Korean J. Chem. Eng., 40(11), 2581-2601 (2023)
DOI: 10.1007/s11814-023-1484-1
pISSN: 0256-1115
eISSN: 1975-7220

REVIEW PAPER

Critical review on graph theory: Estimation of thermodynamic properties of liquid mixtures

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(*Received 12 January 2023 • Revised 21 April 2023 • Accepted 1 May 2023*)

Abstract−The present work deals with a review on graph theory that has been utilized to estimate thermodynamic properties of binary and ternary liquid mixtures. Various topological indices have been used to describe the topology of the chemical species it presents. Elegance and versatility of connectivity parameters of third degree of molecules, $^{3}\xi$, of the various components (derived from their topology) of mixtures are used to estimate (i) existence of components in mixture as well as pure state along with the extent and nature of the interaction between the constituent molecules; (ii) excess molar volume, V^E, excess isentropic compressibility, κ_S^E, excess molar enthalpy, H^E, excess heat capacity, C_P^E, excess Gibb's energy, G^E of binary and ternary liquid mixtures. The present review reports the development of graph theory and its utilization for the determination of V^E, κ_S^E, H^E, C_P^E, G^E of two/three component mixtures (components being non-polar, polar differing in size, shape, polarity and ionic liquids).

Keywords: Connectivity Parameters of Third Degree of a Molecule, Excess Molar Volumes, Excess Isentropic Compressibilities, Excess Molar Enthalpies, Excess Heat Capacities, Excess Gibb's Energies

INTRODUCTION

The mathematization of chemistry has a remarkable history of nearly two centuries. The development of chemistry and its mathematization process has been observed to run parallel to each other at any period of said tenure. In the 20th century, dramatic growth has been observed for the applications of mathematics in chemistry. The advent of quantum chemistry in the 1920s brought in its wake a host of mathematical disciplines, such as matrix theory, group theory and calculus. Chemists have utilized group theory in areas such as crystallography and molecular structure analysis [1]. Graph theory seems to be following in the footsteps of group theory and is currently being exploited in a wide range of applications involving the classification, systematization, enumeration and design of systems of chemical interest [2]. Graph theory is a sub-discipline of mathematics closely related to both topology and combinatorics [3]. It deals with the manner in which constituent atoms of a molecule are connected to each other [4]. Connectivity of atoms in a molecule is the fundamental concept of graph theory. Topological models and graph theoretical concepts have found applications in theoretical physics, chemistry, pharmacology, pharmaceutical chemistry, toxicology, engineering, and computer science [5].

Ever since Cayley and Sylvester [6,7] suggested that the constituent formula of a chemical compound is a special kind of graph, both the mathematical concept of graph theory and modern chemistry have to some level cross fertilized each other [8]. Hosoya [9] suggested that the topological index of a molecule is a sorting trick for the enciphering of its molecular structure. Several researchers [10-13] have observed a good relation amid the physico-chemical properties of a molecule and its topological index. It is understandable as properties such as refractive index, surface tension, boiling point, viscosity, spectroscopical properties of organic molecules are predicted by the comparative occupation of space by atoms in a molecule, which in turn are more or less reflected in its topological index. Modern chemistry thus can be considered as a combinatorial theory applied to atoms and molecules in the formation and rupture of bonds. According to the molecular structure hypothesis, a molecule is a collection of atoms bonded by bonds in the three-dimensional space with properties which can be derived from structural formula. A topological index is a numerical number associated with a graph, i.e., invariant under graph automorphism that describes the graph's topology. Topological indices are remarkable tools for estimating biological activity, physical properties, taxological, pharmacological properties of organic compounds (solid or liquid), and molecular structure is utilized to derive such indices. Researchers [14,15] have observed that although a number of topological indices are identified, yet their utilization has received little consideration. One of the main features of chemical graph theory is to use mathematical tools [16-18], i.e., topological indices of molecules to predict their physical and chemical properties by employing their molecular topology [19,20]. Determination of topological indices (via molecular topology) is the main part of graph theory. As per mathematical amendment of graph theory, the structural formula of a compound (where dots represents atoms and lines the bonds connecting them) called molecular graph provides the entire information about the molecule [21-23]. Graph theoretical methods have been used to compute isomers for alkanes and correlate molecular structure with its chemical properties [24,25]. The question then is how to utilize the topology of the molecules constituting the liquid mixture to estimate thermodynamic prop-

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erties such as excess molar volumes, V^E, excess isentropic compressibility, κ_S^E, excess molar enthalpy, H^E, excess heat capacity, C_P^E and excess Gibb's energy, G^E. Since the molecular graph describing the topology of the components of the mixture has been successfully utilized to develop a theory that reproduced well various thermodynamic properties of liquid mixtures (binary and ternary), henceforth the theory is termed as graph theory. The main objective of the work is to review the development of graph theory (utilizing the concept of connectivity parameter of third degree of a molecule, ${}^3\xi$ derived from its topology) and its amendment for estimating V^E, κ_S^E, H^E, C_P^E and G^E of two/three component mixtures.

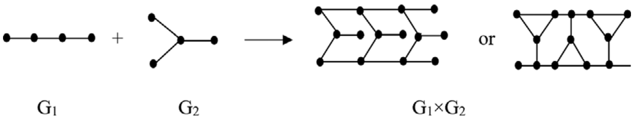
CALL FOR AN APPROACH

V^E, κ_S^E, H^E, C_P^E, G^E of mixtures reflect the origin from ideality due to interactions among unlike molecules [26]. These properties are dependent on concentration of liquid mixtures, temperature and act as an effective tool for the assessment of the behavior of liquid mixtures for their use in industrial applications [27-30]. Such thermodynamic data are also essential for the development of theories/thermodynamic models which are useful for separation processes, optimization of industrial processes and also to design industrial equipment with better precision [31-34]. The estimation of such properties and understanding of fundamental mechanism at molecular level using statistical consideration is quite complex. Various theories/models have been projected to deal with the non-ideality of mixtures. The associated solution (IAS) model [35] deals with the thermodynamic properties of mixtures yielding new molecular species. However, the IAS model does not describe mixtures having significant molecular interactions and a weaker associated binary mixture. Acree [36-40] modified the IAS model by considering chemical and physical interactions among the components of the mixtures. A number of theories/models [41-56] have also been developed to compute various thermodynamic properties of binary liquid mixtures. Most of the approaches are not successful in computing V^E, κ_S^E, H^E, C_P^E, G^E of binary, ternary mixtures. It may be because all these theories/models rely on the evaluation of partition function and assumptions regarding the intermolecular potential (characterizing interactions among dissimilar molecules). Since intermolecular potential functions are computed by laws of limited validity [57], therefore all the approaches of non-electrolytes mixtures [42,43,50,52-55] have limited applicability. The above considerations call for an approach that may not depend on the estimation of prediction of partition functions and assumptions concerning intermolecular potential. Graph theoretical approach was developed for the first time [58] to compute V^E, H^E of non-electrolytic binary mixtures.

GRAPH THEORY

1. Excess Molar Volumes, V^E

Graph theory describes [21-23] the structural formula of a compound as molecular graph where atoms are represented by dots and bonds joining them by lines. If the pure components (1) and (2) of (1+2) mixture are represented by G_1 (e_1, υ_2) or G_1 and G_2 (e_2, υ_2) or (G_2), then the formation of a binary mixture according to the mathematical discipline of graph theory is characterized by interactions between (1) and (2) in the (G_1G_2) molecular graph.



Molecular graphs have been used to obtain topological indices which in turn provide total information contained in molecules. Kier, Singh et al. [58,59-61(a)] have advocated that topological indices, ${}^1\xi$, ${}^2\xi$, ${}^3\xi$ (connectivity parameters of the 1st, 2nd, 3rd degree of a molecule) containing -C-C- skeleton could be utilized to extract information from its molecular graph. If degree of vertices a, b, c etc. of the graph of a molecule is denoted by δ_a, δ_b, δ_c… δ_v etc. then, ${}^1\xi$, ${}^2\xi$, ${}^3\xi$ are given [58,59-61(a)] by

$$ {}^1\xi = \sum_{a<b} (\delta_a \delta_b)^{-0.5} \tag{1}$$

$$ {}^2\xi = \sum_{a<b<c} (\delta_a \delta_b \delta_c)^{-0.5} \tag{2}$$

$$ {}^3\xi = \sum_{a<b<c<d} (\delta_a \delta_b \delta_c \delta_d)^{-0.5} \tag{3}$$

${}^1\xi$, ${}^2\xi$, ${}^3\xi$ parameters rest on the degrees of the nearest vertices (taken 2, 3 and 4 at a time) of molecular graph. ${}^1\xi$ parameter is considered [58] to be a measure of bond length and thus is considered independent of temperature and composition. Estimation of molar volumes, V of many non-electrolytes and their ${}^3\xi$ values (using Eq. (3)) suggests that $({}^3\xi)^{-1}$ of a molecule signifies its probability to interact its surface area efficiently with surface area of other molecule. In view of this, the molar volume of component (i) (i=1 or 2) is expressed by

$$ V_i = \frac{\alpha_i}{{}^3\xi_i} + \beta_i({}^1\xi_i) + \gamma_i \tag{4}$$

where α_i, β_i, γ_i are constants.

Ideal molar volume, $V_{(ideal)}$ for a mixture is expressed by

$$ V_{(ideal)} = x_1\left(\frac{\alpha_1}{{}^3\xi_1} + \beta_1({}^1\xi_1) + \gamma_1\right) + x_2\left(\frac{\alpha_2}{{}^3\xi_2} + \beta_2({}^1\xi_2) + \gamma_2\right) \tag{5}$$

Molar volume of the mixture is expressed by relation

$$ V_m = \alpha/{}^3\xi_m + \beta_m\, {}^1\xi_m + \gamma_m \tag{6}$$

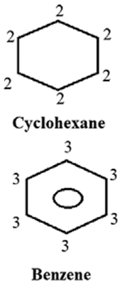
$$ \beta_m\, {}^1\xi_m = x_1\, {}^1\xi_1 \beta_1 + x_2\, {}^1\xi_2 \beta_2 \tag{7}$$

$$ \gamma_m = x_1 \gamma_1 + \gamma_2 x_2 \tag{8}$$

Since $V^E = V_{(ideal)} - V$; V^E for binary mixtures is expressed as [58]:

$$ V^E = \alpha_{12}\left[\sum_{i=1}^{2} (x_i\, {}^3\xi_i)^{-1} - \sum_{i=1}^{2} x_i ({}^3\xi_i)^{-1}\right] \tag{9}$$

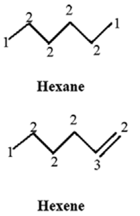
where, x_i (i=1, 2) is mole fraction of component (i). Unknown parameter, α_{12}, determined by using V^E of mixture at equimolar composition was afterward applied to compute V^E values at various compositions. Eq. (9) was successfully applied to determine V^E values for numerous non-electrolytic binary mixtures [62]. Although Eq. (9) was able to define V^E for several (1+2) non-electrolytic mixtures, yet the same was not successful to predict V^E of cyclohexane+benzene mixture [62]. V^E data for this mixture were estimated {via Eq. (9)} to be zero, it was because ${}^3\xi$ parameter estimated by scheme involving only -C-C- skeleton failed to differentiate benzene from cyclohexane. Graph theory was then modified to overcome this limitation. To overcome this constraint, it was suggested [61(b),62] that δ^v(C) (δ^v=valency δ) values instead of δ(C) must be employed to predict ${}^3\xi$ of a molecule. δ^v(C) was obtained using relation δ^v(C)=Z−h [62], where h depicts number of hydrogen atoms attached to atom, Z denotes maximum valency of atom. Such scheme of evaluating ${}^3\xi$ values of a molecule [62] clearly differentiates between benzene and cyclohexane; hexane and hexene.



$${}^3\xi = 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x2} = 1.500$$

$${}^3\xi = 1/\sqrt{3x3x3x3} + 1/\sqrt{3x3x3x3} + 1/\sqrt{3x3x3x3} + 1/\sqrt{3x3x3x3} + 1/\sqrt{3x3x3x3} + 1/\sqrt{3x3x3x3} = 0.666$$

${}^3\xi$ parameters of cyclohexane and benzene



$${}^3\xi = 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x1} + 1/\sqrt{2x2x2x1} + 1/\sqrt{2x2x2x1} + 1/\sqrt{2x2x2x1} + 1/\sqrt{2x2x2x2} = 1.918$$

$${}^3\xi = 1/\sqrt{2x2x2x3} + 1/\sqrt{1x2x2x3} + 1/\sqrt{2x3x2x2} + 1/\sqrt{3x2x2x1} + 1/\sqrt{2x2x2x1} + 1/\sqrt{3x2x2x2} = 1.459$$

${}^3\xi$ parameters of hexane and hexene

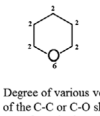
Using above concept of the estimation of ${}^3\xi$ values, Eq. (9) was now able to explain V^E of cyclohexane+benzene mixture. Further, for binary mixtures containing heteroatoms like nitrogen (N) or oxygen (O) or sulfur (S) or chlorine (Cl), it was suggested that ${}^3\xi$ parameters for such molecules be estimated by $\delta^v = Z_M - h_M$, where Z_M symbolizes the maximum valency of N or O or S or Cl atom, h_M represents number of hydrogen atoms connected to such atoms. Accordingly, ${}^3\xi$ values were expressed by

$$ {}^1\xi = \sum_{a<b} (\delta_a^v \delta_b^v)^{-0.5} \tag{10}$$

$$ {}^2\xi = \sum_{a<b<c} (\delta_a^v \delta_b^v \delta_c^v)^{-0.5} \tag{11}$$

$$ {}^3\xi = \sum_{a<b<c<d} (\delta_a^v \delta_b^v \delta_c^v \delta_d^v)^{-0.5} \tag{12}$$

Using δ^v concept ${}^1\xi$ ${}^2\xi$ ${}^3\xi$ parameters of tetrahydropyran were expressed by



Degree of various vertices of the C-C or C-O skeleton of tetrahydropyran

$${}^1\xi = 1/\sqrt{2x2} + 1/\sqrt{2x2} + 1/\sqrt{2x6} + 1/\sqrt{6x2} + 1/\sqrt{2x2} + 1/\sqrt{2x2} = 2.577$$

$${}^2\xi = 1/\sqrt{2x2x2} + 1/\sqrt{2x2x6} + 1/\sqrt{2x6x2} + 1/\sqrt{6x2x2} + 1/\sqrt{2x2x2} + 1/\sqrt{2x2x2} = 1.661$$

$${}^3\xi = 1/\sqrt{2x2x2x6} + 1/\sqrt{2x2x6x2} + 1/\sqrt{2x6x2x2} + 1/\sqrt{6x2x2x2} + 1/\sqrt{2x2x2x2} + 1/\sqrt{2x2x2x2} = 1.076$$

