PREDICTING LIQUID-LIQUID EQUILIBRIUM USING DPD INTERACTION PARAMETERS

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APPROVAL SHEET

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ABSTRACT

Many activity coefficient models are known till now. All models contain parameters whose values are found arbitrarily by curve fitting method. This technique is usually time-consuming. So there is need for introducing a model whose parameters are well defined. A considerable amount of work has been done on DPD module of Materials Studio. Interaction parameters are used as inputs to this module. Earlier, this set of parameters was successfully used to find the interfacial tension of liquids. This same set is now used to find the liquid-liquid equilibrium of binary liquid systems. An equation of Gibbs Excess Free Energy was introduced based on certain conditions and it includes the DPD interactions parameters. These parameters are found using formulae (which are in terms of isothermal compressibility) making them well-defined.

NOMENCLATURE

a – Interaction parameter

r – Distance between two molecules

k_B – Boltzmann Constant

v – Velocity

t – Time

B – Second virial coefficient

K – Isothermal compressibility

ρ – Density

δ – Solublity parameter

f – Fugacity

γ – Activity coefficient

G^{ex} – Excess Gibbs Free Energy

N – Total number of moles

x – Mole fraction

G, τ, A, B, ʌ - Constants

CONTENTS

CHAPTER 1

INTRODUCTION

1.1 MATERIALS STUDIO:

It is developed by a company Acclerys. It is a complete modeling and simulation environment designed for researchers to predict and understand a material's atomic and molecular structure along with its properties and behavior. This software is used for advanced research of various materials such as catalysts, ceramics, polymers, metals, nanotubes and so on.

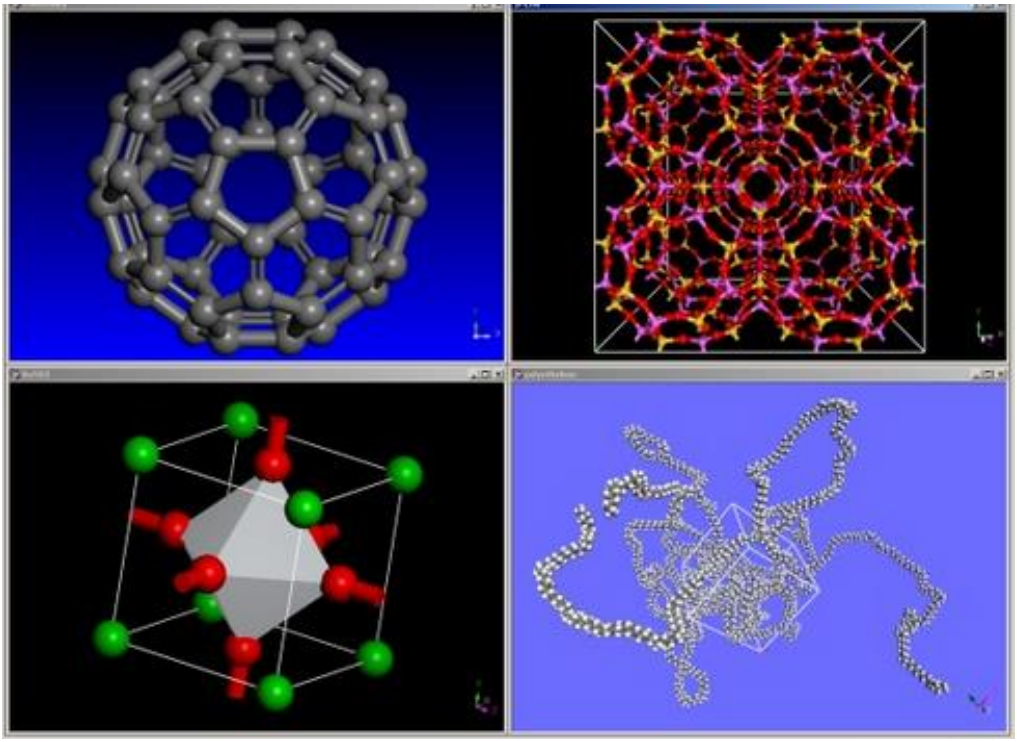

Fig 1: Computer simulations of different materials in Materials Studio

The following are the advantages of this software.

- Accelerate innovation
- Reduce costs
- Improve efficiency
- Solve the most difficult problems easily

Materials studio provides a wide range of tools to solve problems and enables the researchers to predict properties accurately. Different modules are available to deal with different materials.

