary mixtures of normal and substituted alcohols with ethylbenzene and isopropylbenzene at 298.15 and 308.15 K, have been reported by Rattan et al. [318, 320-326]. From experimental results, the isentropic compressibility and its excess value along with the excess viscosity and excess molar Gibbs free energy for the activation of flow have been computed and are presented as
functions of \( x \). The parameter \( d \) of the Grunberg and Nissan expression has also been calculated.

Densities and viscosities of binary mixtures of toluene with acetic acid and propionic acid have been measured at 293.15, 303.15 and 313.15 \( K \) over the complete compositional range by Rattan et al. [319]. The results are discussed in terms of molecular interactions.

The excess molar volumes of chloroform with \( o-, m- \) and \( p- \) xylene and ethylbenzene have been determined in the whole range of composition using a vibrating tube density meter at 298.15 \( K \) by Zhongqi et al. [446]. All the four mixtures exhibit positive values over the entire range of composition at this temperature.

Excess molar volumes of vinyl acetate and toluene, ethylbenzene, \( p- \) xylene, isopropylbenzene, butyl benzene, mesitylene, \( t- \) butylbenzene have been determined from density measurements at 298.15 \( K \) using a vibrating-tube densimeter by Resa et al. [341]. The excess molar volumes are positive over the whole compositional range and increase with the size of the hydrocarbon.

Narayana et al. [237] have reported the ultrasonic velocity of six fluorocarbons at 298.15 \( K \). The deviation of isentropic compressibility exhibited a decreasing trend with increase in the boiling point difference.

Excess volume and viscosity data at 308.15 \( K \) have been measured for binary systems formed by \( o-, m- \) and \( p- \) xylene with \( o- \) nitrotoluene or \( m- \) nitrotoluene by Goud et al. [107]. Excess volumes were measured directly using a dilatometer and viscosities were measured with an Ostwald viscometer. The excess volumes and viscosities are discussed in terms of molecular interactions between like and unlike molecules.

Dilatometric measurements of excess volumes and viscosities have been made for binary liquid mixtures of 1,2-dichloroethane or with benzene, toluene, \( p- \) xylene and quinoline at 298.15 and 308.15 \( K \) and for mixtures of 1,2-dichloroethane with cyclohexane at 308.15 \( K \) by Nath et al. [244, 245]. The values of \( V^e \) have been found to be positive for 1,2-dichloroethane with benzene, toluene, \( p- \) xylene and cyclohexane and negative with quinoline. Grunberg-Nissan parameter was found and
value suggested that the systems containing aromatic hydrocarbons indicate the existence of weak specific interactions between chloroalkanes and aromatics.

Densities, relative permittivties and refractive indices have been measured for the binary mixture γ-butyrolactone + p-xylene from 288.15 to 308.15 K by Avraam et al. [17]. The above quantities are represented with polynomial smoothing curves. Excess volumes, as well as deviations of molar polarization, were calculated and found to be negative, with a minimum at mole fraction 0.5. The Kirkwood correlation factor was also calculated.

The densities and excess molar volumes for tri-n-octylamine (TOA) + propionic acid, TOA + diluent and propionic acid + diluent binary systems have been measured under the full range of composition at 298.15 K, respectively by Yamamoto et al. [439]. The excess molar volumes of TOA + propionic acid + diluent ternary systems were also measured at 298.15 K. Benzene, toluene, p-xylene, ethanol, hexane and cyclohexane were used as the diluent.

Densities and viscosities have been measured for the systems of four oxygenates (acetone, diisopropyl ether, ethanol and methyl ethyl ketone) separately with a five-component hydrocarbon mixture at three temperatures (288.15, 298.15 and 308.15) K and atmospheric pressure by Peng et al. [287]. Excess molar volumes and deviations in viscosity for the mixtures were derived from experimental data and the computed results were fitted to a Redlich-Kister type equation.

Excess molar volumes and excess molar enthalpies for quinoline + benzene, toluene, o-xylene, or p-xylene for the whole range of compositions have been measured at 303.15 K by Kalra et al. [160]. The values of $H_m^E$ and $V_m^E$ for these mixtures suggest that quinoline is partly self-associated and there is strong interaction between quinoline and aromatic hydrocarbons.

Excess volumes and isentropic compressibilities of binary mixtures of p-xylene with 2-propanol, 2-methyl-1-propanol and 3-methyl-1-butanol have been measured at 303.15 K by Sreenivasulu et al. [367]. The excess volume exhibits positive deviation over the whole range of composition in the three mixtures and the deviation in isentropic compressibility exhibits inversion in sign in the three mixtures.
Densities and refractive indices have been measured at 298.15 K for binary mixtures of 1-hexene + o-xylene, + m-xylene, + p-xylene and + ethylbenzene over the entire composition range by Tojo et al. [398]. The results were fitted to a polynomial relation to obtain the coefficients and standard errors. Excess volumes and molar refraction deviations were derived.

The density and viscosity of binary mixtures of propanoic acid + benzene, + toluene and + o-, + m- and + p-xylenes have been measured at 298.15 K by Singh et al. [359]. Excess volumes have been calculated. The interactions existing between the components have been discussed. The results are used to theoretically justify the validity of the viscosity models.

Viscosity coefficient measurements at saturation pressure are reported for ethyl acetate + o-xylene, ethyl acetate + p-xylene, ethyl acetate + p-dioxane and ethyl acetate + tetrahydrofuran over the entire range of composition at 313.15 K by Rathnam [317]. The values of mixture viscosity have been calculated for different compositions by the application of the Katti and Chaudhri equation. It was found that the experimental viscosities are in reasonable agreement with the calculated viscosities and within the uncertainty limits of 10.003 cP. The absolute magnitude of the probable error does not change much from system to system.

The excess volume of mixing for the binary mixtures of the nitroalkanes: nitromethane, nitroethane and 2-nitropropane with symmetrical aromatic hydrocarbons: benzene, p-xylene and mesitylene has been determined by density measurements at 293.15 K by Yadava et al. [438]. The $\overline{v}$ values are positive over the whole mole fraction range except those for the mixtures of nitroethane and 2-nitropropane with benzene and $p$-xylene where they are negative at lower and positive at higher mole fractions of nitroalkanes. The results have been discussed in terms of dipole-induced dipole electrostatic molecular interactions significantly affected by steric factors.

Excess volumes of binary mixtures of triethylamine with benzene, toluene, ethylbenzene and three isomeric xylenes at 313.15 K have been computed from the experimental density data by Rao et al. [314]. $F^E$ decreases when an alkyl group is added to the benzene ring. For isomeric xylenes, it follows the order $m$-xylene > $o$-xylene > $p$-xylene.

197
Viscosities at 25°C have been measured at different molar concentrations for fourteen binary liquid systems representing different types and degrees of interaction between unlike components by Fort et al. [84]. Excess viscosities tend to become less negative and then increasingly positive as the strength of the interaction between unlike molecules increases and the excess viscosity is approximately proportional to the strength of the interaction.

Bloomfield et al. [35] have examined expression connecting the viscosity of binary liquid mixtures with their thermodynamic properties using the concept of the absolute rate and free volume theories of flow.

Kalra et al. [159] have examined the viscosity data of binary mixtures of 1,2-dibromoethane with benzene, o-, m- & p-xylene over the whole composition range at 298.15 K and the interactions existing between the components have been discussed. The deviation in viscosity data has been utilized to evaluate excess volume functions and there is a close agreement between the \( V^e \) values calculated from the viscosity data and those obtained using a dilatometer.

Excess volumes and kinematic viscosities have been measured by means of a vibrating tube densimeter and an Ubbelohde viscometer for 12 binary systems containing 4-methyl-2-pentanone (MIBK) by Fermegiia et al. [80]. Excess volumes have been correlated by means of a polynomial expression, viscosities by means of the Mc Allister equation. The first component in all the binary systems studied is 4-methyl-2-pentanone (MIBK), the second component is 3-pentanone, 2-hexanone, cyclohexanone, \( n \)-heptane, toluene, \( p \)-xylene, ethylcyclohexane, 1,1,1-trichloroethane, \( n \)-butyl acetate, 4-hydroxy-4-methyl-2-pentanone, 1-methoxy-2-propanol (PGM), or 1-acetoxy-2-ethoxyethane. All the systems have been measured at atmospheric pressure and 298.15 K.

Densities and viscosities were measured for the systems of methanol, ethanol, propan-2-ol and 2-methylpropan-2-ol separately with a synthetic \( C_6 \) mixture at temperatures from 298.15 to 318.15 K and atmospheric pressure by Tu et al. [404]. Densities were determined using a vibrating-tube densimeter and viscosities were measured with an automatic Ubbelohde capillary viscometer.