Such scheme of evaluating δ^v values for any kind of molecules from their molecular graph provides an important tool to compute ${}^3\xi$. Graph theory (using modified concept of δ^v) was able to explain the V^E data of heptane+pyridine or 2-picoline or 4-picoline; 1,2-dichloroethane+pyridine or 2-picoline or heptane; aniline+pyridine or 2-picoline or 4-picoline mixtures [63]. Graph theory (Eq. (9)) was then tested for mixtures having one/two associated components (containing N or O or S or Cl). Graph theory was not able to describe V^E data of methanol or ethanol+methylene bromide mixtures [64]. It was because if components of mixtures undergo association/dissociation in mixed state, then their topology may change. Thus, ${}^3\xi$ values of the constituent molecules in mixed state, $({}^3\xi)_m$ may differ from that of pure state. In view of this consideration, Singh et al. [58] modified Eq. (9) and V^E for the mixtures containing associated/non-associated molecules given by relation [64]:

$$V^E = \alpha_{12}\left[\sum_{i=1}^{2}[x_i({}^3\xi_i)_m]^{-1} - \sum_{i=1}^{2}x_i({}^3\xi_i)^{-1}\right] \tag{13}$$

connectivity parameters, ${}^3\xi_i$; $({}^3\xi_i)_m$ (i=1, 2) of component (i) in pure and mixture were estimating by using V^E of (1+2) mixtures using Eq. (13). Characteristic constant, α_{12} of (1+2) mixture was computed by applying V^E at single composition. Eq. (13) was effectively utilized to determine V^E values of methylene bromide+methanol or ethanol mixtures [64]. In estimating state of components, various structures were assumed for methanol, ethanol in pure state as well as in mixture, and their ${}^3\xi'$ values were computed using Eq. (12) (determined via structural concept; Eq. (12)). Only those structures or units of structures were assumed to be the representative structure of ethanol or methanol in pure and mixed state that provided ${}^3\xi'$ value nearer to ${}^3\xi$ {Eq. (13)} value. The computed ${}^3\xi'$ values in pure and mixed states along with α_{12} parameter (utilized using V^E at equimolar composition) were used to determine V^E values of methylene bromide+methanol or ethanol mixtures. Since assessed V^E (graph theory) were comparable with measured values, it was therefore concluded that ${}^3\xi_i$ and $({}^3\xi_i)_m$ (i=1, 2) could be relied upon to obtain evidence about existence of components in pure as well as mixed state. The present study reveals that while methanol occurs as open and cyclic dimer mixture (Fig. 1(a)-(c)), ethanol exists mainly as dimer (Fig. 1(d)-(f)) in pure states; methylene bromide+methanol or ethanol exists as molecular unit (Fig. 1(g)-(h)). Eq. (13) is thus able to describe V^E of mixtures containing associated components. The modified graph theory [64] was successfully applied to (i) extract information regarding components existing in pure as well as in mixture, (ii) extent of interactions in constituent molecules, and (iii) describe V^E of binary mixtures containing polar/non polar components [65-86].

Although Eq. (13) (Modified graph theory) was successful in estimating V^E of binary mixtures (comprised of components varying in polarity), yet it was then of interest to see whether graph theory could determine V^E of ionic liquids/ionic liquid with organic solvents mixtures. For this purpose, we tested graph theory for 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4]+pyridine or 2-, 3-, 4-picoline or pyrrolidin-2-one or 1-methylpyrrolidin-2-one mixtures [87,88] for the estimation of V^E data. The question of interest was to locate a particular point on the $[EMIM]^+$ or $[BF_4]^-$

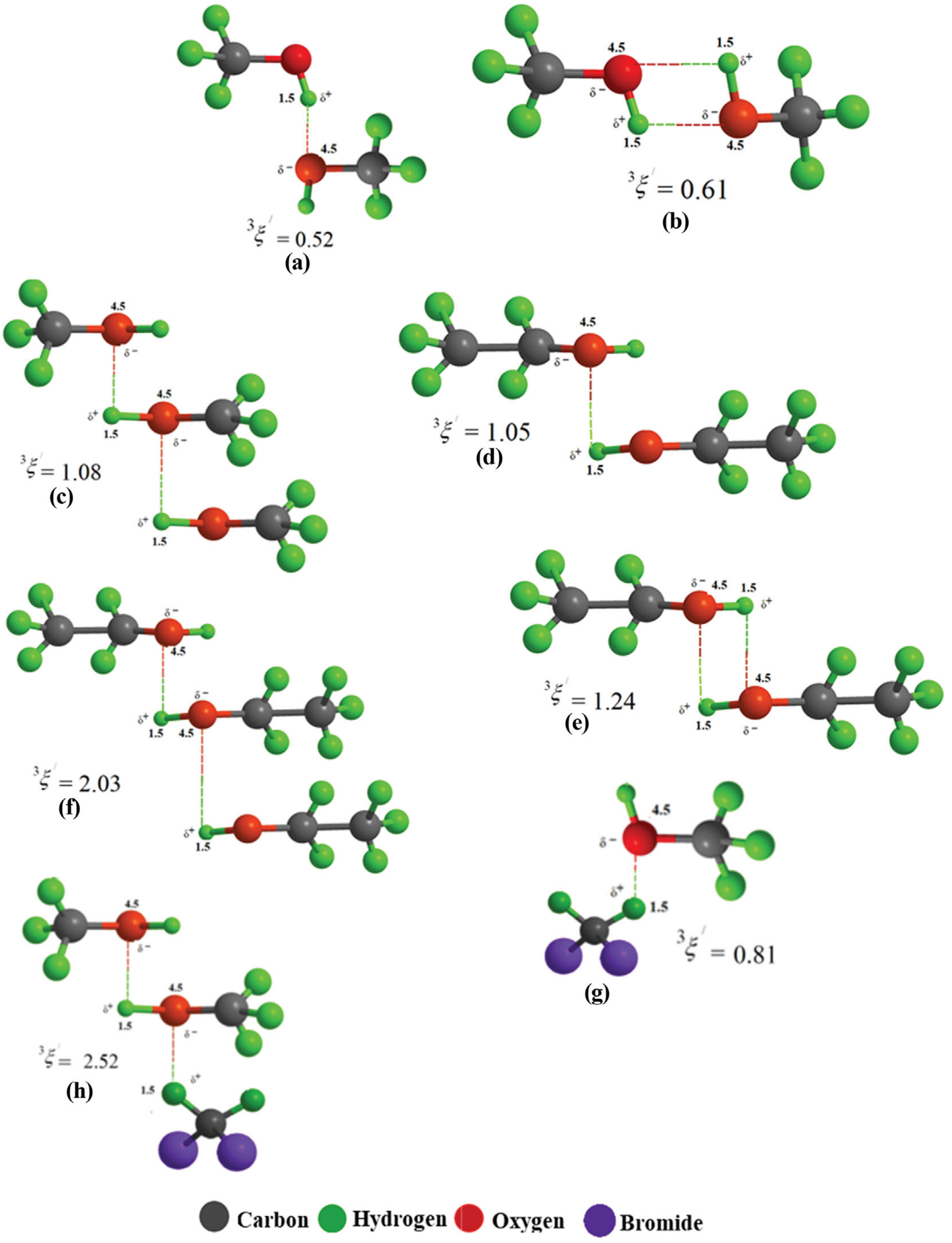


Fig. 1. Connectivity parameters, $^{3}\xi^{\prime}$ of the third degree for various molecular entities.

interacting with counterion or 1-methylpyrrolidin-2-one or pyrrolidin-2-one or pyridine or picolines. The analyses of V^{E} data suggested that hydrogen atom of (C-H {edge}), proton of -CH_3 group (imidazolium ring) are interacting with fluorine atom of $[BF_4]^{-}$. Thus, [EMIM][BF_4] occurs as monomer [87] {Fig. 2(a)}. Further pyrrolidin-2-one [87] {Fig. 2(b)-(d)} 1-methylpyrrolidin-2-one [87] {Fig. 2(e)-(f)} pyridine, 2-, 3-, 4-picoline [88] {Fig. 2(g)-(i); (j)-(m); (n)-(q); (r)-(t)} were found to exist as associated molecular entities. Observations regarding existence of [EMIM][BF_4], 1-methylpyrrolidin-2-one, pyrrolidin-2-one, pyridine and picolines were similar with information obtained from (i) IR, Raman spectral studies, quantum mechanical calculations of [EMIM][BF_4] [89,90] suggesting that $[BF_4]^{-}$ is placed above the imidazolium ring interacts with H-C; proton of the -CH_3 group (imidazolium ring); (ii) Ab-initio calculations of 2-Py [91]; and (iii) X-rays, NMR studies [92] suggest that 1-methylpyrrolidin-2-one is coupled by the bond between -N-CH_3 and keto oxygen atoms (of -C=O) of adjoining molecule (ii) Ab-initio molecular orbital calculations of pyridine

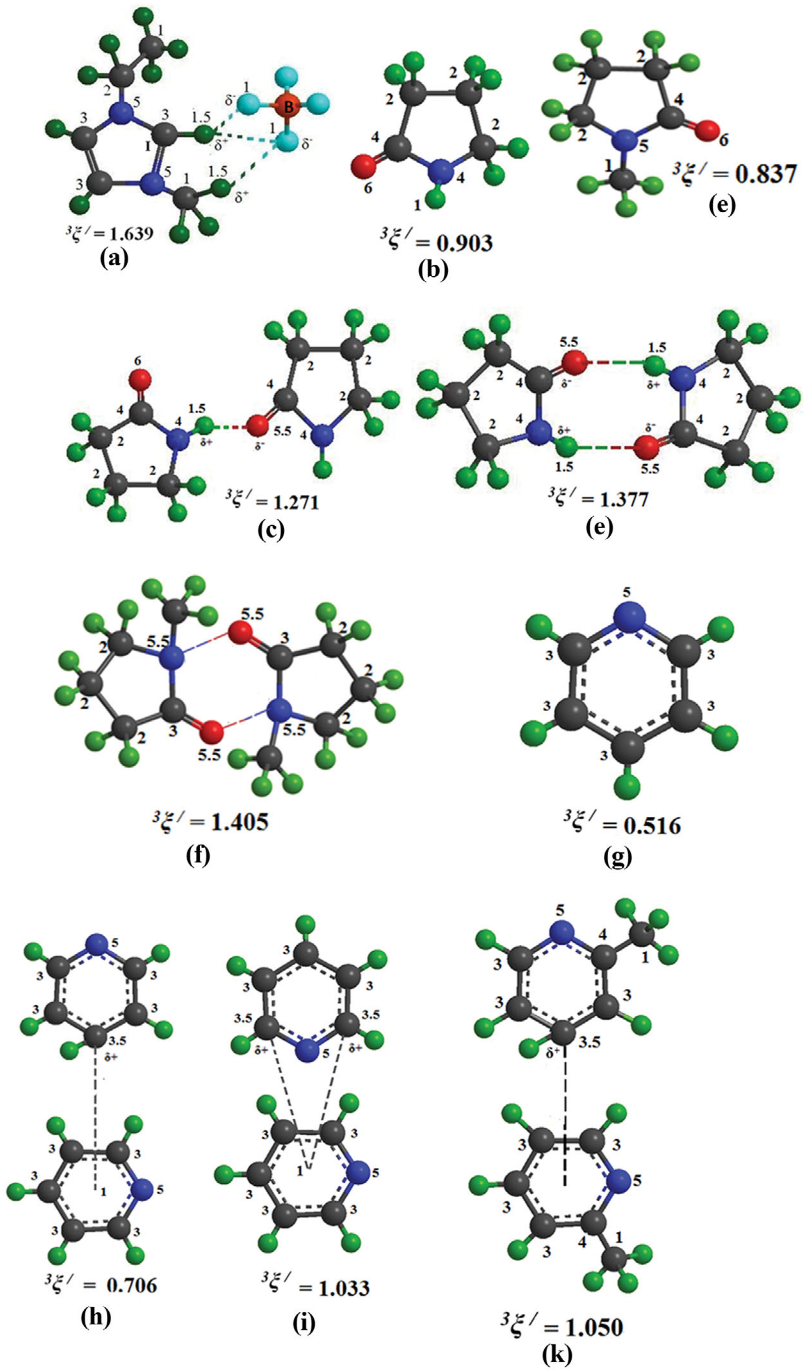


Fig. 2. Connectivity parameters, ${}^3\xi'$ of the third degree for various molecular entities.

and isomeric picolines [93], which suggest that π-electron density at C_6, C_4, C_2 positions in pyridine is lesser than at corresponding positions in benzene. Consequently, either 1/2/3 electron lacking carbon atoms in pyridine or picolines may interact with π-electron cloud of other molecule forming associated molecular entity. Further existence of [EMIM][BF_4] in pyrrolidin-2-one or 1-methylpyrrolidin-2-one or pyridine or 2-, 3-, 4-picoline were found to exist as molecular entities (Fig. 2(u)-(w)) [87,88]. V^E values estimated by Eq. (13) were in agreement with their corresponding measured values. Graph theory thus successfully described V^E of binary mixtures containing ionic liquids or organic solvent [94-101].

Graph theory was next tested to investigate the existence of transition-metal ions in non-electrolytic two component mixtures. Interpretation of V^E data of pyridine saturated with anhydrous cobalt chloride {CoCl} or anhydrous cupric chloride {Cu(Cl)$_2$}+formamide or N,N-dimethylformamide or aniline or 2-methylaniline suggested that CoCl (anhydrous) occurs as ClCo (py) in pyridine; formamide or N,N-dimethylformamide or aniline, 2-methylaniline, coordinate with the central metal in CoCl(Py) in the similar manner with CuCl(Py) [102-104]. Further, estimated V^E of these

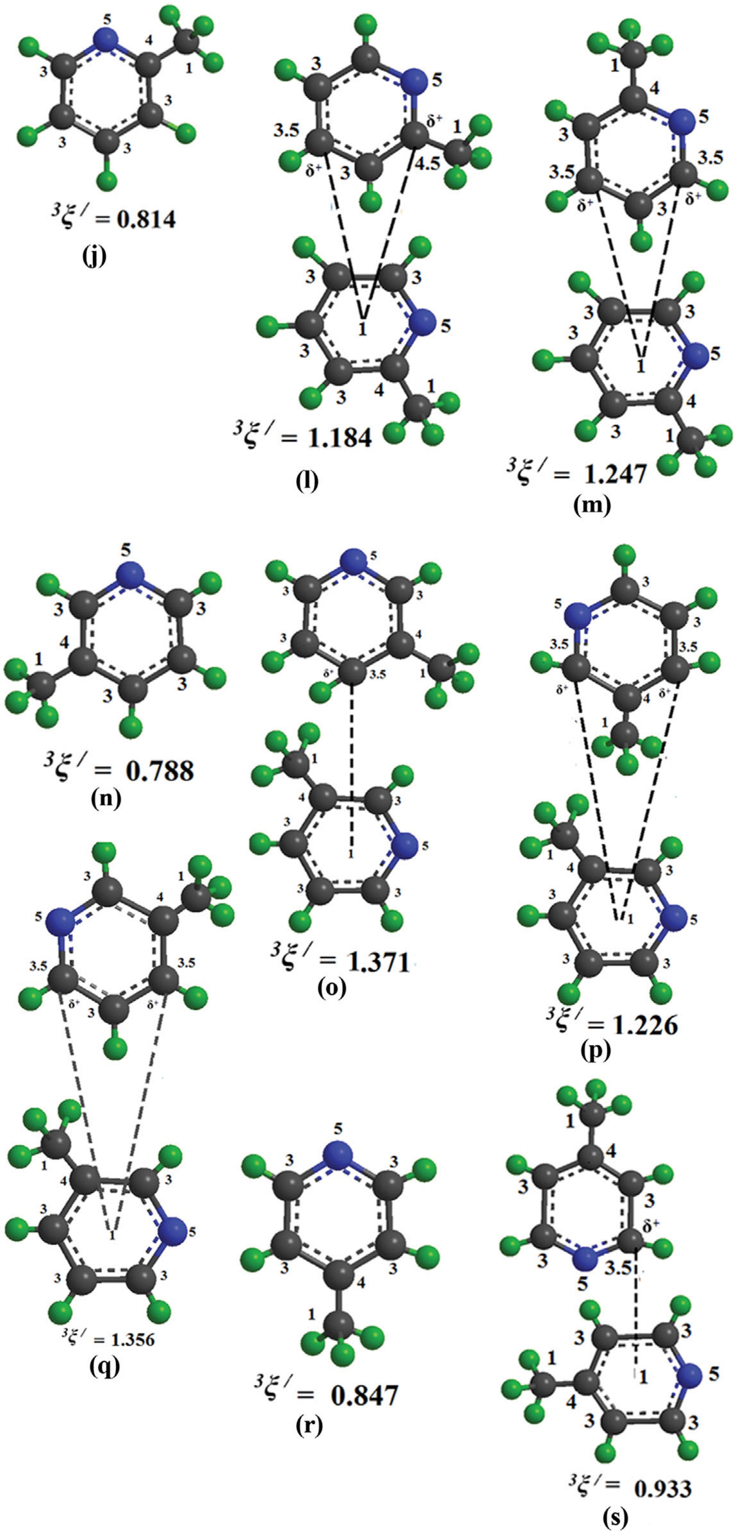


Fig. 2. Continued.

mixtures by graph theory compare well with their measured values.