The following are the quantum modules in Materials Studio.

- CASTEP
- $DMol^3$
- DFTB+
- NMR CASTEP
- ONETEP
- QMERA
- VAMP

Few classical simulation tools are

- Adsorption Locator
- Amorphous Cell
- Blends
- Conformers
- COMPASS
- Forcite Plus
- GULP
- Sorption

Mesoscale simulation modules are

- MesoDyn
- Mesocite

Statistical Modules are

- QSAR
- QSAR Plus
- Synthia

Analytical and crystallization modules are

- Morphology
- Polymorph predictor
- Motif
- Reflex
- Reflex Plus
- Reflex QPA
- X-Cell

1.2 MOLECULAR MODELING:

Molecular modeling uses theoretical methods and computational techniques together to model the behavior of molecules. It is used in a variety of fields like computational chemistry and biology, drug design, materials science etc. It deals with systems ranging from an atom to large biological molecules.

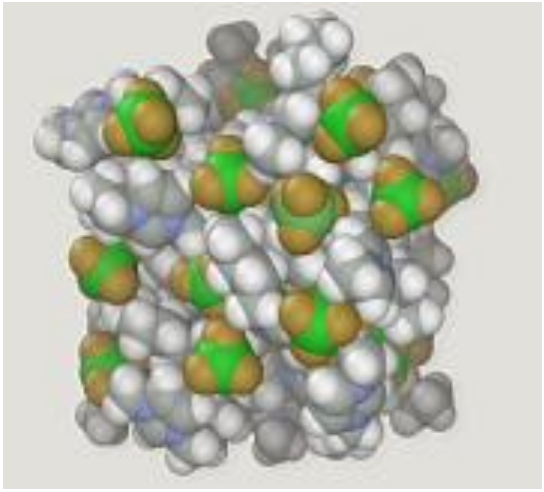

Fig 2: Example of a molecular model of a liquid

1.3 MOLECULAR DYNAMICS:

Molecular Dynamics is a computer simulation of a system of N particles tracking their motion using Newton's equations of motion. As molecular systems contain large number of particles, it is not possible to find their properties analytically. However, MD simulation solves this problem using numerical methods.

In many aspects, MD simulations are very similar to real experiments. While performing a real experiment, we prepare a sample, connect it to measuring instrument and measure the property of interest. If there is a disturbance while measuring, then the measurement is repeated for specific number of times and the average value of the measurement is taken. In the same way, for a MD simulation, we select a system of N particles and solve Newton's equations of motion until the properties do not change with time. After equilibration, the required property measurement is made.

So the simplest form of algorithm of a Molecular Dynamics simulation is as follows:

- We start by considering a system.
- Compute the forces on all particles.
- Integrate the Newton's equations of motion. Steps 2 and 3 are repeated until the system equilibrates for the desired length of time.
- We compute the average values of required parameters and stop.

1.4 DISSIPATIVE PARTICLE DYNAMICS (DPD):

Hoogerbrugge and Koelman have introduced the dissipative particle dynamics method. This method is a coarse-grained scheme. When we have a system of small structure to be run over a long time, a molecular dynamics simulation can be used. A MD simulation is designed to study the dynamics of each atom and molecule in the system in detail. But to study the behavior of certain systems with large number of molecules for a very long time, a MD simulation cannot be chosen. It is computationally slow and time consuming process. In such situations, we consider a DPD simulation. For example, colloidal suspensions contain millions and billions of atoms. A DPD simulation of such a system presents its dynamics much faster compared to a MD simulation. This approach may not provide a correct atomistic description of the molecular motion but it reproduces the correct hydrodynamic behavior on long length and time scales.

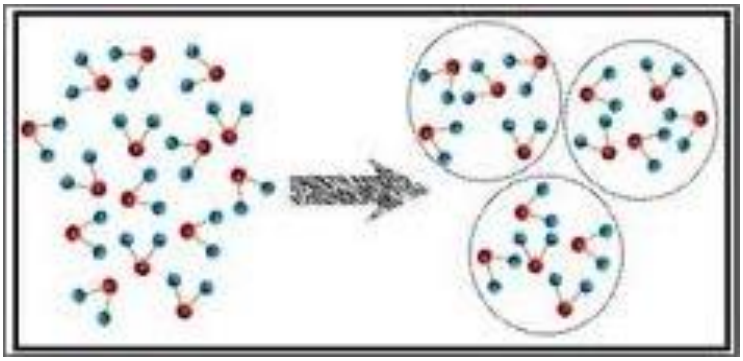

Fig 3: Group of atoms together form beads which are simulated in DPD

In simple terms, one may define a MD simulation as based on atom-atom interactions whereas a DPD simulation is based on bead-bead interactions (Bead is a group of atoms together).