A Picker flow micro calorimeter was used to determine volumetric heat capacities at 298.15 K for the six binary systems formed from the \( C_6 \) alkylbenzenes:
ethylbenzene, o-xylene, m-xylene and p-xylene by Fortier et al. [85]. Excess heat capacities obtained from the results are compared with the meager information available in the literature for the temperature variation of the excess enthalpies of these mixtures.

Molar excess volumes and molar excess enthalpies have been determined at 298.15 K by using a dilatometer and an LKB flow micro calorimeter, respectively, for benzene, toluene, o-xylene, m-xylene, or p-xylene + o-chlorotoluene mixtures by Dahiya et al. [58]. While both the $V^e$ and the $H^e$ values are positive for benzene + chlorotoluene mixtures, they are negative for the rest of the binary mixtures. The data have also been compared with the available literature values.

Kinematic viscosities and densities of 43 binary mixtures containing aromatic and cyclic hydrocarbons, esters, ketones and normal chloroalkanes were measured at 298.15 K over the entire composition range by Petrino et al. [291]. The experimental values of kinematic viscosities have been used to extend the interaction parameters of the UNIFAC-VISCO predictive model.

Excess volumes for binary liquid mixtures of acetone with benzene, toluene, p-xylene and mesitylene at 298.15 and 308.15 K and for mixtures of acetone with cyclohexane at 298.15 K, have been measured by using a dilatometer by Nath et al. [238]. Values of $V^e$ for the various systems have been fitted into least squares equation. At both temperatures, 298.15 and 308.15 K, values of $V^e$ have been found to be negative for acetone-benzene, acetone-toluene and acetone - p-xylene and positive for acetone-mesitylene. For acetone-cyclohexane at 298.15 K, the values of $V^e$ have been found to be positive. The negative values of $V^e$ for the systems of acetone with benzene, toluene and p-xylene suggest the existence of specific interaction between acetone and aromatic hydrocarbons.

The dielectric constants and refractive indexes for binary mixtures of trichloroethylene with benzene, toluene, p-xylene, CCl$_4$ and CHCl$_3$ have been measured at 303.15 K by Nath et al. [242]. Also, the ultrasonic velocities in these binary liquid mixtures have been measured at 303.15 and 313.15 K by using a single crystal interferometer at a frequency of 2 MHz/s. The ultrasonic velocities have been used to calculate the adiabatic compressibilities for these systems at 303.15 and 313.15 K.
Measurements of ultrasonic velocities and adiabatic compressibilities have been made for mixtures of 1,2-dichloroethane with benzene, toluene and quinoline at 303.15 and 313.15 K, for mixtures of 1,2-dichloroethane with \( p \)-xylene at 303.15 and 318.15 K and for mixtures of 1,2-dichloroethane with cyclohexane at 308.15 K by Nath et al. [240].

Excess molar volumes of cyclohexane + benzene, cyclohexane + toluene, cyclohexane + \( p \)-xylene, \( \gamma \)-butyrolactone + benzene, \( \gamma \)-butyrolactone + toluene and \( \gamma \)-butyrolactone + \( m \)-xylene have been measured at 298.15 K by Acree et al. [4]. For the first three systems, \( V^e \) is positive throughout the entire concentration range. \( V^e \) is negative for binary mixtures containing \( \gamma \)-butyrolactone, which indicates significant interaction between \( \gamma \)-butyrolactone and the aromatic hydrocarbon.

The excess volumes of mixing of seven ternary mixtures, viz., (i) carbon tetrachloride (CCl\(_4\)) + \( p \)-xylene + benzene (ii) cyclohexane + CCl\(_4\) + toluene, (iii) cyclohexane + CCl\(_4\) + \( p \)-xylene, (iv) cyclohexane + chloroform (CHCl\(_3\)) + toluene, (v) cyclohexane + CHCl\(_3\) + \( p \)-xylene, (vi) cyclohexane + methylene dichloride (CH\(_2\)Cl\(_2\)) + toluene and (vii) cyclohexane + CH\(_2\)Cl\(_2\) + \( p \)-xylene, have been measured over a wide concentration range by Rastogi et al. [316].

Experimental measurements of density and viscosity of three binary systems, viz., \( p \)-xylene/\( m \)-xylene, \( p \)-xylene/o-xylene and \( m \)-xylene/o-xylene, were performed over the complete concentration ranges, for temperatures between 273.15 and 303.15 K by Serrano et al. [356]. For the same temperature interval, densities and viscosities of three ternary mixtures of the isomers were obtained. The viscosity data was correlated by the McAllister equations, producing excellent representations of both binary and ternary data.

Dynamic viscosities and densities of dilute solutions of glycerol trioleate + chloroform, at 10, 15, 20, 25 and 30 °C and of glycerol trioleate + octane, + \( p \)-xylene, + toluene, at 20, 25, 30, 35 and 40 °C, were measured by Exarchos et al. [78]. The dynamic viscosities and the excess volumes were correlated with the composition and temperature through empirical relations. The excess volumes values were positive for the glycerol trioleate + chloroform system and negative for the other mixtures over the entire range of mole fractions covered in this study.
Measurements of ultrasonic velocities and adiabatic compressibilities at 293.15 and 303.15 K, dielectric constants at 298.15 and 308.15 K and refractive indices at 298.15 K have been made for binary liquid mixtures of tetrachloroethylene with benzene, toluene, $p$-xylene, carbon tetrachloride and cyclohexane by Nath et al. [243].

Molar excess volumes and molar excess enthalpies of various ternary mixtures [nitrobenzene + benzene + $o$-xylene, nitrobenzene + benzene + $p$-xylene] were measured as a function of the composition at 298.15 K by Kalra et al. [158]. The observed data were analysed in terms of Graph theory and of Sanchez-Lacombe and Flory’s theories. The calculated values of excess volumes and excess enthalpies by Graph and by Flory’s theory compare with the experimental values.

Excess molar volumes for binary mixtures ethylbenzene + $o$-xylene, + $p$-xylene, + $m$-xylene; $o$-xylene + $m$-xylene, + $p$-xylene and $m$-xylene + $p$-xylene have been determined from density data using vibrating tube densimeter by Jain et al. [148]. The results have been compared with literature values and with Flory’s theory.

Excess molar volumes of nitromethane with 1,4-dimethylbenzene at 298.15 K were critically evaluated by Marsh [203]. A maxima occurs in the excess volume vs. mole fraction for nitromethane curve at ~ 0.66. Excess molar volumes of nitroethane with 1,4-dimethylbenzene at 298.15 K were critically evaluated. A minima and a maxima occurs in the excess volume vs. mole fraction nitroethane curve at ~ 0.24 and ~ 0.79 respectively.

Viscosity and surface tension data of two binary liquid systems methanol + toluene and methanol + $p$-xylene were determined at 20, 25, 35, 45 °C over the whole compositional range by Wanchoo et al. [418]. The excess values of molar volume, viscosity, Gibbs free energy for the activation of flow and surface tension were evaluated. The Grunberg-Nissan parameter was also calculated. The excess volume values were fitted to Redlich-Kister type of equation. The viscosity data was fitted to the Redlich-Kister type of equation and models of McAllister, Heric and third degree polynomial.

Excess molar volumes were determined as function of composition at 308.15 K by using a direct dilatometric technique for cyclopentanol, cyclohexanol and cycloheptanol with cyclohexane, benzene, toluene and $p$-xylene by Mahl et al. [199].
All the cycloalkanols mixtures with benzene, toluene and p-xylene exhibit positive excess volumes over the whole mole fraction range except for cyclopentanol + toluene and cyclopentanol + p-xylene.

Excess volumes of mixing were measured at 20 °C for mixtures of four aromatic hydrocarbons (benzene, toluene, ethylbenzene and p-xylene) with five alkyl acetates (methyl, ethyl, propyl, butyl and amyl acetates) and two ketones (acetone and 2-butanone) by Qin et al. [306]. The whole composition range was studied for all 28 binary systems. Specific interactions between the carbonyl and aromatic systems lead to rather small excess volumes, frequently even negative ones. Ketones interact more strongly than alkyl acetates.

The volume of mixing, speed of sound and viscosity of binary liquid mixtures composed of butyl acetate + o-xylene, + m-xylene and + p-xylene have been measured at 303.15 K by Venkateswarlu et al. [413]. The excess volumes and deviations in isentropic compressibility and viscosity are discussed in terms of molecular interactions between like and unlike components.

Experimental values of densities, viscosities and refractive indices at 298.15, 303.15 and 308.15 K while speed of sound at 298.15 K for the binary mixtures of 1-chloronaphthalene with benzene, methylbenzene, 1,4-dimethylbenzene, 1,3,5-trimethylbenzene and methoxybenzene are presented over the entire mole fraction range by Aminabhavi et al. [9]. From these data, excess molar volume, deviations in viscosity, speed of sound, isentropic compressibility and Lorenz-Lorentz molar refractivity have been calculated. These results are fitted to the Redlich-Kister type polynomial of the third degree to derive the binary coefficients.