1-1. Effect of Temperature on V^E Data

Graph theory was also employed to study the influence of pressure, temperature on V^E data of binary mixtures. The molar volume, V of liquids varies directly with temperature, T

$$V_1(T_1) \propto (T_1) \tag{14}$$

$$V_1(T_2) \propto (T_2) \tag{15}$$

$$V_1(T_2) = \frac{T_2}{T_1} V_1(T_1) = \frac{T_2}{T_1}\left[\frac{\alpha_{12}}{^3\xi_1} + \beta_1(^1\xi_1) + \gamma_1\right] \tag{16}$$

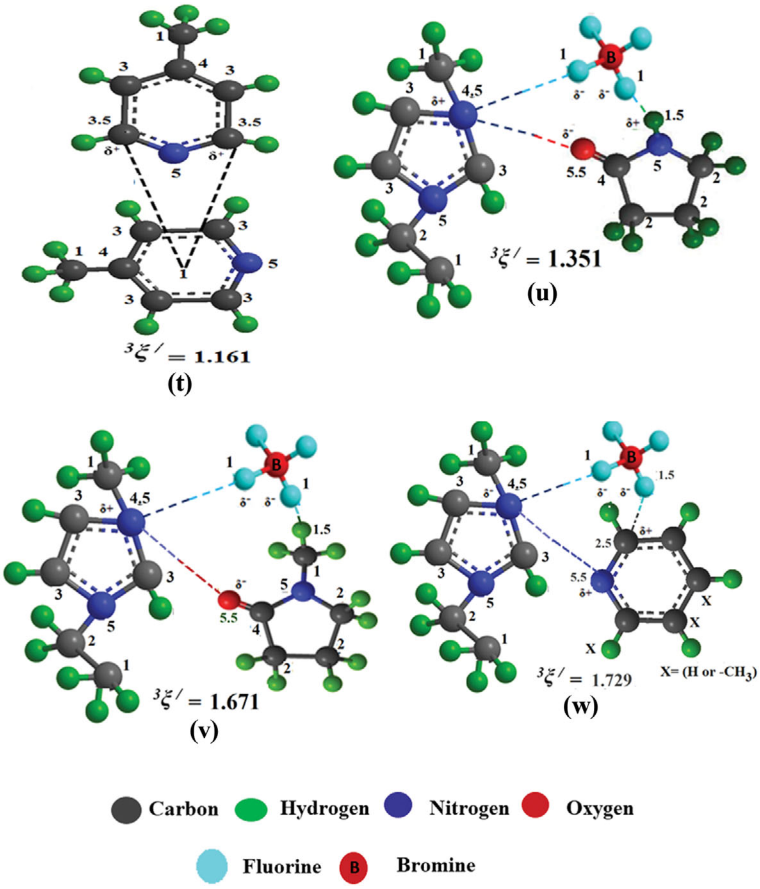


Fig. 2. Continued.

So that V^E (T_2, x) for binary mixture would be given by

$$V^E(T_2, x)=\frac{T_2}{T_1}V^E(T_1, x) \tag{17}$$

V^E (T_2, x) can be estimated if V^E (T_1, x) for a binary mixture at equimolar composition are available. Calculated V^E (T_2, x) values for mixtures were found to be comparable with experimental values [62].

1-2. Effect of Pressure on V^E Data

Molar volume of a molecule decreases with increase in pressure. Decrease in molar volume is governed by applied pressure and its isothermal compressibility. If $V_1(T, P)$, $V_1^{/}(T, P^{/})$ and $K_T(P)$ signify the molar volume at a given T and pressures, P, $P^{/}$ and isothermal compressibility, of a molecule at P, then

$$V_1^{/}(T, P^{/})=V_1(T, P)[1-K_T(P)(P^{/}-P)] \tag{18}$$

K_T is related to pressure by

$$\left(\frac{\partial K_T}{\partial P}\right)_T=-CK_T^2 \tag{19}$$

where C is a constant and has a value nearly 10 for numerous organic liquids. Integration of Eq. (19) provides

$$1/K_T(P^{/})\approx\frac{1}{K_T(P\approx 1\ \text{atm})}+CP^{/} \tag{20}$$

where $K_T(P^{/})$, $K_T(P\approx1\ \text{atm})$ are K_T of a molecule at pressure $(P^{/})$ and atmospheric pressure. In view of this,

$$V_1^{/}(T_1, P^{/})=V_1(T_1, P)\left\{1-\frac{K_T(P^{/}-1)}{1+K_T CP^{/}}\right\} \tag{21}$$

It has been observed that molar volume, $V_1^{/}(T, P^{/})$ for benzene, 1,3-dimethylbenzene, 1,4-dimethylbenzene, chlorobenzene and aniline at $P^{/}$=100, 200, 300, 400, 500 atm etc. pressure {evaluated from Eq. (21)} applying $V_1(T, P=1\ \text{atm})$ values [105] agree well with the corresponding $V_1^{/}(T, P^{/})$ data.

2. Excess Molar Enthalpy, H^E

H^E are due to the replacement of like contacts by dislike contacts. Such unlike contacts in binary mixtures are dependent on the surface area of the constituent components in pure state that take part into effective interactions to form unlike contacts.

If mixing of the components in binary (1+2) mixtures is assumed to be perfectly random, then H^E is expressed [106,107] by

$$H^E=x_1\chi_{12}S_2 \tag{22}$$

where x_1 represents composition of component (1), S_2 is surface area of component (2) that takes part in effective contact with the surface area of component (1) and stated as

$$S_2=\frac{x_2V_2}{\sum_{i=1}^{2}x_iV_i} \tag{23}$$

V_i (i=1, 2), χ_{12} are the molar volume of component of (i) and interaction energy parameter for (1−2) contacts. ${}^3\xi^{-1}$ represents probability of surface area of a molecule to contact with the surface area of another component and was observed to vary inversely proportional [58] to its molar volume, V consequently ${}^3\xi_i$ (i=1, 2) were expressed as

$$\frac{{}^3\xi_1}{{}^3\xi_2}=\frac{V_2}{V_1} \tag{24}$$

Eq. (23), therefore, was given by

$$S_2=\left[\frac{x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right] \tag{25}$$

Thus, H^E of binary mixture was given by the relation:

$$H^E=\left[\frac{x_1x_2\chi_{12}({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right] \tag{26}$$

Eq. (26) contains three parameters: ${}^3\xi_1$, ${}^3\xi_2$ and χ_{12}. The ${}^3\xi$ parameters of a molecule containing four or more than four -C-C- skeleton are predicted via (Eq. (3)). For smaller molecules, ${}^3\xi$ is assumed to be unity. Interaction parameter, χ_{12} was calculated using H^E values at equimolar composition and then utilized to calculate H^E at various mole fractions. The H^E values determined (Eq. (26)) for various binary mixtures of non-electrolytes [58,108] were in agreement with experimental values.

One apparent weakness of Eq. (26) is that it requires H^E either to be positive or negative over entire composition range and thus fails for mixtures where H^E changes sign with composition. The failure of Eq. (26) to determine H^E values was considered due to reason that constituent molecules may not have identical abilities to form 1−2 contacts. In view of this, molar volumes and ${}^3\xi$ of (1+2) mixtures were assumed to follow the relation [109]:

$$\frac{V_2}{V_1}=\kappa_{12}\left(\frac{{}^3\xi_1}{{}^3\xi_2}\right) \tag{27}$$

where κ_{12}, constant characteristic of (1+2) mixture, depicts the ability of dissimilar molecules yielding 1−2 contacts.

H^E for (1+2) mixtures was then stated [109] as:

$$H^E=\left[\frac{x_1x_2\chi_{12}\kappa_{12}({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right] \tag{28}$$

The unknown parameters χ_{12} and κ_{12} were computed by employing H^E at two compositions. Such values of χ_{12} and κ_{12} were then used to calculate H^E at other compositions of mixtures. Modified Eq. (28) described well the H^E for several non-electrolytic binary mixtures [109]. Also Eq. (28) describes well the H^E of pyridine+2-picoline or 3-picoline or 4-picoline or cyclohexane; 3-picoline+cyclohexane; methylene bromide+pyridine or 3-picoline mixtures [110] Although Eqs. (26) and (28) were able to predict H^E data of several binary mixtures containing non-electrolytes, non-electrolytes and salt, yet it was of concern that whether these equations would also be able to compute H^E data of mixtures containing nonelectrolytes, organic solvents and ionic liquids. Further, it was of concern whether topological aspects of the constituent molecules could be utilized to determine κ_S^E, C_P^E of mixtures or not?

3. Excess Molar Enthalpies, H^E, Excess Isentropic Compressibilities, κ_S^E and Excess Heat Capacities, C_P^E of Two Component Mixtures

H^E, κ_S^E and C_P^E of binary mixtures containing various types of organic and ionic liquids can be determined by utilizing the topological aspects of the constituent of the binary mixtures if the processes intricacy in their formation is known. Mixture formation is due to the breakdown and establishment of interactions between the components of the mixtures. While H^E of liquid mixtures are considered to be the collective effect of the contributions due to net destruction and construction of interactions among their constituent molecules, κ_S^E are due to molecular arrangement/interactions of the liquid molecules, and excess heat capacities, C_P^E data are due to degree of randomness/non-randomness raised due to processes like association/dissociation of molecular entities and formation of unlike contacts in mixed state. The molecular graph represents the molecular structure and thus provides entire information regarding the molecule. ${}^3\xi$ of a molecule (estimated via its structural consideration) can therefore be employed to compute H^E, κ_S^E and C_P^E of binary mixtures if the various contributions to each process involving mixture formation are known. The summation of such contributions due to various processes would provide H^E, κ_S^E and C_P^E of the mixtures. An attempt, therefore, has been made from time to time to regulate H^E, κ_S^E and C_P^E of (1+2) mixtures (components varying in polarity, size, shape, association).

3-1. (1_m+2_m) (m is the Degree of Association) Mixtures

Binary (1_m+2_m) mixtures formation was supposed for intricate processes: (i) establishment of (1_m−2_m) (m=2) contacts between unlike molecules; (ii) unlike (1_m−2_m) contact formation lead to breakdown of associated 1_m, 2_m molecular entities to yield their corresponding (a) 1 and (b) 2 molecules, which results in intensification in randomness, and (iii) interactions between 1,2 molecules, resulting in the creation of 1 : 2 molecular complex possessing deficiency in pattern. The contributions because of processes encompass in mixture formation were estimated using the concept of effective contacts among surface areas of the constituent molecules [106, 107] and connectivity parameter, ${}^3\xi$. If χ_{12} is molar compressibility and molar interaction parameters for (1−2) contact, then thermodynamic properties ΔX_i (X=H or κ_S or C_P) because of process (i) are expressed as

$$\Delta X_i(X=H \text{ or } \kappa_S \text{ or } C_P)=x_1S_2\chi_{12} \tag{29}$$

where S_2 is the surface fraction of component 2 in (1_m−2_m) contact and is defined by Eq. (23)

Thus,

$$\Delta X_i(X=H \text{ or } \kappa_S \text{ or } C_P)=\frac{x_1x_2V_2\chi_{12}}{\sum_{i=1}^{2}x_iV_i} \tag{30}$$

If χ_{11}, χ_{22} are molar compressibilities and molar interaction parameters for breakdown of (1_m−1_m) and (2_m−2_m) interactions, which in turn enhance the randomness then thermodynamic properties, the accompanying processes, ii(a-b), are stated as:

$$\Delta X_{ii(a)}(X=H \text{ or } \kappa_S \text{ or } C_P)=x_1S_2'\chi_{11} \tag{31}$$

$$\Delta X_{ii(b)}(X=H \text{ or } \kappa_S \text{ or } C_P)=x_1S_2'\chi_{22} \tag{32}$$

$$\text{where } S_2' \propto x_1S_2 \tag{33}$$

Hence

$$\Delta X_{ii(a)}(X=H \text{ or } \kappa_S \text{ or } C_P)=\frac{x_1^2x_2V_2\chi_{11}}{\sum_{i=1}^{2}x_iV_i} \tag{34}$$

$$\Delta X_{ii(b)}(X=H \text{ or } \kappa_S \text{ or } C_P)=\frac{x_1^2x_2V_2\chi_{22}}{\sum_{i=1}^{2}x_iV_i} \tag{35}$$

If $\chi_{12}^{/}$ is the molar compressibility and molar interaction parameters for interactions among unlike molecules to yield 1 : 2 molecular complex having non-random structure, then ΔX_{iii}(X=H or κ_S or C_P) due to process (iii) are given by

$$\Delta X_{iii}(X=H \text{ or } \kappa_S \text{ or } C_P)=x_1S_2''\chi_{12}^{/} \tag{36}$$

$$\text{where } S_2'' \propto x_2S_2 \tag{37}$$

$$\Delta X_{iii}(X=H \text{ or } \kappa_S \text{ or } C_P)=x_1x_2S_2\chi_{12}^{/} \tag{38}$$

$$\Delta X_{iii}(X=H \text{ or } \kappa_S \text{ or } C_P)=\frac{x_1x_2^2V_2\chi_{12}^{/}}{\sum_{i=1}^{2}x_iV_i} \tag{39}$$