The algorithm of MD consists of only conservative force acting between the particles whereas DPD algorithm consists of a combination of three forces. They are conservative force, dissipative force and random force. Mathematical form of DPD is as follows

$$F_i = \sum_{j \neq i}\left(F_{ij}^C + F_{ij}^D + F_{ij}^R\right) \qquad (1)$$

where F_i is the total force acting on a particle. F_{ij}^C is the conservative force, F_{ij}^D is the dissipative force and F_{ij}^R is the random force. The above forces are defined as follows:

The conservative force $F_{ij}^C = \begin{cases} a_{ij}(1 - r_{ij})\hat{r_{ij}}, & r_{ij} < r_c \\ 0, r_{ij} \geq r_c \end{cases}$

The dissipative force $F_{ij}^{D} = -\gamma w^{D}(r_{ij})(\widehat{r_{ij}}.v_{ij})\widehat{r_{ij}}$

The random force $F_{ij}^{R} = \sigma w^{R}(r_{ij})\theta_{ij}\widehat{r_{ij}}$

where a_{ij} is the maximum repulsion between particles i and j, γ, σ are the magnitudes of frictional and random forces respectively, w^{D}, w^{R} are the distance dependent weight functions, $\widehat{r_{ij}}$ is the unit vector in the direction of r_{ij} and r_c is the cut-off radius beyond which the interactions between particles is considered to be zero.

The weight functions cannot be chosen independently. With respect to the fluctuation-dissipation theorem, the following relations are derived and justified using the Fokker-Planck equation.

$$w^{D}(r_{ij}) = \left[w^{R}(r_{ij})\right]^{2}, \sigma^{2} = 2k_{B}T\gamma \qquad (2)$$

The DPD method is similar to Brownian dynamics method as both include random and dissipative forces. However, the only quantity conserved in Brownian dynamics is the total number of particles. In DPD, the functional forms of frictional and random forces conserve momentum by obeying Newton's third law of motion. This nature is important to ensure maintaining correct hydrodynamics of the system on large length and time scales. Also, the random and dissipative forces together maintain the temperature of the system constant.

For DPD, the standard Velocity-Verlet algorithm cannot be used as the forces between the particles depend of their relative velocities. Later, Groot and Warren came up with a modified Velocity-Verlet algorithm. However, it is not time-reversible unlike the MD algorithms. Later, the modified Velocity-Verlet algorithm obeying time reversibility was introduced. The set of equations are as follows:

The velocities are updated using

$$v\left(t + \frac{\Delta t}{2}\right) = v\left(t - \frac{\Delta t}{2}\right) + \Delta t\frac{f(t)}{m} \qquad (3)$$

The positions are updated using

$$r(t + \Delta t) = r(t) + \Delta t v\left(t + \frac{\Delta t}{2}\right) \qquad (4)$$

The force at time t is calculated using velocity at time t

$$v(t) = \frac{v\left(t+\frac{\Delta t}{2}\right) + v\left(t-\frac{\Delta t}{2}\right)}{2} \qquad (5)$$

When equation (5) is substituted in equation (3), the term $v\left(t+\frac{\Delta t}{2}\right)$ appears on both the sides of the equation. The value of $v\left(t+\frac{\Delta t}{2}\right)$ calculated from the equation has to be same as the value of $v\left(t+\frac{\Delta t}{2}\right)$ used to calculate force at time t. Several iterations are performed to solve these equations of motion. This particular approach ensures that time-reversibility is obeyed. If we use a non-iterative scheme, the velocity that is calculated at time t is not the same as the velocity used to calculate force at that time. Consequently, when we reverse the velocities, particles do not return to their original positions and time-reversibility is not obeyed.

1.4.1 CHOOSING REPULSION PARAMETER:

In order to choose a repulsion parameter, we need to establish the equation of state. We use the virial theorem along with few DPD simulations to finally approach to an equation of state which is a relation between excess pressure and density. From this equation, we get an expression of isothermal compressibility which is used to derive an expression of repulsion parameter or interaction parameter.