Measurements at 25°C of the refractive index at seven wavelengths and the low frequency dielectric constant are reported for mixtures of carbon tetrachloride with benzene, p-xylene and mesitylene by Perez et al. [290]. Dispersion formulas have been obtained for the refractive index and values of the molar refraction and molar polarization are also reported.

Molar excess volumes for m-chloroaniline + benzene, + toluene, + o-xylene, + m-xylene and + p-xylene, m-chloroaniline + benzene + toluene and m-chloroaniline + benzene + o-xylene have been measured as a function of composition at 308.15 K by Sharma et al. [357]. $v^E$ values for the binary mixtures are negative for all the
systems over the entire range of composition and for an equimolar composition vary in the order o-xylene > toluene > m-xylene > benzene > p-xylene. On the other hand while $v^E$ values for m-chloroaniline + benzene + toluene are negative over the whole composition range, those for m-chloroaniline + benzene + o-xylene vary from positive to negative depending on the mole fraction of each of the components.

Densities and molar volumes of solutions of nitrobenzene in 18 weak electron donating solvents were measured as functions of concentration at 25°C by Miller et al. [225]. The data were fitted by a least-square method. No obvious relationship is observed between the electron donating ability of the solvents and densities of the solutions.

Determinations of excess enthalpies in a flow micro calorimeter and of excess volumes in a successive dilution dilatometer were carried out at 298.15 K for binary mixtures of m-dichlorobenzene or o-dichlorobenzene with benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene by Tanaka et al. [374, 375].

Molar excess volumes for methylene bromide + pyridine + β-picoline, pyridine + β-picoline + cyclohexane, benzene + toluene + 1,2-dichloroethane, benzene + o-xylene + 1,2-dichloroethane and benzene + p-xylene + 1,2-dichloroethane have been measured dilatometrically at 308.15 K by Singh et al. [361]. The experimental results are positive over the whole range of composition for all the ternary mixtures.

Measurements of excess volumes, ultrasonic velocities and adiabatic compressibilities at 298.15 and 308.15 K have been made for binary liquid mixtures of 1,1,2,2-tetrachloroethane with benzene, toluene, p-xylene, acetone and cyclohexane and at 303.15 K for binary mixtures of 1,1,2,2-tetrachloroethane with pyridine, anisole, methyl ethyl ketone and 1,4-dioxane by Nath et al. [239, 241]. The values of $v^E$ have been found to be negative for all the binary systems except for 1,1,2,2-tetrachloroethane – cyclohexane system. The results indicate the existence of specific interaction of 1,1,2,2-tetrachloroethane with the aromatic hydrocarbons and acetone.

Excess volumes of mixing for binary mixtures of diethyl ether with toluene, o-, m- and p-xylene as a function of composition and temperature were determined
dilatometrically at 283.15, 293.15 and 303.15 K by Gupta et al. [110]. The values for the excess volume for mixtures are negative and depend on temperature.

The isentropic compressibility, excess volume, excess viscosity and excess molar Gibbs free energy for the activation of flow have been calculated from the experimental values of the speeds of sound and viscosities at 298.15 K for the mixtures of alkyl esters with α-, m- and p-xylene by Katyal et al. [163]. The parameter \( d \), of the Grunberg and Nissan expression has also been calculated. The results indicate the absence of specific molecular interactions.

Isentropic compressibilities, Rao's molar sound functions, molar refractions, excess isentropic compressibilities, excess molar volumes, viscosity deviations and excess Gibbs energies of activation of viscous flow for seven binary mixtures of tetrahydrofuran (THF) with cyclohexane, methylethylcyclohexane, \( n \)-hexane, benzene, toluene, \( p \)-xylene and propylnbenzene over the entire range of composition at 303.15 K have been derived from experimental densities, speeds of sound, refractive indices and viscosities by Oswal et al. [259].

Densities of the binary systems of \( p \)-xylene with ethyl acrylate, butyl acrylate, methyl methacrylate and styrene have been measured as a function of the composition at 298.15 K and atmospheric pressure, using an Anton Paar DMA 5000 oscillating U-tube densimeter by Peralta et al. [288]. The calculated excess volumes were correlated with the Redlich-Kister equation and with a series of Legendre polynomials.

Excess molar enthalpies and excess molar volumes of the binary systems propyl propanoate + \( o \)-xylene, propyl propanoate + \( m \)-xylene and propyl propanoate + \( p \)-xylene at the temperature 298.15 K and atmospheric pressure, over the whole composition range are reported by Perez et al. [289]. The excess magnitudes were correlated to a Redlich-Kister type equation.

The densities of \( o \)-xylene, or \( m \)-xylene, or \( p \)-xylene + dimethyl sulfoxide or cyclohexanone were measured at temperatures (293.15, 303.15, 313.15, 323.15, 333.15, 343.15, 353.15) K and atmospheric pressure by means of a vibrating-tube densimeter by Wang et al. [419, 420]. The \( V^c_m \) results were correlated using the
fourth-order Redlich–Kister equation, with the maximum likelihood principle being applied for the determination of the adjustable parameters.

The excess volumes and velocity of sound have been measured for the mixtures of pyrrolidin-2-one and aromatic hydrocarbons o-xylene, m-xylene, p-xylene and ethylbenzene over the entire range of composition at 303.15 K. $l^E$ values are negative for all the mixtures and vary in the order: o-xylene > ethylbenzene > m-xylene > p-xylene. The results have been analysed by using the well-known Prigogine–Flory–Patterson theory by Mehta et al. [215]. The $K^E$ is negative for all the systems over the entire range of composition and vary in the order o-xylene > m-xylene > ethylbenzene > p-xylene.

The relative permittivity in the ternary mixtures of acetylacetone with benzene + p-xylene has been measured at 303.16 K and 455 kHz frequency by Acharya et al. [3]. The Kirkwood–Frohlich linear correlation factor, excess molar polarization and excess Gibb’s free energy of mixing in these mixtures are calculated using the experimental value of relative permittivity on the basis of Winkelmann–Quitzsch equation. The study reveals that the nonpolar solvent benzene is dominant over p-xylene in the mixtures. The Redlich–Kister relation is used to estimate the ternary interaction parameters, which are in satisfactory agreement with the experimental data.

Experimental values of excess molar enthalpies at 298.15 K and excess molar volumes at 298.15–318.15 K for binary liquid mixtures of methyl methacrylate (MMA) + benzene, + toluene, + p-xylene, + cyclohexane and + diethers (diethyl, diisopropyl and dibutyl) are reported by George et al. [95]. The results show that besides the weakening of dipolar forces among ester molecules, specific but weak interactions of $n \cdots \pi$ and dipole–dipole types are significant in these mixtures (with an exception in MMA+cyclohexane).

The densities, dynamic viscosities, speeds of sound and relative permittivities for dibutyl ether + benzene, or toluene, or p-xylene have been measured at different temperatures over the whole composition range and at atmospheric pressure by George et al. [93]. The mixture viscosities have been correlated with semi empirical equations. Calculations of the speed of sound based on Nomoto’s equation have been
found to be close to experimental values for the three mixtures and at two
temperatures.

Excess molar volume data on mixing for binary mixtures of sulfolane with
toluene, o-xylene, m-xylene, p-xylene, ethylbenzene and 1,2,4-trimethyl benzene have
been measured over the entire composition range at 298.15 K and atmospheric
pressure in order to investigate interactions between molecules by Yu et al. [444]. A
vibrating tube density meter was used. All mixtures exhibit negative excess volumes
with a minimum which occurs approximately at $x = 0.5$. The experimental results
have been correlated using the Redlich–Kister equation and have been qualitatively
discussed.

Excess molar volumes and excess molar enthalpies of nitrobenzene + benzene
+ toluene, or + o-xylene, or + p-xylene ternary mixtures have been measured as a
function of composition dilatometrically and calorimetrically at the temperature
308.15 K by Kalra et al. [157]. The data obtained have been analysed in terms of the
Flory theory.

Densities, excess molar volumes, refractive indices and changes in refractive
index on mixing for ethyl acetate + benzene, or methylbenzene, or ethylbenzene, or
1,4-dimethylbenzene, or 1-methylethylbenzene, or 1,3-5-trimethylbenzene, or
1,1-dimethylethylbenzene have been determined at 298.15 K by Resa et al. [338]. The
excess molar volumes and changes in refractive index have been fitted to
Redlich–Kister polynomials.