Excess X^E(X=H or κ_S or C_P) properties were taken to be the summation of contributions because of processes i, ii(a-b), iii in (1_m+2_m) mixtures. Consequently,

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P)=\sum_{i=i}^{iii}(\Delta X_i)$$

$$=\left[\frac{x_1x_2V_2}{\sum_{i=1}^{2}x_iV_i}\right][\chi_{12}+x_1\chi_{11}+x_1\chi_{22}+x_2\chi_{12}^{/}] \tag{40}$$

Since $\frac{V_2}{V_1}=\frac{{}^3\xi_1}{{}^3\xi_2}$ [58]

Eq. (40) is reduced to

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P)$$

$$=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_1\chi_{22}+x_2\chi_{12}^{/}] \tag{41}$$

For water+pyridine or picolines mixtures [69], it is assumed that $\chi_{12}\cong\chi_{12}^{/}=\chi_{12}^{//}$; $\chi_{11}\cong\chi_{22}=\chi^*$; therefore, Eq. (41) is reduced to

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P)$$

$$=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi_{12}^{//}+2x_1\chi_{12}^{*}] \tag{42}$$

Unknown parameters $\chi_{12}^{//}$ and χ_{12}^{*} were estimated using X^E(X=H or κ_S or C_P) values at equimolar composition. Calculated $\chi_{12}^{//}$, χ_{12}^{*} values were used to determine X^E data at various compositions. The H^E data of N,N dimethylformamide or formamide+aniline or 2-methylaniline (308.15 K) [65], pyridine+aniline or 2-methylaniline or N,N-dimethylformamide or formamide (308.15 K) [66], water+N,N-dimethylformamide or formamide (308.15 K) [67], water+2- or 3- or 4-picoline (298.15 K and 308.15 K) [69], pyridine saturated with anhydrous cupric chloride+N,N-dimethylformamide or formamide or aniline or 2-methylaniline (308.15 K) [104,111], nitrobenzene+aniline or N-methyl aniline or N,N-dimethylaniline (308.15 K) [112] κ_S^E of 1-methylpyrrolidin-2-one+pyrrolidin-2-one, pyrrolidin-2-one or 1-methylpyrrolidin-2-one+2- or 3- or 4-chlorotoluene (293.15, 298.15, 303.15, 308.15 K) [113], 2-chlorotoluene or tetrahydropyran+cyclohexane (298.15, 303.15, 308.15 K) [114], pyrrolidine-2-one+2- or 3- or 4-picoline (293.15. 298.15, 303.15, 308.15 K) [115], cyclopentanone+cyclohexanone (293.15, 298.15, 303.15, 308.15 K) [116], 1-methylpyrrolidin-2-one+piperidine (293.15, 298.15, 303.15, 308.15 K) [117], 1-butyl-2,3-dimethylimidazolium tetrafluoroborate [BDIM][BF_4]+1-methylpyrrolidin-2-one or pyrrolidin-2-one (293.15. 298.15, 303.15, 308.15 K) [118], C_P^E for 1-methyl pyrrolidin-2-one+4- or 3- or 2-picoline or pyridine (293.15, 298.15, 303.15 K) [119], pyrrolidin-2-one or 1-methylpyrrolidin-2-one+2- or 3- or 4-chlorotoluene (293.15, 298.15, 303.15 K) [120], 2-chlorotoluene+pyridine or 4- or 3- or 2-picoline or benzene or toluene or 1,2-dimethylbenzene (298.15, 303.15, 308.15 K) [121], 2-methylaniline+aniline or N-methylaniline mixtures (293.15, 298.15, 303.15, 308.15 K) [122], tetrahydropyran+piperidine (293.15, 298.15, 303.15, 308.15 K) [123], H^E and κ_S^E for 1-methylpyrrolidin-2-one+propan-2-ol or water or propan-1-ol (308.15 K) [81], 1-methylpyrrolidin-2-one or pyrrolidin-2-one+cycloheptanone or cyclohexanone or cyclopentanone (298.15 K; 293.15, 298.15, 303.15, 308.15 K) [82], chloroform+aniline or 2-methylaniline (308.15 K) [124], pyrrolidin-2-one+butan-1-ol or propan-2-ol or propan-1-ol or ethanol (308.15 K) [125], tetrahydropyran+2-methylaniline or aniline or N-methylaniline (308.15 K) [126], 1,3-dioxolane+2-methylaniline or aniline or N-methyl aniline (308.15 K) [127], tetrahydropyran + pyridine or 4- or 3- or 2-picoline mixtures (308.15 K; 298.15, 303.15, 308.15 K) [128], 2-methylaniline+pyridine or 4- or 3- or 2-picoline mixtures (308.15 K; 298.15, 303.15, 308.15 K) [129], 1,4-dioxane+aniline or N-methyl aniline or 2-methylaniline (308.15 K) [130], κ_S^E and C_P^E of 1,3-dioxolane or tetrahydrofuran or 1,4-dioxane+piperidine (293.15, 298.15, 303.15, 308.15 K) [85], 1-methylpiperidine+cycloheptanone or cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [131], piperidine or 1-methylpiperidine+4- or 3- or 2-picoline or 2-pyrrolidinone or pyridine (293.15, 298.15, 303.15 , 308.15 K) [132,133], H^E, κ_S^E and C_P^E of 1,3-dioxolane+1-methylpyrrolidin-2-one or cycloheptanone or cyclohexanone mixtures (308.15 K; 293.15, 298.15, 303.15 K; 308.15 K) [83], [EMIM][BF_4] or 1-butyl-3-methylimidazolium tetrafluoroborate [BMIM][BF_4]+[BDIM][BF_4], [BMIM][BF_4]+[EMIM][BF_4]; (298.15 K; 293.15, 298.15, 303.15, 308.15 K) [99] , 2-chlorotoluene+N,N-dimethylformamide or N-methylformamide or formamide (308.15 K; 298.15, 303.15, 308.15 K) [134], acetone+cyclopentanone or cyclohexanone or cycloheptanone (298.15 K; 293.15, 298.15, 303.15, 308.15 K) [135], 2-chlorotoluene+tetrahydropyran or 1,3-dioxolane or 1,4-dioxane (308.15 K; 298.15, 303.15, 308.15 K) [136], piperidine+cyclopentanone or cyclohexanone or cycloheptanone (308.15 K; 293.15, 298.15, 303.15, 308.15 K) [137] were verified by means of Eq. (42). Inferred results suggest that calculated H^E, κ_S^E, C_P^E values of the above said mixtures via Eq. (42) were in agreement with their measured values.

3-2. ($1+2_m$) (m is the Degree of Association) Mixtures

For ($1+2_m$) mixture comprised of non-associated (1) and associated (2) components, interaction parameter for the breakdown of associated (1_m) entity, was considered to be zero, i.e. χ_{11}=zero. Eq. (41) for ($1+2_m$) mixtures was defined by

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{22}+x_2\chi'_{12}] \tag{43}$$

It was assumed that interaction parameter for the formation of (1−2) contact is nearly equal to interaction parameter for the disruption of (2−2) contacts i.e. $\chi_{12}\cong\chi_{22}=\chi'''_{12}$. Eq. (43) then was expressible by,

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi'''_{12}+x_2\chi'_{12}] \tag{44}$$

Unknown parameters χ'''_{12}, χ'_{12} {predicted in the manner as described for Eq. (42)} were subsequently used to determine excess thermodynamic data at various compositions. Various investigators verified Eq. (44) for estimating H^E, κ_S^E and C_P^E data of mixtures containing components being monomer and dimer respectively. H^E for N-methyl aniline or aniline or N,N-dimethyl aniline+methylene bromide (308.15 K) [68], methylene bromide+nitrobenzene (308.15 K) [70], nitromethane+isopropanol or butanol (308.15 K) [74]; 1,4-dioxane+butan-2-ol or butan-1-ol or propan-2-ol or propan-1-ol (308.15 K) [75], 1,3-dioxolane+formamide or N,N-dimethylformamide (298.15 K) [138], 1,3-dioxolane+butan-1-ol or butan-2-ol or propan-1-ol (308.15 K) [139], [EMIM][BF_4]+formamide (298.15 K) [140], κ_S^E of 1,4-dioxane or 1,3-dioxolane or methylbenzene or benzene+N,N-dimethylformamide or formamide (308.15 K) [141], benzene+2- or 3- or 4-chlorotoluene (293.15, 298.15, 303.15, 308.15 K) [142], C_P^E of [EMIM][BF_4]+1-methylpyrrolidin-2-one or pyrrolidin-2-one or pyridine; pyrrolidin-2-one+pyridine (293.15, 298.15, 303.15, 308.15 K) [143], H^E, κ_S^E of [EMIM][BF_4]+N-methylaniline or 2-methylaniline or aniline (298.15 K; 293.15, 298.15, 303.15, 308.15 K) [94], [EMIM][BF_4]+N-methylformamide or dimethylsulphoxide or N,N-dimethylformamide or acetone (298.15 K; 293.15, 298.15, 303.15, 308.15 K) [95,96], κ_S^E and C_P^E of 2-methylaniline+aniline or N-methylaniline (293.15, 298.15, 303.15, 308.15 K) [97], H^E, κ_S^E and C_P^E of [BDIM][BF_4] or [BMIM][BF_4] or [EMIM][BF_4]+cyclohexanone or cyclopentanone or (298.15 K; 293.15, 298.15, 303.15, 308.15 K) [98,100, 101] mixtures were examined in terms of Eq. (44). Calculated thermodynamic values (H^E, κ_S^E, C_P^E) were found to be comparable with measured data.

3-3. (1_m+2) (m is the Degree of Association) Mixtures

In the binary mixtures containing constituent (1) as associated entity and (2) as non-associated (2) entity (monomer), interaction parameter for the rupture of associated entity (2_m) i.e., χ_{22} would be Zero. Consequently, there would be no contribution to excess thermodynamic properties, X^E due to process ii (b). In view of said consideration, Eq. (41) for (1_m+2) mixtures reduced to

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}] \tag{45}$$

Further, interaction parameter for the establishment of unlike (1–2) contact were considered to be approximately equal to the interaction parameter for the estrangement of associated entity (1) i.e. $\chi_{12}\cong\chi_{11}=\chi'''_{12}$ Eq. (45) was written as

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_1)\chi''''_{12}+x_2\chi'_{12}] \tag{46}$$

Parameters χ''''_{12}, χ'_{12} were calculated in the same manner as explained for Eq. (42) and (44). χ''''_{12}, χ'_{12} were then used to compute X^E at various compositions. It was then worthwhile to see how Eq. (46) was applicable to predict H^E, κ_S^E and C_P^E of various (1_m+2) mixtures? For this purpose, researchers analyze H^E of methanol or ethanol+methylene bromide (298.15, 308.15 K) [64], 3-nitrotoluene or 2-methylaniline+1,3-dimethylbenzene or 1,4-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene or benzene (308.15 K) [71,76], nitrobenzene+1,4-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene or benzene mixtures (298.15, 308.15 K) [73], water+1,4-dioxane (303.15 K) [144], 1,4-dimethylbenzene or 1,3-dimethylbenzene+1,4-dioxane (308.15 K) [145], κ_S^E of 2-chlorotoluene+methylbenzene or 1,2-dimethylbenzene (298.15, 303.15, 308.15 K), tetrahydropyran+benzene or methylbenzene or 1,2-dimethylbenzene (298.15, 303.15 K) [146], C_P^E of tetrahydropyran+benzene or methylbenzene or 1,2-dimethylbenzene (298.15, 303.15, 308.15 K) [147], 1-methylpyrrolidin-2-one+benzene; benzene+3- or 4-chlorotoluene (293.15, 298.15, 303.15 K) [148], H^E, κ_S^E of pyrrolidin-2-one+1,4-dimethylbenzene or 1,3-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene or benzene (308.15 K) [77], 1-methyl pyrrolidin-2-one+1,2-dimethylbenzene or 1,3-dimethylbenzene or 1,4-dimethylbenzene (308.15 K) [80], tetrahydropyran+1,4-dimethylbenzene or 1,3-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene or benzene (308.15 K) [149] mixtures in terms of Eq. (46). The obtained results indicated that the computed H^E, κ_S^E and C_P^E values at various values of composition were in agreement with their corresponding measured data.

In the interpretation of H^E, κ_S^E data for 2-methylaniline+heptane or hexane or cyclohexane mixtures (containing associated organic solvent and inert solvent) at 308.15 K [150], it was observed that interaction parameter for the establishment of unlike (1−2) contact was too large in comparison to interaction parameter for the physical interaction between unlike molecules, i.e., $\chi_{12}\gg\chi'_{12}=\chi_{12}$, Eq. (45) for such mixtures was therefore expressed as

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}] \tag{47}$$

Eq. (47) effectively assessed H^E and κ_S^E data of 2-methylaniline+heptane or hexane or cyclohexane mixtures. However, in the analyses of C_P^E of pyrrolidin-2-one or 1-methylpyrrolidin-2-one+cyclohexane (293.15, 298.15, 303112.15, 308.15 K) [151], tetrahydropyran or 2-chlorotoluene+cyclohexane (298.15, 303.15, 308.15 K) [152], H^E and κ_S^E of tetrahydropyran+heptane or hexane or cyclohexane (308.15 K) [78], 1-methylpyrrolidin-2-one+cyclohexane (308.15 K) [79] mixtures, Eq. (47) was not successful in determining their thermodynamic H^E, κ_S^E and C_P^E data. This was because in these mixtures the interaction parameter for physical interaction, χ'_{12}, between the unlike constituent molecule was not negligible in comparison to interaction parameter for the establishment of unlike 1−2 contacts, χ_{12}. In such mixtures it was assumed that $\chi_{12} \approx \chi_{11} = \chi^*_{12}$. In view of this, Eq. (45) was reduced to

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_1)\chi^*_{12}+x_2\chi_{12}] \tag{48}$$

Eq. (48) was now able to describe H^E, κ_S^E and C_P^E of the above said mixtures.

3-4. (1+2) Binary Mixtures

In (1+2) mixtures, components (1) and (2) exist as monomer. Interaction parameters, χ_{11} and χ_{22} in such mixtures, were therefore non-existent; consequently, χ_{11} or χ_{22}=zero. Eq. (41) for these mixtures was then given by the relation:

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_2\chi'_{12}] \tag{49}$$

Eq. (49) was successfully utilized to estimate κ_S^E of 1,4-dioxane or 1,3-dioxolane+methylbenzene or benzene (308.15 K) [141], H^E and κ_S^E for 1,3-dioxolane+1,4-dimethylbenzene or 1,3-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene or benzene (298.15 K) [153,154] mixtures.