The virial theorem used in Groot-Warren paper is

$$p = \rho k_B T + \frac{2\pi}{3}\rho^2 \int_0^1 f(r)g(r)r^3 dr \qquad (6)$$

where g(r) is the radial distribution function, f(r) is the conservation force.

A system of single molecule 'A' of size 20X10x10 was considered with repulsion parameter a = 15 and was run for 2,00,000 time steps with density ρ = 1. The simulations yield values of radial distribution function for various radii. Therefore, excess pressure ($p - \rho k_B T$) or virial coefficient is calculated using the corresponding output data. To obtain the equation of state, the density was varied from ρ = 1 to ρ = 8 with repulsion parameters a = 15, 25 and 30.

General virial equation is

$$p = \rho k_B T + k_B T \rho^2 B \qquad (7)$$

where B is the virial coefficient.

Comparing equations (6) and (7), we get

$$k_B T B = \frac{2\pi}{3} I$$

Where $I = \int_0^1 f(r)g(r)r^3 dr$

$$B = \frac{2\pi I}{3k_B T}$$

At T = 273K, in DPD $k_B T = 1$

Therefore, $\boldsymbol{B = \frac{2\pi}{3} I}$ (8)

Substituting B in equation (7) gives

$$B = \frac{p - \rho k_B T}{\rho^2}$$

For r = 0, DPD simulation cannot be run. Therefore, the values of virial coefficients are calculated theoretically.

A sample calculation is shown below.

1) For ρ = 0
   - Calculate f(r) using the below relation
     $$f(r) = a(1 - r)$$
   - Calculate g(r) using the below relation as given in Groot-Warren paper
     $$g(r) = exp\left[\frac{-\frac{1}{2}a(1-r)^2}{k_B T}\right]$$
   - Calculate g(r)*f(r)*r^3

2) For ρ > 0,
   - Calculate f(r) using the below relation
     $$f(r) = a(1 - r)$$
   - Values of g(r) are obtained from DPD simulations for various r values
   - Calculate g(r)*f(r)*r^3

The value of integral I for values from r = 0 to r = 1 is obtained by applying Simpsons rule. Then, virial coefficient is calculated using equation (3).

To validate our results of virial coefficient from Groot-Warren paper, we consider expression of virial coefficient from statistical mechanics.

From statistical mechanics,

$$B = 2\pi \int_0^1 \big(1 - g(r)\big) r^2 dr \quad (9)$$

where $g(r) = exp\left[\frac{-\frac{1}{2}a(1-r)^2}{k_B T}\right]$ (10)

substituting equation (10) in equation (9), we get

$$\boldsymbol{B = 2\pi I} \quad (11)$$

where $I = \int_0^1 \big(1 - g(r)\big) r^2 dr$

Table 1 : Values of virial coefficient at a = 25 and ρ = 3. Column 4 indicates values calculated from statistical mechanics and Column 5 indicates values calculated from Groot-Warren paper. We see that values of virial coefficient are similar.

r	**g(r)**	**f(r)**	**(1-g(r))^r^2**	**f(r)g(r)r^3**
0	0.000003726	25	0	0
0.1	0.00004	22.5	0.01	0.0000009
0.2	0.000335	20	0.0399	0.000537
0.3	0.002187	17.5	0.0898	0.001034
0.4	0.011108	15	0.1582	0.010665
0.5	0.043937	12.5	0.239	0.068651
0.6	0.135335	10	0.3113	0.292324
0.7	0.324652	7.5	0.3309	0.835168
0.8	0.606531	5	0.2518	1.552718
0.9	0.88479	2.5	0.0952	1.0608351
1	1	0	0	0
			Value of integral = 0.152743	Value of integral = 0.458811
			B = 0.035369	**B = 0.038418**

The same procedure is followed for other values of ρ and repulsion parameter.