Excess molar volumes have been measured by means of a continuous dilution
dilatometer for γ-butyrolactone + benzene, or toluene, or o-xylene, or m-xylene, or
p-xylene, or ethylbenzene, or styrene at 298.15 K by Wang et al. [421]. The $V'_m$
values are negative over the entire range of composition for all the binary mixtures.
The results were compared with the results for binary mixtures containing other polar
liquids and showed that the interactions between γ-butyrolactone molecules and
aromatic hydrocarbon molecules are very strong.

Molar excess Gibbs free energy of mixing values for 1-propanol or
2-propanol + benzene, toluene, o- m- or p-xylene at 298.15 K have been calculated by
the Barker method from vapour pressure data measured by a static method by
Gupta et al. [115]. The free energies of mixing for these binary systems are also predicted in terms of the Mecke-Kempter type of association model with a Flory contribution term using two interaction parameters. The predicted values agree reasonably well with the experimental values.

Excess volumes have been measured by means of a continuous-dilution dilatometer for \(n, n\)-dimethylacetamide or benzonitrile + benzene or toluene or \(o\)-xylene or \(m\)-xylene or \(p\)-xylene or ethylbenzene or styrene at the temperature 298.15 \(K\) by Haijun et al. [117, 118]. \(V^e_m\) values are negative over the entire range of composition for all the binary mixtures.

Excess molar volumes at 298.15 \(K\) are reported for the binary systems containing toluene, \(p\)-xylene or pseudo-cumene + 2-propanone, 2-butane, 2-pentane, 2-octane or 2-decanone by Francesconi et al. [86]. All experimental curves present negative excess volumes, with the sole exception of the pseudo-cumene + 2-propanone mixture. The experimental data are examined by an extended cell model.

Excess volume data for binary liquid mixtures of acetophenone with some substituted aromatic hydrocarbons have been measured dilatometrically as a function of composition at 303.15 \(K\) by Surendranath et al. [373]. The hydrocarbons include benzene, toluene, three isomeric xylenes, chlorobenzene, bromobenzene and nitrobenzene. The values of \(V^e_m\) were found to be negative in the mixtures of acetophenone with benzene, toluene, \(o\)-xylene, \(m\)-xylene, \(p\)-xylene and chlorobenzene and positive in the systems containing bromobenzene and nitrobenzene.

The excess volumes and enthalpies of mixing of binary mixtures of 1,2-dibromoethane with benzene, toluene, \(o\)-xylene, \(m\)-xylene and \(p\)-xylene have been measured experimentally over the whole composition range at 298.15 \(K\) by Spah et al. [364]. Qualitatively, the data have been explained on the basis of electron donor/acceptor interactions between 1,2-dibromoethane and the aromatic hydrocarbons and also on the basis of the loss of favourable orientational order of the pure components.

Excess volumes at 303.15 \(K\) have been measured for binary liquid mixtures of \(n\)-pentylacetate with \(n\)-hexane, \(n\)-octane, \(n\)-hexadecane, isooctane, cyclopentane,
cyclohexane, methylcyclohexane, benzene, toluene, \( p \)-xylene or ethylbenzene by Awwad et al. [18]. Excess volume values are positive for all mixtures examined except for \( n \)-pentylacetate with \( p \)-xylene or with ethylbenzene. For \( n \)-pentylacetate with toluene, the \( V^E \) curve has three extrema: \( V^E \) values are positive in both the dilute regions and negative in the mole fraction range of toluene from 0.2 to 0.8.

Excess molar volumes at 298.15 K are reported for seven binary mixtures of \( n \)-methylpyrrolidone with benzene, toluene, ethylbenzene, \( o \)-xylene, \( m \)-xylene, \( p \)-xylene and mesitylene by Mashhadani et al. [208]. The excess molar volumes are negative over the whole mole fraction range. The results are discussed in terms of the complex-forming ability. The experimental results are compared with values predicted from the Flory theory and found to be in poor agreement.

Excess volumes of benzene +, toluene +, ethylbenzene +, \( o \)-xylene +, \( m \)-xylene +, \( p \)-xylene + and mesitylene + \( n \)-formylmorpholine were obtained from precise density measurements at 298.15 K by Awwad et al. [19]. The excess volumes are negative over the whole mole-fraction range. The significance of these results is discussed in terms of the complex-forming ability of the components.

Molar excess volumes and molar excess enthalpies of binary methylenebromide + benzene, + toluene and + \( o \)-, + \( m \)- and + \( p \)-xylene mixtures have been determined at 298.15 and 308.15 K by Singh et al. [360]. The results suggest that these mixtures are characterized by specific interactions between the components.

A semi-continuous dilatometer for measuring excess volume is described. Excess volumes of \( p \)-xylene + \( n \)-hexane + \( n \)-octane, + \( n \)-decane, + \( n \)-dodecane, + \( n \)-tetradecane and + \( n \)-hexadecane have been measured at 298.15 K as a function of composition by Alonso et al. [6].

Excess enthalpies, excess volumes and excess Gibbs free energies have been measured for benzene + \( p \)-xylene over the entire composition range at 288.15, 298.15, 308.15, 313.15 and 318.15 K by Ott et al. [274, 275]. \( V^E \) was obtained with a Sodev vibrating-tube densimeter, \( T^E \) with a Picker flow micro calorimeter and \( G^E \) was calculated from solid + liquid phase equilibria measurements. Measurements were also made of the heat capacity of liquid \( p \)-xylene as a function of temperature using the heat-capacity unit of the Picker flow micro calorimeter.
Excess volumes of mixing for binary mixtures of 1,2-dichloroethane with benzene, toluene, o-, m- and p-xlenes have been determined at 308.15 K over the complete composition range by Nigam et al. [249]. The excess volumes are positive for all these mixtures and varies in the order m-xylene > o-xylene > p-xylene > benzene > toluene.

Excess volumes for tetrachloroethylene + benzene, + toluene, + p-xylene, + cyclohexane and + carbon tetrachloride have been measured dilatometrically at 303.15 K by Rastogi et al. [315]. $f^E$ was found to be positive for tetrachloroethylene + benzene, + toluene, + cyclohexane and negative for tetrachloroethylene + p-xylene. For tetrachloroethylene + carbon tetrachloride, the $f^E$ is found to be positive at low mole fractions of C2Cl4 and negative at high mole fractions.

The viscosities of the mixtures of 1,2-dibromoethane + cyclohexane, + benzene, + toluene, + o-xylene, + m-xylene and + p-xylene have been measured at 298.15 and 308.15 K as a function of composition by Dhillon et al. [64]. The viscosity data have been analysed in the light of approaches developed by Hind and Grunberg. Using Eyring kinematic scheme, the viscosity data have been employed to calculate activation energies of flow.

A dilution dilatometer for determining excess volumes at high dilutions of ethanol in the range $x(C_2H_5OH) = 1 \times 10^{-3}$ to $8 \times 10^{-2}$, is described by Marsh et al. [202]. Excess volumes for ethanol + cyclohexane, + n-hexane, + benzene, + carbon tetrachloride, + cyclopentane and + p-xylene are reported at temperatures from 283.15 to 318.15 K. The excess volumes are highly unsymmetrical, with the function $f^E/\alpha(1-\alpha)$ showing a very rapid increase at low mole fractions of ethanol. The limiting partial molar excess volumes of ethanol in the various non-polar solvents show a similar trend to that observed for the limiting partial molar excess enthalpy of ethanol in the same solvents.

Excess enthalpies and excess volumes were measured at 25 °C for the systems o-xylene + m-xylene, o-xylene + p-xylene and m-xylene + p-xylene by Lam et al. [176]. Analyses of the results in terms of the theories of Flory and of Barker are described.

Excess enthalpies and volumes of the four binary systems formed by mixing toluene with benzene, o-xylene, m-xylene and p-xylene were measured at 25 °C by
Murakami et al. [231]. These results along with similar results for benzene + isomeric xylene systems were analyzed in terms of the theories of Flory and of Barker. Each approach provides a reasonable, but limited, basis for correlation of the results.