For (1+2) mixtures containing one of the components as nonpolar, there will be no chemical interaction between the unlike molecules, i.e., χ'_{12}=zero. X^E data were therefore defined by

$$X^E(X=H \text{ or } \kappa_S \text{ or } C_P) = \left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}] \tag{50}$$

Unknown parameter, χ_{12}, was computed by employing X^E data, preferably at equimolar composition. The calculated parameter was then used to compute excess thermodynamic data at other compositions. H^E data of methylene bromide+cyclohexane (308.15 K) [155], κ_S^E of 1,3-dioxolane+heptane or hexane or cyclohexane or benzene (298.15 K) [156] mixtures were comparable to their corresponding experimental values.

4. Activity Coefficients, γ and Gibb's Energies of Mixing, G^E of Binary Mixtures

An accurate knowledge regarding activity coefficients of the constituent molecules in the mixture provides a significant tool to obtain information regarding the change in interactions due to the mixing of components in the mixture. It was therefore worthwhile to utilize topological considerations of the components of mixtures for estimating their activity coefficients, γ and Gibb's energies of mixing, G^E of binary mixtures. To achieve said purpose, we was supposed that the change in energy due to mixing of components (1) and (2) depends on interactional energy mole^{-1} (say) χ_{12} and surface fraction, S_2, of the component (2) that form a contact with the surface area of component (1). Also, thermal energy has an effect on the magnitude of χ_{12}. The activity coefficient of component (1), γ_1, on the basis of above assumptions was expressed by [157-159]:

$$\ln\gamma_1 = x_2\chi_{12}V_2/RT\sum_{i=1}^{2}x_iV_i \tag{51}$$

where V_i (i=1, 2) is the molar volume of constituent (i). Standard state of component (1) was taken as that of pure (1), i.e., as $x_2 \rightarrow 0$; $\gamma_1 \rightarrow 1$.

The activity coefficient of the second component was evaluated via Gibbs Duhem equation in the form

$$\ln\gamma_2 = (\chi_{12}V_2/RTV_1)\left[\ln\left(\frac{\sum_{i=1}^{2}x_iV_i}{x_2V_2}\right) - x_1V_1/\sum_{i=1}^{2}x_iV_i\right] \tag{52}$$

If both components of the mixture have nearly identical molar volumes, then there should not be a drastic change in their surrounding in mixed state. As $\frac{V_2}{V_1} = \frac{{}^3\xi_1}{{}^3\xi_2}$, Eqs. (51) and (52) are then expressed as

$$\ln\gamma_1 = x_2\chi_{12}({}^3\xi_1/{}^3\xi_2)/RT[x_1+x_2({}^3\xi_1/{}^3\xi_2)] \tag{53}$$

$$\ln\gamma_2 = [\chi_{12}({}^3\xi_1/{}^3\xi_2)/RT] \left[\ln\left(\frac{\sum x_1+x_2({}^3\xi_1/{}^3\xi_2)}{x_2({}^3\xi_1)^{-1}}\right) - x_1({}^3\xi_1/{}^3\xi_2)/x_1+x_2({}^3\xi_1/{}^3\xi_2)\right] \tag{54}$$

Eqs. (53) and (54) were obtained by assuming that components of (1+2) mixture have almost same molar volumes and there was in no remarkable change in their surroundings (due to mixing of components).

Eqs. (53) and (54) failed to predict γ_1, γ_2 for mixtures having components of different molar volumes. For such mixtures γ_1, γ_2 were determined not only by considering (1−2) interactions but also taking into consideration the work done to accommodate 2nd component into the matrix of the 1st component. Work done necessary to accommodate the 2nd component into vicinity of 1st was then considered to be proportional not only to the difference in the molar volumes of the components but also to the interactions of 2nd component with 1st in the cavity. In view of this, the net work done, G_W^E, due to the accommodation of the 2nd component into the matrix of the 1st component was expressed by

$$G_W^E = \beta x_1x_2V_1V_2(1-V_2/V_1)/(\sum x_iV_i) \tag{55}$$

where β is constant. The activity coefficients of components in (1+2) mixture, due to this effect, were expressed by

$$(\ln\gamma_1)_w = \frac{1}{RT}[\partial(n_TG_W^E)/\partial n_1]_{n_2,\,T,\,P} \tag{56}$$

$$(\ln\gamma_2)_w = \frac{1}{RT}[\partial(n_TG_W^E)/\partial n_2]_{n_1,\,T,\,P} \tag{57}$$

Further, effects due to (1−2) interactions (Eq. (51)) and difference in the molar volumes of components (1) and (2) were presumed to have an independent impact on γ_1, γ_2; then $\ln\gamma_1$ and $\ln\gamma_2$ were given by [159]

$$\mathrm{RT}\ln\gamma_1=[\chi_{12}\mathrm{x}_2\mathrm{V}_2/\textstyle\sum \mathrm{x}_i\mathrm{V}_i]+\beta \mathrm{V}_1\mathrm{V}_2^2\mathrm{x}_2^2(1-\mathrm{V}_2/\mathrm{V}_1)/(\textstyle\sum \mathrm{x}_i\mathrm{V}_i)^2 \qquad (58)$$

$$\mathrm{RT}\ln\gamma_2=[\chi_{12}\mathrm{V}_2/\mathrm{V}_1]\left[\ln\frac{\sum \mathrm{x}_1\mathrm{V}_1}{\mathrm{x}_2\mathrm{V}_2}-\frac{\mathrm{x}_1\mathrm{V}_1}{\sum \mathrm{x}_1\mathrm{V}_1}\right]$$
$$+[\beta \mathrm{x}_1^2\mathrm{V}_1^2\mathrm{V}_2(1-\mathrm{V}_2/\mathrm{V}_1)/(\textstyle\sum \mathrm{x}_i\mathrm{V}_i)^2] \qquad (59)$$

Since $\frac{\mathrm{V}_2}{\mathrm{V}_1}=\frac{{}^3\xi_1}{{}^3\xi_2}$ [58]. Consequently, Eqs. (58) and (59) were reduced to [126]

$$\mathrm{RT}\ln\gamma_1=\left[\frac{\chi_{12}\mathrm{x}_2({}^3\xi_1/{}^3\xi_2)}{\mathrm{x}_1+\mathrm{x}_2({}^3\xi_1/{}^3\xi_2)}\right]+\left[\frac{\beta(1/{}^3\xi_1)({}^3\xi_1/{}^3\xi_2)^2\mathrm{x}_2^2(1-{}^3\xi_1/{}^3\xi_2)}{\mathrm{x}_1^2+\mathrm{x}_2^2({}^3\xi_1/{}^3\xi_2)^2}\right] \qquad (60)$$

$$\mathrm{RT}\ln\gamma_2=[\chi_{12}({}^3\xi_1/{}^3\xi_2)]\left[\ln\left(\frac{\mathrm{x}_1+\mathrm{x}_2({}^3\xi_1/{}^3\xi_2)}{\mathrm{x}_2({}^3\xi_1/{}^3\xi_2)}\right)-\frac{\mathrm{x}_1}{\mathrm{x}_1+\mathrm{x}_2({}^3\xi_1/{}^3\xi_2)}\right]$$
$$+\frac{\beta\mathrm{x}_1^2(1/{}^3\xi_2)[(1-{}^3\xi_1/{}^3\xi_2)]}{\mathrm{x}_1^2+\mathrm{x}_2^2({}^3\xi_1/{}^3\xi_2)^2} \qquad (61)$$

As Gibb's energies of mixing, G^E, of the binary (1+2) binary mixture is given by,

$$\mathrm{G}^E=\mathrm{RT}\textstyle\sum \mathrm{x}_i(\ln\gamma_i) \qquad (62)$$

Unidentified parameters χ_{12}, β (Eqs. (60) and (61)) were estimated by means of using γ_1, γ_2 at equimolar composition. These parameters were then utilized to predict γ_1, γ_2 and G^E at other values of x_1. Results suggest that activity coefficients for few binary mixtures were in agreement [159] with their measured values. Activity coefficients and G^E of 1,4-dioxane or tetrahydropyran or 1,3-dioxolane+N-methylaniline or 2-methylaniline or aniline (308.15 K) [126,127,130] were estimated using Eqs. (60)-(62). The results indicated that the activity coefficients (γ_i; i=1, 2) and G^E data of the examined mixtures had been judged well with their measured values. The assessment between measured and calculated values implied that Eqs. (60)-(62) can be utilized for estimating γ_i and G^E of binary mixtures (components varying even in polarity, shape, size).

Next question of interest was whether activity coefficients of components can be estimated if only the activity coefficient at infinite dilution is known. As $\mathrm{x}_1\rightarrow0$; $\mathrm{x}_2\rightarrow1$, the activity coefficient of component (1) at infinite dilution in (2) (in view of Eq. (58)) was expressed by

$$\ln\gamma_1^\infty=[\chi_{12}/\mathrm{RT}]+[\beta\mathrm{V}_1(1-\mathrm{V}_2/\mathrm{V}_1)/\mathrm{RT}] \qquad (63)$$

The activity coefficients of the 1st and the 2nd components of binary mixture were then expressed in terms of $\ln\gamma_1^\infty$ by equations:

$$\ln\gamma_1=[\chi_{12}\mathrm{x}_2\mathrm{V}_2/\mathrm{RT}\textstyle\sum \mathrm{x}_i\mathrm{V}_i][1-\mathrm{x}_2\mathrm{V}_2/\textstyle\sum \mathrm{x}_i\mathrm{V}_1]$$
$$+[(\ln\gamma_1^\infty)\mathrm{V}_2^2\mathrm{x}_2^2/(\textstyle\sum \mathrm{x}_i\mathrm{V}_i)^2] \qquad (64)$$

$$\ln\gamma_2=[\chi_{12}\mathrm{V}_2/\mathrm{RTV}_1][\ln\{\textstyle\sum \mathrm{x}_i\mathrm{V}_i/\mathrm{x}_2\mathrm{V}_2\}-\{\mathrm{x}_1\mathrm{V}_1/\textstyle\sum \mathrm{x}_i\mathrm{V}_i\}$$
$$-\{\mathrm{x}_1^2\mathrm{V}_1^2/(\textstyle\sum \mathrm{x}_i\mathrm{V}_i)^2\}]+[(\ln\gamma_1^\infty)\mathrm{x}_1^2\mathrm{V}_2\mathrm{V}_1/(\textstyle\sum \mathrm{x}_i\mathrm{V}_i)^2] \qquad (65)$$

γ_1^∞ can be determined easily by gas-liquid chromatography [160, 161], Eqs. (64) and (65) can be used to predict γ_1 and γ_2 of the components of binary mixtures at any value of x_1. The γ_1 etc. data of binary mixtures estimated by using experimental activity coefficients at (x_i=0.5) via Eqs. (64) and (65) were found to be in agreement with experimental data [159]. Graph theory thus provides a very simple method that successfully reproduces the experimental activity coefficients data for the components of binary mixture when only the activity coefficient at equimolar composition is known.

5. Excess Molar Volumes, V_{123}^E, for Ternary Mixtures

V^E for binary mixtures (graph theory) is expressed by Eq. (13). In view of this equation, V_{123}^E for ternary mixtures was expressed [162] by:

$$\mathrm{V}_{123}^E=\alpha_{123}\left[\sum_{i=1}^{3}[\mathrm{x}_i({}^3\xi_i)_m]^{-1}-\sum_{i=1}^{3}\mathrm{x}_i({}^3\xi_i)^{-1}\right] \qquad (66)$$

α_{123} signifies a constant characteristic of a ternary (1+2+3) mixture. Since, ternary mixture was rumored to be comprised of binary (1+2), (2+3) and (1+3) mixtures, therefore, α_{12}, α_{23}, α_{13}, characteristic parameters of (1+2), (2+3) and (1+3) mixtures were expressed in terms of α_{123} by the relation:

$$\alpha_{123}=\alpha_{12}+\alpha_{23}+\alpha_{13} \qquad (67)$$

As 1, 2 molecules in (1+2) mixture can pack themselves in two either 12 or 21 ways, therefore, three molecules 1, 2 and 3 were considered to provide six different binary arrangements: 12, 21; 23, 32; 13, 31 in three binary mixtures. These packing arrangements result in ${}^6\mathrm{C}_2$ or fifteen 123 ternary combinations. However, in general 1, 2 and 3 molecules pack themselves only in three 123 or 231 or 321 ways. Thus, ternary packing arrangements (obtained via binary packing arrangements) were five times higher than the actual ternary packing arrangements. Consequently, α_{123} was expressed by

$$\alpha_{123}=0.2\ (\alpha_{12}+\alpha_{23}+\alpha_{13}) \qquad (68)$$

Eq. (66) was then modified to

$$\mathrm{V}_{123}^E=0.2(\alpha_{12}+\alpha_{23}+\alpha_{13})\left[\sum_{i=1}^{3}[\mathrm{x}_i({}^3\xi_i)_m]^{-1}-\sum_{i=1}^{3}\mathrm{x}_i({}^3\xi_i)^{-1}\right] \qquad (69)$$

Eq. (69) can be utilized to determine V_{123}^E for the ternary mixtures if α_{12}, α_{23} and α_{13} for (1+2), (2+3), (1+3) for binaries are known. α_{12}, α_{23} and α_{13} for several binaries (by using their V^E data) could then be exploited to compute V_{123}^E of ternary mixtures. Graph theory (Eq. (69)) described well V_{123}^E data of methylene bromide+benzene+1,2-dimethybenzene or 1,4-dimethoxybenzene or methylbenzene; methylene bromide+methylbenzene+1,2-dimethybenzene or 1,4-dimethoxybenzene (298.15, 308.15 K) [162]; methylene bromide+pyridine+3-picoline; cyclohexane+pyridine+3-picoline; benzene+methylbenzene+1,2-dichloroethane; benzene+1,2-dimethylbenzene+1,2-dicholoroethane; benzene+1,4-dimethylbenzene+1,2-dichloroethane (298.15 K) [163]; 1,2-dichloroethane+pyridine+2-picoline; 1,2-dichloroethane+heptane+2-picoline or pyridine; heptane+pyridine+4-picoline; aniline+pyridine+2-picoline or 4-picoline (298.15 K) [164]; benzene+methylbenzene or 1,2-dimethylbenzene or 1,4-dimethylbenzene+2-chlorotoluene; methylbenzene+1,2-dimethylbenzene+2-chlorotoluene (308.15 K) [165]. In those cases where the comparison between the two (measured and calculated) values was not good, the predicted values were of similar order of magnitude. Minute observations implied that V^E_{123} values predicted for benzene+1,4-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene+2-chlorotoluene; methylbenzene+1,2-dimethylbenzene+2-chlorotoluene (308.15 K) [165] mixtures were of similar sign as that of measured values but the calculable agreement was not good. Failure of the Graph theory to determine V^E_{123} correctly for said ternary mixtures was because interactions occurring among the components of mixtures were not taken into consideration. NMR studies of benzene+2-chlorotoluene and 1,2-dimethylbenzene+benzene+2-chlorotoluene mixtures [165] revealed that addition of 1,2-dimethylbenzene to an equimolar benzene+2-chlorotoluene mixture does bring into play attractive-repulsive interactions between 1, 2 and 3 molecules. In view of the interactions between the constituent molecules α_{123} of 1,2-dimethylbenzene or 1,4-dimethylbenzene+benzene or methylbenzene+2-chlorotoluene mixtures was defined by

$$\alpha_{123}=0.2\ (a\alpha_{12}+b\alpha_{23}+c\alpha_{13}) \qquad (70)$$

where a, b, c are constants characteristic of (1+2+3) mixtures that depict the change in interaction due to addition of 3rd, 1st, 2nd in (1+2), (2+3), (1+3) mixtures. The V^E_{123} values evaluated by Graph theory using a, b, c values reproduced well the experimental data.