6.2 Predictive Methods

6.2.1 Excess Molar Volume by Flory’s statistical theory

Flory et al. [1, 81, 82] have obtained a relatively simple equation of state, adequate for pure liquids and for liquid mixtures whose molecular components vary in size and shape. The theory assumes that the molecules are made up of equal segments, the effective number being \( r \). Each segment has \( S \) intermolecular contact sites capable of interacting with neighbouring sites. In the liquid state, the volume per mole of segments is denoted by \( v \) and the corresponding “hard core” or “characteristic” volume by \( v^* \). The molar values of these are indicated by:

\[
V = r \, v \tag{6.4}
\]

and

\[
V^* = r \, v^* \tag{6.5}
\]

The reduced volume of a mole of segment is:

\[
\tilde{v} = v / v^* = V / V^* \tag{6.6}
\]

Assuming a Van der Waal’s relationship for the dependence of the energy on volume \( (E = -\sqrt{v}) \), an equation of state has been obtained as a function of the reduced parameters:

\[
\tilde{p} \, \tilde{v} / \tilde{T} = \left[ \left( \tilde{v}^{1/3} / (\tilde{v}^{1/3} - 1) \right) - (1 / \tilde{v}^{1/3}) \right] \tag{6.7}
\]

where

\[
\tilde{v} = V / V^* , \quad \tilde{T} = T / T^* , \quad \tilde{p} = P / P^* \]

Here \( P^* \), \( V^* \) and \( T^* \) are the characteristic parameters. At \( p = 0 \), Eq. 6.7 becomes:

\[
\tilde{T} = (\tilde{v}^{1/3} - 1) / \tilde{v}^{4/3} \tag{6.8}
\]

By differentiating Eq. 6.7 with respect to \( \tilde{T} \) at constant \( p \), one obtains:
\[(a T)^{-1} = \left[\frac{(4/3) - \nu^{1/3}}{\nu^{1/3} - 1}\right]\]

or

\[(\nu^{1/3} - 1) = (a T / 3) (1 + a T)^{-1} \quad (6.9)\]

On differentiating Eq. 6.7 with respect to \( \hat{p} \) at constant \( T \) and extrapolating to \( p = 0 \), one gets

\[P^* = \gamma T \hat{\nu}^2\]

\[= \left(\alpha / K_T\right) T \hat{\nu}^2 \quad (6.10)\]

where \( K_T \) and \( \gamma \) are the isothermal compressibility and the thermal pressure coefficient respectively. \( \alpha \), the thermal expansion coefficient, is defined as:

\[\alpha = -(1/V) (\partial V / \partial T)_p = -(1/p) [(\rho_1 - \rho_2)/(T_1 - T_2)] \quad (6.11)\]

where \( \rho_1 \) and \( \rho_2 \) represent the densities at temperatures \( T_1 \) and \( T_2 \) respectively.

**Binary mixtures**

For a binary mixture, the molecular segment is defined in correspondence for the two species such that \( r_1 \) and \( r_2 \) are in the ratio of the respective molar core volumes \( V_1^* \) and \( V_2^* \) i.e. \( r_1 / r_2 = V_1^* / V_2^* \). Similarly \( S_1 \) and \( S_2 \) are the ratio of the molecular surface areas of contact per segment.

\[S_1 / S_2 = (V_2^* / V_1^*)^{1/3} \quad (6.12)\]

It can be shown that the reduced temperature of a mixture of two species of molecules at mole fraction \( x_i \) is given by:

\[T = (\phi_1 P_1^* T_1 + \phi_2 P_2^* T_2) / (\phi_1 P_1^* + \phi_2 P_2^* - \phi_2 \theta_2 X_{12}) \quad (6.13)\]

where the segment fractions \( \phi_1 \) and \( \phi_2 \) are defined by:

\[\phi_2 = 1 - \phi_1 = x_2 / [x_2 + x_1 (r_1 / r_2)] \quad (6.14)\]

and the site fraction \( \theta_2 \) by:

\[\theta_2 = x_2 / [\phi_2 + \phi_1 (S_1 / S_2)] \quad (6.15)\]
The parameter $X_{ni}$ can be treated as an adjustable parameter and it is determined from the experimental value of an excess quantity in the bulk phase, for a particular mixture.

The excess molar volume is related to the reduced volume by the equation:

$$\tilde{\nu} - \tilde{\nu}^0 = \tilde{\nu}^E = \frac{V^E}{(x_1v'_1 + x_2v'_2)}$$

(6.16)

and $\tilde{\nu}^0$ is the ideal reduced volume and is given by:

$$\tilde{\nu}^0 = \phi_1\tilde{\nu}_1 + \phi_2\tilde{\nu}_2$$

(6.17)

and $\tilde{\nu}^E$ can be written to adequate approximation as:

$$\tilde{\nu}^E = \left(\frac{\partial \tilde{\nu}}{\partial T}\right)(\tilde{T} - \tilde{T}^0) = \left(\tilde{\nu}^0\right)^{7/3}[(4/3) - (\tilde{\nu}^0)^{1/3}]^{-1}(\tilde{T} - \tilde{T}^0)$$

(6.18)

where

$$\tilde{T}^0 = [\tilde{\nu}^{0^{7/3}} - 1]^{4/3}$$

(6.19)

Therefore, the expression for $V^E$ is written as:

$$V^E = \left[(\tilde{\nu}^0)^{7/3} / \left\{(4/3) - (\tilde{\nu}^0)^{1/3}\right\}\right] (x_1v'_1 + x_2v'_2) \times$$

$$\left\{\left[\phi_1\tilde{\nu}'_1 + \phi_2\tilde{\nu}'_2\right] / \left[\phi_1\tilde{\nu}'_1 + \phi_2\tilde{\nu}'_2 - \phi_2X_{12}\right]\right\} - \left\{((\tilde{\nu}^0)^{1/3} - 1) / (\tilde{\nu}^0)^{4/3}\right\}$$

(6.20)

### 6.2.2 Viscosity

A large number of correlations have been suggested to estimate liquid viscosities when no experimental data are available. Binary liquid mixture viscosities have been represented in terms of pure component viscosity and a parameter due to interaction between the mixture constituents. Out of a large number, a few are reliable and most generally used are discussed here. In many cases, large errors are noted and it is usually recommended that experimental values should be sought before resorting to estimation or predictive techniques.

**Orrick and Erbar Method**

This method [335] employs a group contribution technique to estimate $A$ and $B$ in the following equation:

$$212$$
The group contributions for obtaining $A$ and $B$ are given for liquids [335]. For liquids that have a normal boiling point below 293.15 K, the value of $\rho$ at 293.15 K is used and for liquids whose freezing point is above 293.15 K, $\rho$ at the melting point should be employed. Compounds containing nitrogen or sulphur cannot be treated. Orrick and Erbar tested this method for 188 organic liquids. The errors varied widely but they reported an average deviation of 15 %.

**Van Velzen, Cardozo and Langenkamp’s method**

In an unusually detailed study of the effect of structure on liquid viscosities, Van Velzen et al. [411, 412] proposed a modification of Eq. 6.22 given under:

$$
\ln(\eta_i / \rho, M) = A + B / T
$$

(6.21)

where

$\eta_i$ = liquid viscosity, cP

$\rho$ = liquid density at 20° C, g.cm$^{-3}$

$M$ = molecular weight

$T$ = temperature, K

And $B$ and $T_0$ are related to the structure. To determine these parameters, one must first find the equivalent chain length $N^*$, where

$$
N^* = N + \Sigma \Delta N_i
$$

(6.24)

$N$ is the actual number of carbon atoms in the molecule and $\Delta N$ represents structural contributions [335]. If the structural or functional group $\Delta N_i$ appears $n_i$
times in the molecule, $\eta$, corrections must be added. In the tabulation of $\Delta N$, contributions, some entries are to be used every time the functional group appears; other entries represent additional corrections to be used to modify the basic group contribution.

**Grunberg and Nissan Method [335]**

Grunberg and Nissan suggested the following expression for a binary mixture:

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 d$$

(6.25)

where $x$ is the liquid mole fraction and $d$ is an interaction parameter which is a function of the components 1 and 2 as well as the temperature (and, in some cases, the composition). This relation has probably been more extensively examined than any other liquid mixture viscosity correlation. Isdale [146] has presented the results of a very detailed testing using more than 2000 experimental mixture datum points. When the interaction parameter was regressed from experimental data, non associated mixtures and many mixtures containing alcohols, carboxylic acids and ketones were fitted satisfactorily. The overall root mean square deviation for the mixtures tested was 1.6 %.

**Teja and Rice Method [383, 384]**

Based on a corresponding states treatment for mixture compressibility factors [385, 386], Teja and Rice proposed an analogous form for liquid mixture viscosity:

$$\ln(\eta_m \epsilon_m) = \ln(\eta \epsilon)^{y} + \left[ \ln(\eta \epsilon)^{y} - \ln(\eta \epsilon)^{y'} \right] \left[ (\omega_m - \omega^{y})/(\omega^{y} - \omega^{y'}) \right]$$

(6.26)

where the subscripts $r_1$ and $r_2$ refer to two reference fluids, $\eta$ is the viscosity, $\omega$ the acentric factor and $\epsilon$ is an energy potential parameter defined as:

$$\epsilon = V_\epsilon^{2/3} / (T_\epsilon M)^{1/2}$$

(6.27)

The variable of composition is introduced in four places: the definitions of $\omega_m$, $V_\epsilon$, $T_\epsilon$ and $M_m$. The rules suggested by the authors to compute these mixture parameters are:
where \( \psi_{ij} \) is an interaction parameter of order unity which must be found from experimental data. It is important to note that, in the use of Eq. 6.26 for a given mixture at a specified temperature, the viscosity values for the two reference fluids \( \eta^{(e)} \) and \( \eta^{(v)} \) are to be obtained not at \( T \), but at a temperature equal to \( T [(T_c)^{v \backslash c} / T_c] \) for \((r_1)\) and \(T [(T_c)^{v \backslash c} / T_c] \) for \((r_2)\).

The reference fluids \((r_1)\) and \((r_2)\) may be chosen different from the actual components in the mixture. It is normally advantageous to select them from the principal components in the mixture. In fact, for a binary of 1 and 2, if \((r_1)\) is selected as component 1 and \((r_2)\) as component 2, then, by virtue of Eq. 6.31, Eq. 6.26 simplifies to:

\[
\ln (\eta_{w,m}) = x_1 \ln(\eta_{e}^{(1)}) + x_2 \ln(\eta_{e}^{(2)})
\]  

(6.34)

The authors claim good results for many mixtures ranging from strictly non-polar to highly polar aqueous-organic systems. For non-polar mixtures, errors averaged about 1 percent. For non-polar–polar and polar–polar mixtures, the average rose to about 2.5 percent.
Przedziecki Method [305]

The authors have proposed the following equation for predicting the viscosity:

\[
\eta_L = \frac{\nu}{[E(V - V_0)]} \tag{6.35}
\]

where

\[\eta_L = \text{liquid viscosity, } cP\]
\[V = \text{liquid molar volume, } cm^3.mol^{-1}\]

and the parameters \(E\) and \(V_0\) are defined below.

\[E = -1.12 + \left[ \frac{V_c}{(12.94 + 0.10M - 0.23P_c + 0.0424 T_f - 11.58(T_f / T_c))} \right] \tag{6.35a}\]

\[V_0 = 0.0085 \omega T_c - 2.02 + \left[ \frac{V_m}{(0.342(T_f / T_c) + 0.894)} \right] \tag{6.35b}\]

where

\[T_c = \text{critical temperature, } K\]
\[P_c = \text{critical pressure, bar}\]
\[V_c = \text{critical volume, } cm^3.mol^{-1}\]
\[M = \text{Molecular weight, } g.mol^{-1}\]
\[T_f = \text{freezing point, } K\]
\[\omega = \text{acentric factor}\]
\[V_m = \text{liquid molar volume at } T_f, \text{ } cm^3.mol^{-1}\]

The authors recommend that the two liquid volumes i.e. \(V_m\) and \(V\) should be estimated from \(T_f\) and \(T\) by Gunn-Yamada method [109]. In this procedure, one accurate value of \(V\) is required in the temperature range of applicability of Eq. 6.35. This datum point was defined as \(V^*\) at \(T^*\); then at any other temperature \(T\),
\[ V(T) = \left[ \frac{f(T)}{f(T^*)} \right] V^* \]  

(6.36)

where

\[ f(T) = H_1 (1 - \omega H_2) \]  

(6.36a)

\[ H_1 = 0.33593 - 0.33953 T_r + 1.51941 T_r^2 - 2.02512 T_r^3 + 1.11422 T_r^4 \]  

(6.36b)

\[ H_2 = 0.29607 - 0.09045 T_r - 0.04842 T_r^2 \]  

(6.36c)

The Eq. 6.35 was employed to estimate liquid viscosities for various compounds. Large errors were noted for alcohols whereas for other compounds, the errors varied widely. Large errors were normally noted at low temperatures. This problem was emphasized by Luckas and Lucas \cite{192}, who suggested that Eq. 6.35 should not be used below \( T_r \) values of about 0.55.

**Letsou & Stiel Method**

Letsou and Stiel \cite{179} proposed for saturated liquids,

\[ \eta_{sSL} \xi = (\eta_{sSL} \xi)^{(0)} + \omega (\eta_{sSL} \xi)^{(1)} \]  

(6.37)

where the parameters \((\eta_{sSL} \xi)^{(0)}\) and \((\eta_{sSL} \xi)^{(1)}\) are functions only of reduced temperature and \( \xi \) is given as:

\[ \xi = 0.176 \left[ T_r / (M^2 P_s^t) \right]^{0.6} \]  

(6.37a)

Letsou and Stiel have tabulated these functions; but to a close approximation, from \( 0.76 < T_r < 0.98 \) they can be expressed as:

\[ (\eta_{sSL} \xi)^{(0)} = 10^{-3} (2.648 - 3.725 T_r + 1.309 T_r^2) \]  

(6.37b)

\[ (\eta_{sSL} \xi)^{(1)} = 10^{-3} (7.425 - 13.39 T_r + 5.933 T_r^2) \]  

(6.37c)

The units have been converted to yield \( \eta_{sSL} \) in centipoises even though \( \xi \) from Eq. 6.37a has the dimensions of micropoises. This correlation was developed from data on only 14 liquids, mostly simple hydrocarbons. The authors report average
errors of about 3 percent for most materials up to \( T_r \approx 0.92 \); larger errors were found as the critical point was approached. In general, however, the technique is a simple one to use and yields estimates that are often surprisingly good.

**Liu and Wang Model [183]**

A revised free-volume model of liquids was proposed by Liu [182], from which an equation to correlate liquid viscosity for a pure substance was obtained [445].

\[
\phi = B_0 (\tilde{V} - 1) \exp(C / VRT) \quad (6.38)
\]

where \( \phi \) is the fluidity (the reciprocal of viscosity \( \eta \)), \( \tilde{V} \) the reduced volume given as:

\[
\tilde{V} = V / V_o \quad (6.38a)
\]

where \( V_o \) is a parameter describing molecular volume and \( B_0 \) and \( C \) are constants for the substance of interest. Eq. 6.38 satisfactorily represents viscosities for 83 substances, with 1044 data points, including those for polar, non-polar, organic and inorganic compounds with an overall deviation of 1.3 percent.

For a mixture, Eq. 6.38 can be written as:

\[
V_m \ln \phi_m = B'_m V_m + V_m \ln(\tilde{V}_m - 1) + C_m / RT \quad (6.39)
\]

with \( B' = \ln B_0 \). Apparently, for a pure substance \( i \), Eq. 6.38 becomes:

\[
V_i \ln \phi_i = B'_i V_i + V_i \ln(\tilde{V}_i - 1) + C_i / RT \quad (6.40)
\]

Then, after rearrangement,

\[
\ln \phi_m = \sum_i \theta_i \ln \phi_i + B'_m V_m - \sum_i \theta_i B'_i + \ln[(\tilde{V}_m - 1) / \Pi_i \tilde{V}_i (\tilde{V}_i - 1)^{\theta_i}] + (C_m - \sum_i x_i C_i) / V_m RT \quad (6.41)
\]

where \( \theta_i \) is defined as:

\[
\theta_i = x_i V_i / V_m \quad (6.41a)
\]

\[
B'_m = \sum_i \theta_i B'_i \quad (6.41b)
\]
For binary systems, the mixing rule for $C_m$ is:

$$C_m = \sum_i \sum_j x_i x_j C_{ij} = x_1^2 C_1 + 2 x_1 x_2 C_{12} + x_2^2 C_2 \quad (6.41c)$$

From Eqs. 6.41-6.41c, the working equation is obtained:

$$\ln \phi_m = \sum_i \ln \phi_i + \ln \left( \frac{[\tilde{V}_m - 1]}{\Pi_i (\tilde{V}_i - 1)^{\beta_i}} \right) + x_1 x_2 G_{12} / V_m RT$$

$$= \ln \left( \frac{Z_0 \ln \phi_m}{\left( \frac{V_m - 1}{n} \right)} \right)$$

$$= x_1 x_2 G_n / V_m RT$$

$$= \ln \left( \frac{Z_0 \ln \phi_m}{\left( \frac{V_m - 1}{n} \right)} \right)$$

$$= \sum_i \theta_i \ln \phi_i + \ln \left( \frac{[\tilde{V}_m - 1]}{\Pi_i (\tilde{V}_i - 1)^{\beta_i}} \right) + x_1 x_2 G_{12} / V_m RT$$

where $G_{12} = 2 C_{12} - C_1 - C_2$, $\tilde{V}_m = V_m / V_{\phi_m}$

(6.42a)

The mixing rule for $V_{\phi_m}$ is given by:

$$V_{\phi_m} = \sum_i \sum_j x_i x_j V_{\phi_i} \quad (6.43)$$

The combining rule for $V_{\phi_i}$ is:

$$V_{\phi_i} = (1 - k_{ij}) \left( V_{\phi_i}^{1/3} + V_{\phi_j}^{1/3} \right) / 8 \quad (6.44)$$

where $k_{ij}$ as well as $G_{12}$ in Eq. 6.42 are the binary interaction parameters in this model.