6. Excess Molar Enthalpies, H^E_{123} for Ternary Mixtures

The energetics of the ternary mixtures was then studied by graph theory. To compute H^E_{123} for ternary (1+2+3) mixture it was assumed that the ternary mixture is characterized by the following contacts:

$$1\underline{23}=12' \qquad (71)$$

$$2\underline{31}=23' \qquad (72)$$

$$3\underline{12}=31' \qquad (73)$$

so that H^E_{123} may be the summation of H^E contribution due to 12', 23', 31' and 12, 23, 31 contacts. The contribution due to each of the said unlike contacts was assumed to be additive. Consequently, H^E_{123} was expressed [166] by

$$H^E_{123}\propto(H^E_{12'}+H^E_{12'}+H^E_{31'}+H^E_{12}+H^E_{23}+H^E_{31}) \qquad (74)$$

$$H^E_{123}=K(H^E_{12'}+H^E_{12'}+H^E_{31'}+H^E_{12}+H^E_{23}+H^E_{31}) \qquad (75)$$

K symbolizes constant of proportionality; $H^E_{12'}$ etc., signify the involvement to H^E_{123} because of 1−2' etc. contacts. The $H^E_{12'}$ for an (1+2') mixture was expressed by

$$H^E_{12'}=\frac{x_1x_2\chi'_{12}K_{12'}({}^3\xi_1/{}^3\xi_{2'})}{x_1+x_1x_2K_{12'}({}^3\xi_1/{}^3\xi_{2'})} \qquad (76)$$

$K_{12'}({}^3\xi_1/{}^3\xi_{2'})$ depicts the probability of interacting surface area of 2' with 1. For an (1+2+3) mixture containing x_1, x_2 and x_3 mole fractions, $K_{12'}({}^3\xi_1/{}^3\xi_{2'})$ is specified by

$$K_{12'}({}^3\xi_1/{}^3\xi_{2'})=x_2K_{12}({}^3\xi_1/{}^3\xi_2)+x_1K_{13}({}^3\xi_1/{}^3\xi_3) \qquad (77)$$

If interactions do not exist between components of the mixture, H^E_{123} is given by:

$$H^E_{123}=K\left[\sum x_1x_2\chi'_{12'}\frac{x_2K_{12}({}^3\xi_1/{}^3\xi_2)+x_3K_{13}({}^3\xi_1/{}^3\xi_3)}{x_1+x_2[x_2K_{12}({}^3\xi_1/{}^3\xi_2)+x_3K_{13}({}^3\xi_1/{}^3\xi_3)]}\right.$$

$$\left.+\sum\frac{x_1x_2\chi'_{12}K_{12}({}^3\xi_1/{}^3\xi_2)}{x_1+x_2K_{12}({}^3\xi_1/{}^3\xi_2)}\right] \qquad (78)$$

$\chi'_{12'}$ etc. represent the interaction energy of 1 : 2' etc. unlike contacts. Since non-specific interactions occurred among the components of ternary mixtures, it was justified to assume

$$\chi'_{12'}=\chi'_{12}+\chi'_{13} \qquad (79)$$

$$\chi'_{23'}=\chi'_{23}+\chi'_{21} \qquad (80)$$

$$\chi'_{31'}=\chi'_{31}+\chi'_{32} \qquad (81)$$

Eq. (78) is then given by

$$H^E_{123}=K\left[\sum x_1x_2(\chi'_{12'}+\chi'_{13})\frac{x_2K_{12}({}^3\xi_1/{}^3\xi_2)+x_3K_{13}({}^3\xi_1/{}^3\xi_3)}{x_1+x_2[x_2K_{12}({}^3\xi_1/{}^3\xi_2)+x_3K_{13}({}^3\xi_1/{}^3\xi_3)]}\right.$$

$$\left.+\sum\frac{x_1x_2\chi'_{12}K_{12}({}^3\xi_1/{}^3\xi_2)}{x_1+x_2K_{12}({}^3\xi_1/{}^3\xi_2)}\right] \qquad (82)$$

The H^E_{123} of a ternary mixture thus should be figured from the H^E data of the (1+2), (2+3), (3+1) mixtures if K is known. K is considered to be dependent on unlike contacts and thus is taken same for all the ternary mixtures. Further, K=0.2 best reproduces the H^E_{123} of data of benzene+cyclohexane+heptane [167] ternary mixture and the same is used to determine H^E_{123} for numerous ternary mixtures. H^E_{123} assessed by Graph theory for methylene bromide+benzene+methylbenzene or 1,2-dimethoxybenzene or 1,4-dimethylbenzene; methylene bromide+methylbenzene+1,2-dimethoxybenzene or 1,4-dimethylbenzene (308.15 K) [166]; 1,2-dichloroethane+pyridine+2-picoline; 1,2-dichloroethane+heptane+2-picoline or pyridine; heptane+pyridine+2-picoline; aniline+pyridine+2-picoline or 4-picoline (298.15, 308.15 K) [168]; methylene bromide+pyridine+3-picoline; pyridine+3-picoline+cyclohexane; benzene+methylbenzene+1,2-dichloroethane; benzene+1,2-dimethylbenzene+1,2-dichloroethane; benzene+1,4-dimethylbenzene+1,2-dichloroethane (298.15 K) [169]; benzene+methylbenzene or 1,2-dimethylbenzene or 1,4-dimethylbenzene+2-chlorotoluene; toluene+1,2-dimethylbenzene+2-chlorotoluene (308.15 K) [165] mixtures compare well with their measured data. However, Singh et al. [166] observed that H^E_{123} for methylene bromide+benzene+1,4-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene; methylene bromide+methylbenzene+1,4-dimethylbenzene or 1,2-dimethylbenzene (298.15 K) (determined via Eq. (82)) were not in good agreement with their corresponding experimental data. It was explained by the fact that a decrease in temperature may result in specific interactions among molecules. H^E_{123} for methylene bromide+methylbenzene+1,4-dimethylbenzene or 1,2-dimethylbenzene (negative at 298.15 K in comparison to positive at 308.15 K) support said view point. Thus, incapability to compute H^E_{123} at 298.15 K for the said mixtures was due to the failure of assumptions (Eqs. (79)-(81)) made in computing $\chi'_{12'}$ etc. For methylene bromide+benzene+1,2-dimethylbenzene or 1,4-dimethylbenzene or methylbenzene (298.15 K) $\chi'_{12'}$ etc. were expressed by

$$\chi'_{12'}=(1/7)(\chi'_{12}+\chi'_{13}) \qquad (83)$$

$$\chi'_{23'}=(1/7)(\chi'_{23}+\chi'_{21}) \qquad (84)$$

$$\chi'_{31'}=(1/7)(\chi'_{31}+\chi'_{32}) \tag{85}$$

H^E_{123} values for these mixtures (calculated from Eq. (82)) utilizing modified $\chi'_{12'}$ etc. values {Eqs. (83)-(85)} made effective improvement between calculated and measured values. However, for methylene bromide+methylbenzene+1,4-dimethylbenzene or 1,2-dimethylbenzene mixtures H^E_{123} data were found to be in agreement with experimental values by making assumption $\chi'_{12'}=-(\chi'_{12}+\chi'_{13})$.

Graph approach thus predicts well the V^E_{123} and H^E_{123} of mixtures comprised of components which do not characterize specific interactions. However, theory failed to explain the V^E_{123} and H^E_{123} data of mixtures containing specific interactions among the constituent molecules or containing associated molecular entities. To overcome this limitation, it was proposed that various thermodynamic properties like V^E_{123}, $(\kappa^E_S)_{123}$, H^E_{123} and $(C^E_P)_{123}$ of ternary mixtures can be estimated by graph theory if the existence of components and processes intricate in the mixture formation is known. These considerations prompted researchers to determine V^E_{123}, $(\kappa^E_S)_{123}$, H^E_{123} and $(C^E_P)_{123}$ of mixtures comprising ionic liquids, polar solvents, non -polar solvents.

7. Excess Molar Volume, V^E_{123}, Excess Isentropic Compressibility, $(\kappa^E_S)_{123}$, Excess Molar Enthalpy, H^E_{123} and Excess Heat Capacity, $(C^E_P)_{123}$ for Ternary Mixtures

Graph theory has been efficaciously employed to describe V^E, (κ^E_S), H^E, (C^E_P) of binary mixtures. It was then of concern to see whether the said approach can be extended to estimate V^E_{123}, $(\kappa^E_S)_{123}$, H^E_{123} and $(C^E_P)_{123}$ of ternary mixtures. As discussed in binaries, V^E_{123}, $(\kappa^E_S)_{123}$, H^E_{123}, $(C^E_P)_{123}$ of ternary mixtures can be computed, if several processes in (1+2+3) mixture formation are known. Such processes depend on the state of components and interactions taking place among the unlike molecules. Various mathematical expressions obtained for estimating thermodynamic data of mixtures containing components differing in degree of association are described below.

7-1. $(1_m+2_m+3_m)$ (m is the Degree of Association) Ternary Mixtures

If 1, 2 and 3 molecules exist as associated molecular entities 1_m, 2_m, 3_m (m=2; m represents the degree of association), respectively, then $(1_m+2_m+3_m)$ mixture formation be presumed to encompass processes (i) creation of dissimilar (a) 1_m–2_m; (b) 2_m–3_m; (c) 1_m–3_m contacts; (ii) estrangement of (a) 1_m (b) 2_m (c) 3_m entities to form their respective molecules; and (iii) Such molecules interact to form molecular (a) 1 : 2 (b) 2 : 3 and (c) 1 : 3 complexes. If χ_{12}, χ_{23}, χ_{13} are molar volume, molar compressibility and molar interaction energy parameters for unlike 1_m-2_m, 2_m-3_m, 1_m-3_m contacts, which in turn enhance non-randomness, then the contribution to $\Delta X_{i(a\text{-}c)}$ (X=V or κ_S or H or C_P) because of processes i(a-c) is given [170-172] by

$$\Delta X_{i(a\text{-}c)}=x_1S_2\chi_{12}+x_2S_3\chi_{23}+x_3S_1\chi_{13} \tag{86}$$

Since $S_{i\,(i=1,2,3)}$ is defined by Eq. (23), consequently Eq. (86) is reduced to

$$\Delta X_{i(a\text{-}c)}=\frac{x_1x_2V_2\chi_{12}}{\sum_{i=1}^{2}x_iV_i}+\frac{x_2x_3V_3\chi_{23}}{\sum_{i=2}^{3}x_iV_i}+\frac{x_1x_3V_1\chi_{13}}{\sum_{i=1}^{3}x_iV_i} \tag{87}$$

Further, if χ_{11}, χ_{22}, χ_{33} are molar volumes, molar compressibilities, molar interaction parameters for rupture of associated entities which enhances randomness, then, $\Delta X_{ii(a\text{-}c)}$ (X=V or κ_S or H or C_P) because of processes ii(a-c) is stated [170-172] by

$$\Delta X_{ii(a\text{-}c)}=x_1S'_2\chi_{11}+x_2S'_3\chi_{22}+x_3S'_1\chi_{33} \tag{88}$$

In view of $S'_{i\,(i=1,2,3)}$ defined by Eq. (33), Eq. (88) is expressed by

$$\Delta X_{ii(a\text{-}c)}=\frac{x_1^2x_2V_2\chi_{11}}{\sum_{i=1}^{2}x_iV_i}+\frac{x_2^2x_3V_3\chi_{22}}{\sum_{i=2}^{3}x_iV_i}+\frac{x_3^2x_1V_1\chi_{33}}{\sum_{i=1}^{3}x_iV_i} \tag{89}$$

If χ'_{12}, χ'_{23} and χ'_{13} are molar volumes, molar compressibilities and molar interaction parameters for the interactions between 1, 2; 2, 3; and 1, 3 molecules to form molecular 1 : 2, 2 : 3 and 1 : 3 complexes having non-random structure, then, $\Delta X_{iii(a\text{-}c)}$ (X=V or κ_S or H or C_P) due to processes iii(a-c) is given [170-172] by

$$\Delta X_{iii(a\text{-}c)}=x_1S''_2\chi'_{12}+x_2S''_3\chi'_{23}+x_3S''_1\chi'_{13} \tag{90}$$

where $S''_1=x_1S_1$; $S''_2=x_2S_2$; $S''_3=x_3S_3$. Consequently Eq. (90) is expressible by

$$\Delta X_{iii(a\text{-}c)}=\frac{x_1x_2^2V_2\chi'_{12}}{\sum_{i=1}^{2}x_iV_i}+\frac{x_2x_3^2V_3\chi'_{23}}{\sum_{i=2}^{3}x_iV_i}+\frac{x_3x_1^2V_1\chi'_{13}}{\sum_{i=1}^{3}x_iV_i} \tag{91}$$

Excess thermodynamic properties, X^E_{123} are due to the summation of contributions because of i(a-c), ii(a-c) and iii(a-c) processes in $(1_m+2_m+3_m)$ mixtures. Consequently,

$$\begin{aligned}X^E_{123}=\sum_{i=I}^{III}\Delta X_i=&\left[\frac{x_1x_2V_2}{\Sigma_{i=1}^{2}x_iV_i}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}]\\&+\left[\frac{x_2x_3V_3}{\Sigma_{i=2}^{3}x_iV_i}\right][\chi_{23}+x_2\chi_{22}+x_3\chi'_{23}]\\&+\left[\frac{x_1x_3V_1}{\Sigma_{i=1}^{3}x_iV_i}\right][\chi_{13}+x_3\chi_{33}+x_1\chi'_{13}]\end{aligned} \tag{92}$$

where V_i (i=1, 2, 3) is the molar volume of components (i). Further, $\frac{V_2}{V_1}=\frac{{}^3\xi_1}{{}^3\xi_2}$ [58]; Eq. (92) is therefore expressed as

$$\begin{aligned}X^E_{123}=&\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}]\\&+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][\chi_{23}+x_2\chi_{22}+x_3\chi'_{23}]\\&+\left[\frac{x_1x_3({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][\chi_{13}+x_3\chi_{33}+x_1\chi'_{13}]\end{aligned} \tag{93}$$

If $\chi_{12}\cong\chi'_{12}=\chi^*_{12}$; $\chi_{23}\cong\chi'_{23}=\chi^*_{23}$; $\chi_{13}\cong\chi'_{13}=\chi^*_{13}$ and $\chi_{11}\cong\chi_{22}\cong\chi_{33}=\chi^*$ then Eq. (93) is reduced to

$$\begin{aligned}X^E_{123}=&\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi^*_{12}+x_1\chi^*]\\&+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][(1+x_3)\chi^*_{23}+x_2\chi^*]\\&+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][(1+x_1)\chi^*_{13}+x_3\chi^*]\end{aligned} \tag{94}$$

7-2. (1_m+2_m+3) Ternary Mixtures

In ternary mixtures containing 1, 2 molecules as associated entity and 3 as non-associated entity, no energy would be required to dissociate molecule 3, i.e., contribution to χ_{33} in Eq. (93) would be zero. Eq. (93) for (1_m+2_m+3) is therefore stated [173,174] as

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][\chi_{23}+x_2\chi_{22}+x_3\chi'_{23}]$$
$$+\left[\frac{x_1x_3({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][\chi_{13}+x_1\chi'_{13}] \tag{95}$$

If $\chi_{12}\cong\chi'_{12}=\chi^*_{12}$; $\chi_{23}\cong\chi'_{23}=\chi^*_{23}$; $\chi_{13}\cong\chi'_{13}=\chi^*_{13}$ and $\chi_{11}\cong\chi_{22}=\chi^*$ then X^E_{123} data are expressed by

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi^*_{12}+x_1\chi^*]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][(1+x_3)\chi^*_{23}+x_2\chi^*]$$
$$+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][(1+x_1)\chi^*_{13}] \tag{96}$$

7-3. (1_m+2+3_m) Ternary Mixtures

In (1_m+2+3_m) ternary mixtures while 1 and 3 components are associated molecular entities, molecule 2 is non-associated, thus the interaction parameter for the disruption of molecule 2, i.e., χ_{22} would be zero. Eq. (93) for (1_m+2+3_m) mixtures is defined [175, 176] by

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][\chi_{23}+x_3\chi'_{23}]$$
$$+\left[\frac{x_1x_3({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][\chi_{13}+x_3\chi_{33}+x_1\chi'_{13}] \tag{97}$$

If $\chi_{12}\cong\chi'_{12}=\chi^*_{12}$; $\chi_{23}\cong\chi'_{23}=\chi^*_{23}$; $\chi_{13}\cong\chi'_{13}=\chi^*_{13}$ and $\chi_{11}\cong\chi_{33}=\chi^*$ then X^E_{123} for such mixtures is given by the relation:

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi^*_{12}+x_1\chi^*]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][(1+x_3)\chi^*_{23}]$$
$$+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][(1+x_1)\chi^*_{13}+x_3\chi^*] \tag{98}$$

7-4. (1+2_m+3_m) Ternary Mixtures

In mixtures containing one component as monomer say, (1), and two components as associated molecular entities, say 2, 3, there would be no contribution to interaction energy for the rupture of component 1, i.e., χ_{11} would be zero. In view of this, Eq. (93) for (1+2_m+3_m) mixtures is expressed [177,178] as

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_2\chi'_{12}]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][\chi_{23}+x_2\chi_{22}+x_3\chi'_{23}]$$
$$+\left[\frac{x_1x_3({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][\chi_{13}+x_3\chi_{33}+x_1\chi'_{13}] \tag{99}$$

$\chi_{12}\cong\chi'_{12}=\chi^*_{12}$; $\chi_{23}\cong\chi'_{23}=\chi^*_{23}$; $\chi_{13}\cong\chi'_{13}=\chi^*_{13}$ and $\chi_{22}\cong\chi_{33}=\chi^*$ then thermodynamic properties are expressible by

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi^*_{12}]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][(1+x_3)\chi^*_{23}+x_2\chi^*]$$
$$+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][(1+x_1)\chi^*_{13}+x_3\chi^*] \tag{100}$$

7-5. (1_m+2+3) Ternary Mixtures

Since two components, namely, 2 and 3, in (1_m+2+3) mixture are non-associated molecular entities, therefore the contribution to interaction energy for the rupture of components 2 and 3, i.e., χ_{22}, χ_{33}, would be zero. Due to these considerations, Eq. (93) is stated [179,180] as

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][\chi_{23}+x_3\chi'_{23}]$$
$$+\left[\frac{x_1x_3({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][\chi_{13}+x_1\chi'_{13}] \tag{101}$$

If $\chi_{12}\cong\chi'_{12}=\chi^*_{12}$; $\chi_{23}\cong\chi'_{23}=\chi^*_{23}$; $\chi_{13}\cong\chi'_{13}=\chi^*_{13}$ and $\chi_{11}\cong\chi_{22}\cong\chi_{33}=\chi^*$ then X^E_{123} for such mixtures is defined by

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][(1+x_2)\chi^*_{12}+x_1\chi^*]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][(1+x_3)\chi^*_{23}]$$
$$+\left[\frac{x_3x_1({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][(1+x_1)\chi^*_{13}] \tag{102}$$

In mixtures containing a third component as non-polar solvent (cyclohexane, n-alkanes) the interaction energy due to the formation of 2 : 3 and 1 : 3 molecular complexes, i.e., χ'_{23} and χ'_{13} would be zero. Eq. (101) is reduced [181] to

$$X^E_{123}=\left[\frac{x_1x_2({}^3\xi_1/{}^3\xi_2)}{x_1+x_2({}^3\xi_1/{}^3\xi_2)}\right][\chi_{12}+x_1\chi_{11}+x_2\chi'_{12}]$$
$$+\left[\frac{x_2x_3({}^3\xi_2/{}^3\xi_3)}{x_2+x_3({}^3\xi_2/{}^3\xi_3)}\right][\chi_{23}]+\left[\frac{x_1x_3({}^3\xi_3/{}^3\xi_1)}{x_3+x_1({}^3\xi_3/{}^3\xi_1)}\right][\chi_{13}] \tag{103}$$

If $\chi_{12}\cong\chi'_{12}=\chi^*_{12}$ then X^E_{123} were given as

$$\mathrm{X}^{E}_{123}=\left[\frac{\mathrm{x}_1\mathrm{x}_2(^3\xi_1/^3\xi_2)}{\mathrm{x}_1+\mathrm{x}_2(^3\xi_1/^3\xi_2)}\right][(1+\mathrm{x}_2)\chi^{*}_{12}+\mathrm{x}_1\chi_{11}]$$
$$+\left[\frac{\mathrm{x}_2\mathrm{x}_3(^3\xi_2/^3\xi_3)}{\mathrm{x}_2+\mathrm{x}_3(^3\xi_2/^3\xi_3)}\right][\chi_{23}]+\left[\frac{\mathrm{x}_1\mathrm{x}_3(^3\xi_3/^3\xi_1)}{\mathrm{x}_3+\mathrm{x}_1(^3\xi_3/^3\xi_1)}\right][\chi_{13}] \tag{104}$$

7-6. (1+2+3_m) Ternary Mixtures

(1+2+3_m) mixtures are comprised of two components, 1 and 2, as non-associated and 3rd component as associated entity; consequently, there is no contribution to interaction energies due to the rupture of components 1 and 2, i.e., χ_{11}, χ_{22}=zero. For such mixtures Eq. (93) is given [182] by

$$\mathrm{X}^{E}_{123}=\left[\frac{\mathrm{x}_1\mathrm{x}_2(^3\xi_1/^3\xi_2)}{\mathrm{x}_1+\mathrm{x}_2(^3\xi_1/^3\xi_2)}\right][\chi_{12}+\mathrm{x}_2\chi^{/}_{12}]$$
$$+\left[\frac{\mathrm{x}_2\mathrm{x}_3(^3\xi_2/^3\xi_3)}{\mathrm{x}_2+\mathrm{x}_3(^3\xi_2/^3\xi_3)}\right][\chi_{23}+\mathrm{x}_3\chi^{/}_{23}]$$
$$+\left[\frac{\mathrm{x}_1\mathrm{x}_3(^3\xi_3/^3\xi_1)}{\mathrm{x}_3+\mathrm{x}_1(^3\xi_3/^3\xi_1)}\right][\chi_{13}+\mathrm{x}_3\chi_{33}+\mathrm{x}_1\chi^{/}_{13}] \tag{105}$$

$\chi_{12}\cong\chi^{/}_{12}=\chi^{*}_{12}$; $\chi_{23}\cong\chi^{/}_{23}=\chi^{*}_{23}$; $\chi_{13}\cong\chi^{/}_{13}=\chi^{*}_{13}$, X^{E}_{123} for these mixtures is given by

$$\mathrm{X}^{E}_{123}=\left[\frac{\mathrm{x}_1\mathrm{x}_2(^3\xi_1/^3\xi_2)}{\mathrm{x}_1+\mathrm{x}_2(^3\xi_1/^3\xi_2)}\right][(1+\mathrm{x}_2)\chi^{*}_{12}]$$
$$+\left[\frac{\mathrm{x}_2\mathrm{x}_3(^3\xi_2/^3\xi_3)}{\mathrm{x}_2+\mathrm{x}_3(^3\xi_2/^3\xi_3)}\right][(1+\mathrm{x}_3)\chi^{*}_{23}]$$
$$+\left[\frac{\mathrm{x}_3\mathrm{x}_1(^3\xi_3/^3\xi_1)}{\mathrm{x}_3+\mathrm{x}_1(^3\xi_3/^3\xi_1)}\right][(1+\mathrm{x}_1)\chi^{*}_{13}+\mathrm{x}_3\chi_{33}] \tag{106}$$

7-7. (1+2+3) Ternary Mixtures

All the components in (1+2+3) mixtures exist as non-associated entities;, therefore, interaction energies for the rupture of 1, 2 and 3 components, i.e., χ_{11}=χ_{22}=χ_{33}=zero. These considerations reduce [183] Eq. (93) to

$$\mathrm{X}^{E}_{123}=\left[\frac{\mathrm{x}_1\mathrm{x}_2(^3\xi_1/^3\xi_2)}{\mathrm{x}_1+\mathrm{x}_2(^3\xi_1/^3\xi_2)}\right][\chi_{12}+\mathrm{x}_2\chi^{/}_{12}]$$
$$+\left[\frac{\mathrm{x}_2\mathrm{x}_3(^3\xi_2/^3\xi_3)}{\mathrm{x}_2+\mathrm{x}_3(^3\xi_2/^3\xi_3)}\right][\chi_{23}+\mathrm{x}_3\chi^{/}_{23}]$$
$$+\left[\frac{\mathrm{x}_1\mathrm{x}_3(^3\xi_3/^3\xi_1)}{\mathrm{x}_3+\mathrm{x}_1(^3\xi_3/^3\xi_1)}\right][\chi_{13}+\mathrm{x}_1\chi^{/}_{13}] \tag{107}$$

If $\chi_{12}\cong\chi^{/}_{12}=\chi^{*}_{12}$; $\chi_{23}\cong\chi^{/}_{23}=\chi^{*}_{23}$; $\chi_{13}\cong\chi^{/}_{13}=\chi^{*}_{13}$ then thermodynamic properties, X^{E}_{123}, are related by

$$\mathrm{X}^{E}_{123}=\left[\frac{\mathrm{x}_1\mathrm{x}_2(^3\xi_1/^3\xi_2)}{\mathrm{x}_1+\mathrm{x}_2(^3\xi_1/^3\xi_2)}\right][(1+\mathrm{x}_2)\chi^{*}_{12}]$$
$$+\left[\frac{\mathrm{x}_2\mathrm{x}_3(^3\xi_2/^3\xi_3)}{\mathrm{x}_2+\mathrm{x}_3(^3\xi_2/^3\xi_3)}\right][(1+\mathrm{x}_3)\chi^{*}_{23}]$$
$$+\left[\frac{\mathrm{x}_3\mathrm{x}_1(^3\xi_3/^3\xi_1)}{\mathrm{x}_3+\mathrm{x}_1(^3\xi_3/^3\xi_1)}\right][(1+\mathrm{x}_1)\chi^{*}_{13}] \tag{108}$$