For a symmetric system whose constituent molecules are similar in size and polarities, i.e., the interaction between molecules do not differ considerably, both the parameters $k_{12}$ and $G_{12}$ can be consequently taken as zero. Therefore a predictive model for the binary systems can be written as:

$$\ln \phi_m = \sum_i \theta_i \ln \phi_i + \ln \left( \frac{[\tilde{V}_m - 1]}{\Pi_i (\tilde{V}_i - 1)^{\beta_i}} \right)$$

(6.45)

**McAllister's Technique**

McAllister [210] adopted a semi theoretical Eyring approach for finding liquid mixture viscosity. In this case, the interaction between the layers of molecules in the velocity gradient involves activated jumps of molecules between layers. A molecule moving in this manner is treated as if it were undergoing a chemical reaction and pushing or squeezing of these moving particles require that it overcomes the potential (free)- energy barrier $\Delta G^*$ in the process.
The McAllister’s equation is as given under:

\[
\ln \nu = x_1^1 \ln \nu_1 + 3x_1^2 x_1 \ln \nu_{12} + 3x_1 x_1^2 \ln \nu_{21} + x_1^3 \ln \nu_2 - \ln (x_1 + x_2 M_2 / M_1) \\
+ 3x_1^2 x_2 \ln [(2 + M_2 / M_1) / 3] + 3x_1 x_2^2 \ln [(1 + 2M_2 / M_1) / 3] \\
+ x_2^3 \ln (M_2 / M_1)
\]  

(6.46)

For the mixture,

\[
\nu = (hN / M_{avg}) e^{M^{*}/RT} 
\]

(6.46a)

For pure component 1,

\[
\nu_1 = (hN / M_1) e^{AG_1^{'} / RT} 
\]

(6.46b)

\[
\nu_{12} = (hN / M_{12}) e^{AG_{12}^{'} / RT} 
\]

(6.46c)

\[
\nu_{21} = (hN / M_{21}) e^{AG_{21}^{'} / RT} 
\]

(6.46d)

\[
M_{12} = (2M_1 + M_2) / 3 
\]

(6.46e)

\[
M_{21} = (M_1 + 2M_2) / 3 
\]

(6.46f)

where

- \( \nu \) = kinematic viscosity, stoke or centistoke
- \( M \) = molecular weight
- \( x \) = mole fraction in the liquid phase
- \( h \) = Planck constant
- \( N \) = Avogadro number
- \( \Delta G \) = molal free energy of activation for viscosity, cal/mol

**Wedlake and Ratcliffe Method [424]**

The ideal viscosity of a mixture is first defined by:-

\[
(\ln \eta)_{ideal} = \sum x_i \ln \eta_i 
\]

(6.47)

Real mixtures deviate from ideality, giving rise to an excess quantity \( \beta \):

220
\[ \ln \eta - (\ln \eta)_{obs} = (\ln \eta)^\delta = \beta \] (6.48)

This excess is attributed to two causes. Firstly, it is assumed that interactions between the various groups making up the molecules give rise to a “group contribution” \( \beta^G \). Secondly, the manner in which the groups are joined together to form the molecules is assumed to generate a “structural contribution”, \( \beta^S \). The effects are assumed additive so that:

\[ \beta = \beta^S + \beta^G \] (6.49)

Furthermore, all \( \beta^s \)'s are split into the individual contributions of each molecular species \( i \). By definition:

\[ \beta_i = \left( \frac{\partial (\ln \eta) / \partial \eta_i}{\partial \eta} \right)_{c, e} - \ln \eta_i \] (6.50)

and

\[ \beta_i = \beta^S_i + \beta^G_i \] (6.50a)

which ensures

\[ \beta = \sum_i x_i \beta_i \] (6.51)

and

\[ \beta^G = \sum_i x_i \beta^G_i \] (6.52)

\[ \beta^S = \sum_i x_i \beta^S_i \] (6.53)

The structural contribution \( \beta^S_i \) is taken as:

\[ \beta^S_i = a_s(N_i - \bar{N})^2 / \bar{W} \] (6.53a)

So that

\[ \beta^S = (a_s / \bar{W}) \sum_i x_i (N_i - \bar{N})^2 \] (6.54)

where the average molecular weight, \( \bar{W} \) and average number of groups, \( \bar{N} \), are defined by:

\[ \bar{W} = \sum_i x_i W_i \] (6.54a)

\[ \bar{N} = \sum_i x_i N_i \] (6.54b)

221
The group contribution $\beta_i^{G}$ is expressed in terms of the contributions, $B_k$, of the individual groups making up molecules $i$:

$$\beta_i^{G} = \sum_k N_{ki} (B_k - B_k^*)$$ (6.55)

where

$N_{ki} =$ number of groups of type $k$ in molecular species $i$.

The standard state value $B_k^*$ is the value of $B_k$ at a group composition corresponding to pure molecular $i$ and must be included since $\beta_i = 0$ for pure $i$.

Here

$a =$ group solution model parameters

$B_k =$ individual group contribution of group $k$

$n_i, n_j =$ number of moles of components $i$ and $j$ in system

$N_i =$ total number of groups in molecular species $i$

$W_i =$ molecular weight of component $i$

$\beta =$ excess viscosity property

**Powell and Eyring Method [296]**

A shearing force, $f$, when applied across the two layers of molecules, causes the flow to take place, as a single molecule squeezes past its neighbours and drops into a vacant equilibrium position (a hole) at a distance, $\lambda$, from its original position. Fluidity or reciprocal viscosity is defined as the difference in velocity per unit shear:

$$\phi = 1/\eta = \Delta u / \lambda, f$$ (6.56)

where

$f =$ shearing force

$\Delta u =$ difference in velocity

The difference in velocity is given by the distance a molecule moves in one
jump multiplied into the net rate of jumping given as:

$$\Delta u = \lambda (k'_f - k'_b)$$ \hspace{1cm} (6.57)

where

$$\lambda = \text{distance between equilibrium positions}$$

$$k'_f, k'_b = \text{specific reaction rate in forward direction, in backward direction}$$

If the free energy of activation for a molecule jumping under no external force is $\Delta F^\dagger$, the forward process is helped by the work due to a force $f$ acting on an area $\lambda_2 \lambda_3$ through a distance $\lambda / 2$ and the reverse process is hindered by the same amount, so that:

$$k'_f = \frac{kT}{h} e^{-\Delta F^\dagger / RT} \left( e^{+\beta f \lambda_2 \lambda_3} \right)$$ \hspace{1cm} (6.57a)

$$k'_b = \frac{kT}{h} e^{-\Delta F^\dagger / RT} \left( e^{-\beta f \lambda_2 \lambda_3} \right)$$ \hspace{1cm} (6.57b)

where

$$h = \text{Planck constant}$$

$$k = \text{Boltzmann constant, } R / N$$

$$\lambda_1, \lambda_2, \lambda_3 = \text{intermolecular distances}$$

$$\Delta F^\dagger = \text{free energy change of activation}$$

Upon combining Eqs. 6.56 – 6.57b and expanding the second exponentials, the viscosity equation is obtained in its final form:

$$\phi = \frac{1}{\eta} = (\lambda^2 \lambda_2 \lambda_3 / \lambda_1 h) e^{-\Delta F^\dagger / RT}$$ \hspace{1cm} (6.58)

To a close approximation, the factor involving $\lambda$’s is simply the volume of a molecule and Eq. 6.58 takes the more usable form:

$$\phi = \frac{(V / Nh)}{e^{-\Delta F^\dagger / RT}}$$ \hspace{1cm} (6.59)

$$= \frac{(V / Nh)}{e^{\Delta F^\dagger / RT}}$$ \hspace{1cm} (6.59a)
where

\[ N = \text{Avogadro number} \]
\[ V = \text{molal volume} \]
\[ \Delta S^1 = \text{entropy change of activation} \]
\[ \Delta H^1 = \text{heat change of activation} \]

Correlation with Thermodynamic Properties: According to this model of the flow process, some of the same bonds are broken in flow as in vaporisation; however, the flowing molecule does not gain the entropy of the expansion into the vapor, neither does it have charged against it the work \( RT \) per mole of expansion against the atmosphere. The thermodynamic property with which the free energy of activation is to be correlated is then:

\[ \Delta F_{vap} + T\Delta S_{vap} - RT = \Delta E_{vap} \tag{6.60} \]

where

\[ \Delta F_{vap} = \text{free energy change of vapourisation} \]
\[ \Delta S_{vap} = \text{entropy change of vapourisation} \]
\[ \Delta E_{vap} = \text{energy change of vapourisation} \]

The result may be used as an empirical formula to predict viscosities from heats of vaporisation:

\[ \eta = \left( \frac{Nh}{V} \right) e^{\Delta S_{vap}/2.45RT} \tag{6.61} \]

**Katti and Chaudhri Method [162]**

From the Powell and Eyring model [296] for the viscosity of a pure liquid:

\[ \eta = \left( \frac{\lambda}{\alpha} \right)^2 \left( \frac{hN}{V} \right) e^{f/RT} \tag{6.62} \]

\( \eta \) = the absolute viscosity

\( \lambda \) = the distance between the adjacent layers of the molecules

\( \alpha \) = the distance through which the shearing force acts
the molar volume

\( h \) = the Planck’s constant

\( N \) = the Avagadro’s number

\( f \) = the molar free energy of activation of flow

Eq. 6.62 can be written as:

\[
\frac{f}{RT} = \ln \left( \frac{\eta V}{hN} \left( \alpha/\lambda \right)^2 \right)
\]

(6.63)

If for the mixture one assumes:

\[
\frac{f_i}{RT} = x_i \left( \frac{f_i}{RT} \right) + x_2 \left( \frac{f_2}{RT} \right)
\]

(6.64)

and

\[
\ln(\alpha_i/\lambda_i) = x_i \ln(\alpha_i/\lambda_i) + x_2 \ln(\alpha_i/\lambda_2)
\]

(6.65)

\[
\ln \eta_i V_i = x_i \ln \eta_i V_i + x_2 \ln \eta_2 V_2
\]

(6.66)

However, for regular solutions, \( f_i \) would not be a linear function of \( f_i \) and \( f_2 \). Instead there would be an additional term \( W \) given by the relation:

\[
\frac{f_i}{RT} = x_i \ln(f_i/RT) = x_i \ln(f_2/RT) + x_2(W/RT)
\]

(6.67)

and defined as the interaction energy for the activation of flow. Eq. 6.66 then takes the form:

\[
\log \eta_i V_i = x_i \log \eta_i V_i + x_2 \log \eta_2 V_2 + x_2(W_{i\text{mix}}/RT)
\]

(6.68)

where \( W_{i\text{mix}} \) is calculated at equimolar concentration for each system:

\[
(\Delta \log \eta_i V_i)_{\text{exp}} = \log \eta_i V_i - x_i \log \eta_i V_i - x_2 \log \eta_2 V_2
\]

(6.69)

**Polynomial Equation**

In addition to above models, the viscosity can be fitted into following type of polynomial equation:

\[
\eta = A_1 + A_2 x + A_3 x^2 + A_4 x^3
\]

(6.70)

The constants of the above polynomial equation can be determined by the method of least squares.
6.2.3 Calculation of ultrasonic velocity using empirical relations

Free Length theory

Jacobson [147] has obtained an empirical equation:

\[ u L_f \rho^{1/2} = K \] (6.71)

or

\[ L_f (K \rho)^{1/2} = K \] (6.71a)

between ultrasonic velocity \( u \) and free length \( L_f \) in a liquid or a liquid mixture, where \( K \) is a temperature dependent constant and \( \rho \) is the experimental density. The intermolecular free length in liquids has been defined by:

\[ L_f' = 2V_a / Y \] (6.72)

where \( V_a \) is the available volume and \( Y \), the total molecular surface in one mole is given by:

\[ Y = (36\pi N V_a^3)^{1/3} \] (6.73)

\( V_a \) and \( V_a \) parameters are calculated using equation:

\[ V_a = V(1 - (T/T_c))^{3/4} \] (6.73a)

\[ V_a = V - b = V - SB \] (6.73b)

where \( S \) is the collision factor so that \( SB \) corresponds to the excluded volume \( b \). The value of \( b \) is related to the critical volume by \( b = V_c / 4 \).

Employing the free length \( L_f' \) and surface areas per mole \( Y \) of pure liquids, the free length in the mixture \( L_f'(mix) \) has been calculated from the relation:

\[ L_f'(mix) = 2(V - \sum x_i V_{a,i}) / \sum x_i Y_i \] (6.74)

and \( u \), by substituting \( L_f'(mix) \) values in Eq. 6.71.
Junjie’s expression

Zhang Junjie [216] has obtained the following equation for ultrasonic velocities in binary liquid mixtures:

\[
u = \frac{[(x_1 M_1 / \rho_1) + (x_2 M_2 / \rho_2)]}{\sqrt{[(x_1 M_1 + x_2 M_2)^{1/2}(x_1 M_1 / \rho_1 u_1^2) + (x_2 M_2 / \rho_2 u_2^2)]^{1/2}}}
\] (6.75)

using the following equations:

\[
u^2 = (-\rho / V) \left( \frac{\partial V}{\partial P} \right)
\] (6.76)

\[
V = \frac{(x_1 M_1 + x_2 M_2)}{\rho}
\] (6.77)

\[
V^k = V - (x_i V_i + x_2 V_2)
\] (6.78)

\[
V_i = M_i / \rho_i
\] (6.79)

\[
V_2 = M_2 / \rho_2
\] (6.80)

Excess molar volumes and its derivatives have been neglected in deriving the Eq. 6.75. This equation is used for computing \( u \) for the binary mixtures.

Nomoto’s relation

Nomoto [216] has obtained a relation for the calculation of ultrasonic velocity by assuming the linearity of the molecular ultrasonic velocity as:

\[
R = x_1 R_1 + x_2 R_2
\] (6.81)

where Rao’s constant \( R \) is related to the molecular weight \( M \) and density \( \rho \) by:

\[
R_i = M_i u_i^{1/3} / \rho_i = V_i u_i^{1/3}
\] (6.82)

In the case of mixtures, \( R \) can be written as:

\[
R_{mix} = \frac{\bar{M}}{\rho} u^{1/3}
\] (6.83)

where \( \bar{M} (=\sum x_i M_i) \), \( \rho \) and \( u \) represent the molecular weight, density and ultrasonic velocity of the mixtures respectively. Using the analysis of [33, 328] in Eq. 6.83, we get:

\[
u = (R_{mix} V)^{1/3} = [(x_1 R_i + x_2 R_2) / (x_1 V_i + x_2 V_2)]^{1/3}
\] (6.84)
This formula holds true for such mixtures for which the linearity of molecular sound velocity and additivity of molar volumes is comparatively good. Eq. 6.84 has been employed for the calculation of \( u \) for the mixtures.

**Flory’s statistical theory (Binary mixtures)**

Patterson and Rastogi [284] have extended the corresponding states theory to deal with surface tension, expressing characteristic surface tension as:

\[
\sigma^* = k^{1/3} P^{*4/3} T^{*1/3} \tag{6.85}
\]

where \( k \) is the Boltzman constant and \( P^* \), \( T^* \) are the characteristic pressure and temperature respectively. The reduced surface tension equation in the case of a Van der Waal’s liquid can be written as:

\[
\bar{\sigma} (\bar{\nu}) = M \bar{\nu}^{-4/3} - \left[ (\bar{\nu}^{1/3} - 1) / (\bar{\nu}^{1/3} - 0.5) \right] \ln \left( \frac{\bar{\nu}^{1/3} - 0.5}{\bar{\nu}^{1/3} - 1} \right) \tag{6.86}
\]

where \( M \) is the fraction of nearest neighbors which a molecule loses on moving from the bulk of the liquid to the surface and its most suitable value is 0.29. Thus surface tension of a liquid in terms of Flory’s theory can be described as:

\[
\sigma = \sigma^* \bar{\sigma} (\bar{\nu}) \tag{6.87}
\]

According to Auerbach [282] relation, the ultrasonic velocity \( u \) can be related to the surface tension of the liquid as:

\[
u = \left[ \sigma / (6.3 \times 10^{-4} \rho) \right]^{2/3} \tag{6.88}
\]

The Eq. 6.86 with same value of \( M \) can be applied to mixtures assuming that the mixture behaves as a pure liquid. The reduced volume \( \bar{\nu} \) over the whole composition range is given by:

\[
\bar{\nu} = V \left( x_1 V_1^* + x_2 V_2^* \right) \tag{6.89}
\]

where \( V \) is the molar volume of the mixture. The characteristic parameters \( P^* \), \( V^* \) and \( T^* \) for a mixture are defined as:

\[
< V^* > = x_1 V_1^* + x_2 V_2^* \tag{6.90}
\]

\[
< P^* > = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 X_{12} \tag{6.91}
\]

\[
< T^* > = < P^* > / \left[ \{(\phi_1 P_1^*/T_1^*) + (\phi_2 P_2^*/T_2^*) \} \right] \tag{6.92}
\]