The estimation of X^{E}_{123} data in terms of Eqs. (94), (96), (98), (100), (102), (104), (106), (108) can be determined if four/three unknown parameters, χ^{*}_{12}, χ^{*}_{23}, χ^{*}_{13}, χ^{*} in these equations are known. Such parameters are estimated using X^{E}_{123} at three/four arbitrary mole fractions and then used to compute X^{E}_{123} data at various compositions for numerous mixtures. Mathematical expressions (Eqs. (94), (96), (98), (100), (102), (104), (106), (108)) were tested by several researchers to compute X^{E}_{123} data of (i) (1_m+2_m+3_m); (ii) (1_m+2_m+3); (iii) (1_m+2+3_m); (iv) (1+2_m+3_m); (v) (1_m+2+3); (vi) (1+2+3_m); and (vii) (1+2+3) mixtures (components being associated/non-associated entities). Investigators utilized (i) Eq. (94) to estimate V^{E}_{123}, $(\kappa^{E}_{S})_{123}$ of 2-methylaniline+tetrahydropyran+N,N-dimethylformamide or N-methylformamide or 2- or 3- or 4-picoline or pyridine (298.15, 303.15, 308.15 K) [170,173,184,185]; [BDIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$] or [BMIM][$\mathrm{BF_4}$]+cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [186]; tetrahydropyran+piperidine+cyclohexanone or cycloheptanone (293.15, 298.15, 303.15, 308.15 K) [187]; 1,3-dioxolane+N-methylpyrrolidi-2-one or 1,4-dioxane+cycloheptanone or cyclohexanone (293.15, 298.15, 303.15, 308.15 K) [188]; piperidine or 1-methylpiperidine+pyrrolidine-2-one+2- or 3- or 4-picoline (293.15, 298.15, 303.15, 308.15 K) [115]; [BDIM][$\mathrm{BF_4}$] or [BMIM][$\mathrm{BF_4}$]+cyclohexanone+cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [116]; piperidine or 1-methylpiperidine+pyrrolidin-2-one+pyridine (293.15, 298.15, 303.15, 308.15 K) [131]; 1-methylpyrrolidin-2-one+piperidine+cycloheptanone or cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [117]; [EMIM][$\mathrm{BF_4}$] or [BDIM][$\mathrm{BF_4}$]+N-methylpyrrolidin-2-one+pyrrolidin-2-one (293.15, 298.15, 303.15, 308.15 K) [118]; [BMIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$]+cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [189]; 2-chlorotoluene+tetrahydropyran+N-methylformamide or N,N-dimethylformamide (298.15, 303.15, 308.15 K) [114]; H^{E}_{123} of 2-methylaniline+tetrahydropyran+pyridine or 2- or 3- or 4-picoline or benzene or methylbenzene (308.15 K) [171]; 1,4-dioxane or 1-methylpyrrolidin-2-one+1,3-dioxolane+cycloheptanone or cyclohexanone (308.15 K) [190]; [BMIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$]+cyclopentanone or cyclohexanone [191]; [BDIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$] or [BMIM][$\mathrm{BF_4}$]+cyclohexanone or cyclopentanone (298.15 K) [192]; $(\mathrm{C}^{E}_{P})_{123}$ 1,3-dioxolane+1-methylpyrrolidin-2-one or 1,4-dioxane+cycloheptanone or cyclohexanone (293.15, 298.15, 303.15, 308.15 K) [172]; [BDIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$] or [BMIM][$\mathrm{BF_4}$]+cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [193], [BDIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$]+1-methylpyrrolidin-2-one or pyrrolidin-2-one [194]; 1-methylpiperidine (1)+pyrrolidin-2-one (2)+pyridine, 2-, 3-, 4-picolines [195]; H^{E}_{123}, $(\mathrm{C}^{E}_{P})_{123}$ of tetrahydropyran+piperidine+cyclohexanone or cycloheptanone (293.15, 298.15, 303.15, 308.15 and 308.15 K) [123]; V^{E}_{123}, $(\kappa^{E}_{S})_{123}$ and $(\mathrm{C}^{E}_{P})_{123}$ of [BMIM][$\mathrm{BF_4}$]+[BDIM][$\mathrm{BF_4}$]+[EMIM][$\mathrm{BF_4}$] (293.15, 298.15, 303.15, 308.15 K) [196]; 1-methylpiperidine+pyrrolidin-2-one+cycloheptanone or cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [131]; (ii) Eq. (96) to determine V^{E}_{123} of 2-methylaniline+1,4-dioxane+1,4-dimethylbenzene or 1,3-dimethylbenzene or methylbenzene or benzene (308.15 K) [197]; 1,4-dioxane or 1,3-dioxolane+methylbenzene or benzene+aniline (308.15 K) [198]; H^{E}_{123} of 1,4-dioxane or 1,3-dioxolane+aniline+methylbenzene or benzene (308.15 K) [174]; 2-methylaniline+1,4-dioxane+1,4-dimethylbenzene or 1,3-dimethylbenzene or methylbenzene or benzene (308.15 K) [145]; V^E_{123}, $(\kappa^E_S)_{123}$ of 2-methylaniline+tetrahydropyran+benzene or methylbenzene (298.15, 303.15, 308.15 K) [173] (iii) Eq. (98) to compute V^E_{123}, $(\kappa^E_S)_{123}$ of methyl benzene or benzene+pyrrolidin-2-one+propan-1-ol (308.15 K) [175]; methyl benzene or benzene or cyclohexane+1-methyl pyrrolidin-2-one+propan-1-ol or propan-2-ol (308.15 K) [176,199]; (iv) Eq. (100) to calculate V^E_{123} of water+1,4-dioxane or 1,3-dioxolane dimethylformamide or formamide (308.15 K) [200]; $(\kappa^E_S)_{123}$ of water+1,4-dioxane or 1,3-dioxolane+water+formamide or dimethylformamide (308.15 K) [201]; H^E_{123} of [EMIM][BF$_4$]+2-methylaniline+pyridine or 2 - or 3- or 4-picoline (298.15 K) [178]; [EMIM][BF$_4$]+2-methyl aniline+N-methyl aniline or aniline; [EMIM][BF$_4$]+water+N,N-dimethyl formamide or formamide (298.15 K) [140]; [EMIM][BF$_4$]+1-methyl pyrrolidin-2-one or pyrrolidin-2-one+cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [202]; [EMIM][BF$_4$]+1-methyl pyrrolidin-2-one or pyrrolidin-2-one+water or pyridine (298.15 K) [203]; $(C^E_P)_{123}$ of [EMIM][BF$_4$]+1-methylpyrrolidin-2-one or pyrrolidin-2-one+cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [204]; [EMIM][BF$_4$]+2-methylaniline+N-methylaniline or aniline (293.15, 298.15, 303.15, 308.15 K) [122]; V^E_{123}, $(\kappa^E_S)_{123}$ of 1,4-dioxane or 1,3-dioxolane+water+propan-2-ol or propan-1-ol (308.15 K) [205,206]; [EMIM][BF$_4$]+pyrrolidin-2-one or 1-methylpyrrolidin-2-one+water (293.15, 298.15, 303.15, 308.15 K) [207]; [EMIM][BF$_4$]+2-methylaniline+pyridine or 2- or 3- or 4-picoline (293.15, 298.15, 303.15, and 308.15 K) [208]; [EMIM][BF$_4$]+1-methyl pyrrolidin-2-one or pyrrolidin-2-one+cyclohexanone or cyclopentanone (293.15, 298.15, 303.15, 308.15 K) [209]; V^E_{123}, $(\kappa^E_S)_{123}$, $(C^E_P)_{123}$ of [EMIM][BF$_4$]+pyridine+pyrrolidin-2-one or 1-methyl pyrrolidin-2-one (293.15, 298.15, 303.15, and 308.15 K) [177]; (v) Eq. (102) to determine V^E_{123}, $(\kappa^E_S)_{123}$ of 1-methylpyrrolidinone+benzene+methylbenzene (308.15 K) [79]; tetrahydropyran+benzene+1,4-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene; tetrahydropyran+methylbenzene+1,2-dimethylbenzene or 1,4-dimethylbenzene (308.15 K) [180,210]; 2-pyrrolidinone+benzene+1,4-dimethylbenzene or methylbenzene (308.15 K) [211]; V^E_{123} and H^E_{123} of nitrobenzene+benzene+1,4-dimethylbenzene or 1,2-dimethylbenzene or methylbenzene (298.15 K) [179]; (vi) Eq. (104) to compute V^E_{123} of benzene+1,3-dioxolane+heptane or hexane or cyclohexane (298.15 K) [212]; V^E_{123} and $(\kappa^E_S)_{123}$ of benzene+2-methylaniline+heptane or hexane or cyclohexane (308.15 K) [181]; 1-methylpyrrolidin-2-one+benzene or methylbenzene+cyclohexane (308.15 K) [79] benzene+tetrahydropyran+heptane or hexane or cyclohexane (308.15 K) [213]; V^E_{123} and H^E_{123} of nitrobenzene+benzene+heptane or hexane or cyclohexane (298.15 K) [214]; (vii) Eq. (106) to determine V^E_{123} and $(\kappa^E_S)_{123}$ of 1,4-dioxane or 1,3-dioxolane+methylbenzene or benzene+N,N-dimethylformamide or formamide (308.15 K) [141,182]; (viii) Eq. (108) to compute V^E_{123} of 1,3-dioxolane+methylbenzene+1,2-dimethylbenzene or 1,4-dimethylbenzene (298.15 K) [183]; V^E_{123} and $(\kappa^E_S)_{123}$ of 1,3-dioxolane+benzene+methylbenzene or 1,2-dimethylbenzene or 1,4-dimethylbenzene (298.15 K) [215]; 2-methylaniline+tetrahydropyran+pyridine or benzene or methylbenzene. A check of estimated V^E_{123}, $(\kappa^E_S)_{123}$, H^E_{123}, $(C^E_P)_{123}$ for various ternary mixtures (i-viii) revealed that determined X^E_{123} values determined by graph theory {Eqs. (94), (96), (98), (100), (102), (104), (106), (108)} fairly compare with corresponding measured values. Agreement among calculated and measured values supports (i) assumptions made in the processes involved in mixtures formation: (ii) mathematical expressions obtained for such processes in terms of ${}^3\xi$ and interaction energy parameters.

8. Excess Gibb's Energies of Mixing, G^E_{123} for Ternary Mixtures

The approach was next extended to predict G^E_{123} data of three component mixtures. A ternary mixture (1+2+3) was regarded as a mixture of two components (1+L), where L=2+3. Thus, a ternary mixture containing n_1 moles of 1, n_2 moles of 2 and n_3 moles of 3 was assumed to be a mixture of n_1 moles of 1 and $n'=(n_2+n_3)$ moles of a (hypothetical liquid) L. While component 1 in a ternary mixture was considered to be characterized by (1−1) interactions; hypothetical liquid (L) characterized by 2–2 or 3–3 and 2–3 interactions. If the component 2 in L has no preference for any particular site on the surface of 3, then the whole of the surface of 3 or 2 molecules is available for making contact with 2 or 3 for establishing 2−3 contacts. The total contact volume, v in (1+L) mixture is then expressed [216] by

$$v=n_1V_1+n_2V_2+n_3V_3+n_2V_3+n_3V_2=n_1V_1+(n_2+n_3)(V_2+V_3) \tag{109}$$

where

$$V=v/(n_1+n_2+n_3) \tag{110}$$

Activity coefficients signify unlike interactions. Consequently, activity coefficients of 1 in (1+L) (L=2+3) mixture would involve contributions due to 1−L, i.e., 1−2 and 1−3 interactions. Further, 1−2 and 1−3 interactions are presumed to make independent impact to γ_1. $\ln\gamma_1$ is therefore, expressible by

$$\ln\gamma_1=\ln(\gamma_1)_{1-2}+\ln(\gamma_1)_{1-3} \tag{111}$$

$\ln(\gamma_1)_{1-2}$ in the (1+2+3) mixtures is assumed to be dependent on the (i) ratio of the molar volume of 1 in the mixture to the total contact volume; (ii) the efficacy of 1−2 contact in (1+2+3) mixture; (iii) interaction energy, χ_{12} per mole of 1−2 contact; (iv) the thermal energy. In view of these assumptions, $\ln(\gamma_1)_{1-2}$ [158] is defined by

$$\ln(\gamma_1)_{1-2}=\frac{x_1V_1(x_1/RT)f_{12}}{x_1V_1+(x_2+x_3)(V_2+V_3)} \tag{112}$$

In the same way $\ln(\gamma_1)_{1-3}$ is given as

$$\ln(\gamma_1)_{1-3}=\frac{x_3V_3(x_3/RT)f_{13}}{x_1V_1+(x_1+x_3)(V_1+V_3)} \tag{113}$$

where f_{12} etc. reflect the efficacy of 1−2 etc. contacts.

In view of the above Eq. (111) is expressed by

$$\ln\gamma_1=\frac{x_1V_1(\chi_{12}/RT)f_{12}+x_3V_3(\chi_{13}/RT)f_{13}}{P} \tag{114}$$

$$P=x_1V_1+(x_2+x_3)(V_2+V_3) \tag{115}$$

Making assumptions that the basic arguments made in deriving Eq. (111) are valid, activity coefficients of 2 and 3 in (1+2+3) mixtures are also expressed as

$$\ln\gamma_2=\frac{x_1V_1(\chi_{12}/RT)f_{12}+x_3V_3(\chi_{13}/RT)f_{13}}{P} \tag{116}$$

$$\ln\gamma_3=\frac{x_1V_1(\chi_{13}/RT)f_{13}+x_2V_2(\chi_{23}/RT)f_{23}}{P} \tag{117}$$

Since

$$G_{123}^{E}=RT\sum_{i=1}^{3}(x_1\ln\gamma_1) \tag{118}$$

Further, it is assumed that $f_{12}=f_{21}$, $f_{23}=f_{32}$, $f_{13}=f_{31}$

As

$$g_{123}=G_{123}^{E}/RT \tag{119}$$

$$g_{123}=\frac{1}{P}[(x_1x_2(\chi_{12}/RT)(V_2+V_1)f_{12}+x_1x_3(\chi_{13}/RT)(V_1+V_3)f_{13} \\ +x_2x_3(\chi_{23}/RT)(V_2+V_3)f_{23})] \tag{120}$$

Eq. (120) is comprised of parameters χ_{12}, χ_{23}, χ_{13}; f_{12}, f_{23}, f_{13} of binaries (1+2); (2+3); (1+3) of ternary mixtures. Such parameters are estimated using free energy data of binary mixtures using Eqs. (60) and (61) and then subsequently utilizing to calculate g_{123} data for (1+2+3) mixtures at various compositions. Singh et al. [216] tested Eq. (120) to determine g_{123} data of water+ethylene glycol+ethanol; acetone+ethanol+water; ethanol+chloroform+1,4-dioxane mixtures. Analysis of results suggests that calculating g_{123} for water+ethylene glycol+ethanol; acetone+ethanol+water compares reasonably well with corresponding g_{123} data [217,218]. However, for estimating g_{123} values for ethanol+chloroform+1,4-dioxane mixture are of the same sign and magnitude.

ADVANTAGES OF GRAPH THEORY OVER CONVENTIONAL THEORIES

Unlike conventional theories/approaches, such as (i) Cell model for liquid mixtures; (ii) Flory theory; (iii) Flory-Prigogine-Patterson theory; (iv) Sanchez and Lacombe theory etc., graph theory does not rely on the evaluation of the partition function and intermolecular potential function depicting interaction between dissimilar molecules. Theory simply needs information of $^3\xi$; V^E, κ_S^E, H^E, C_P^E preferably at one/two compositions for estimating the thermodynamic properties at several mole fractions. Various models/theories of liquid mixtures do not describe V^E, κ_S^E, H^E, C_P^E of mixtures (i) holding strong interactions between unlike molecules; (ii) ionic liquids and organic solvents; (iii) ionic liquid mixtures. Graph theory has been shown to be quite successful in estimating V^E, κ_S^E, H^E, C_P^E and G^E of above said mixtures comprising polar, nonpolar solvents and ionic liquids.

CONCLUSIONS

Thermodynamics of liquid mixtures (components being polar, non-polar solvents, ionic liquids) is of great relevance for the utilization of such mixtures in numerous technological and engineering applications. Thermodynamic models/theories of liquid mixtures are highly desirable for describing their behavior. Graph theory has been successfully exploited to (1) obtain knowledge regarding the existence of components in mixed and pure state (by analyzing V^E data of binary mixtures); (ii) get information about the extent and nature of interactions among the constituent molecules; (iii) compute V^E, κ_S^E, H^E, C_P^E and G^E data of binary mixtures (iii) estimate V_{123}^E, $(\kappa_S^E)_{123}$, H_{123}^E, $(C_P^E)_{123}$ and G_{123}^E for ternary mixtures.

The present review article summarizes the development of Graph theory first for binary mixtures containing non-electrolytes and then its amendment for estimating V^E, κ_S^E, H^E, C_P^E and G^E of mixtures containing associated/non-associated components. The review also deals with the extension of Molelwyn-Huggins concept of interactions between the surfaces of the binary mixtures to ternary mixtures to obtain mathematical expressions which describe well V_{123}^E, $(\kappa_S^E)_{123}$, H_{123}^E, $(C_P^E)_{123}$ and G_{123}^E data of various ternary mixtures (components differing in degree of association). The present review thus provides a comprehensive study regarding the development and amendment of graph theory for its applicability to binary and ternary liquid mixtures, which may in turn be helpful for the readers who lack familiarity with the present theory.

The production of biofuels/biodiesel is crucial to India as it is the only way we can participate in the global energy grade. Currently, biofuel/biodiesel production systems are over engineered because the predictions of process stimulators are unreliable. Thermophysical and thermodynamical data of biofuel/biodiesel/petrol/diesel and their blends with diesel or petrol or alkanols may provide information about their behavior, which could be useful for industrial utilization. Graph theory may be helpful in establishing the behavior of biofuel/biodiesel and their blends with diesel or petrol or alkanols by estimating thermodynamics properties.

ACKNOWLEDGEMENTS

V. K. Sharma, Dr. Sunita are grateful to Council of Scientific and Research (CSIR) for the award of Emeritus Scientist and Research Associate (Reference No. 21 (1061/18/EMR-II).

NOTES

The authors declare no competing interest.

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