Table 2: Values of virial coefficient at different values of density and repulsion parameter.

rho	**a = 15**	**a = 25**	**a = 30**
0	0.0509	0.0384	0.0343
3	0.091911	0.092272	0.092518
4	0.095564	0.096176	0.096435
5	0.095271	0.098345	0.098562
6	0.099162	0.099691	0.099928
7	0.100139	0.10065	0.100815
8	0.100876	0.101296	0.101435

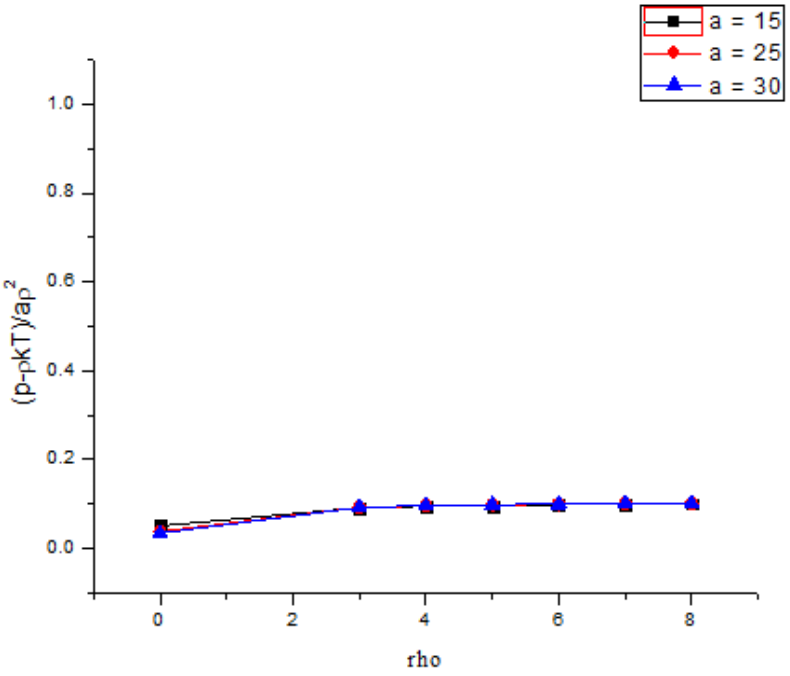

Fig 4: Excess pressure for different repulsion parameter values when divided by ρ^2 shows scaling.

Conclusions that can be drawn from the above graph are as follows:

- Systems with ρ >2 follow a simple scaling relation. Further, systems with ρ = 3 and above correspond to a constant value of excess pressure.
- The simple scaling relation for systems with ρ = 3 and above is given by

$$p = \rho k_B T + \alpha a \rho^2 \quad (\alpha = 0.101 \pm 0.001) \qquad (12)$$

- For defining isothermal compressibility of a system, the model chosen in Groot-Warren paper is Weeks-Chandler-Anderson perturbation theory of liquids. According to this theory,

$$K^{-1} = \frac{1}{k_B T}\left(\frac{\partial p}{\partial \rho}\right) \text{ T} \qquad (13)$$

  Derivative of equation (12) with respect to density at constant temperature gives an expression for isothermal compressibility.

$$K^{-1} = 1 + \frac{2\alpha a \rho}{k_B T} \qquad (14)$$

- Density for a simulation is a free parameter. As density increases, the number of interactions for each particle increases. Also, required CPU time per timestep and per

unit of volume increases. Therefore, lowest density for which the above simple scaling relation holds is generally considered i.e ρ = 3.

- Expression for repulsion parameter is obtained by rearranging equation (14)

$$\boldsymbol{a = \frac{(K^{-1}-1)k_B T}{2\alpha\rho}} \quad (15)$$

1.5 FORCEFIELD:

In molecular modeling, a forcefield is a mathematical function used to describe the potential energy of a system of particles. The total potential energy of a system is the combination of covalent and non-covalent interactions between the particles in the system. The basic functional form of a forcefield is given as

$$E_{total} = E_{covalent} + E_{non-covalent}$$

Energy due to covalent interactions arise due to the bonds, angles and dihedrals whereas energy due to non-covalent interactions arise due to the vander waals and long range electrostatic forces between the particles in the system.

$$E_{covalent} = E_{bonds} + E_{angles} + E_{dihedrals}$$

$$E_{non-covalent} = E_{vander\ waals} + E_{electrostatic}$$

A forcefield has two different components which together describe the interactions between particles. The two components are

- A set of equations used to derive potential energy
- Parameters in these equations

There are three different types of force fields. They are

- All Atom Force field:
    i. This forcefield includes explicit representation of all atoms, including non-polar hydrogens.
    ii. There are parameters present for every single atom in the system
- United Atom Forcefield:
    i. This forcefield does not include explicit representation of non-polar hydrogen atoms.
    ii. Therefore, parameters are present for all atoms except non-polar hydrogen atoms.
- Coarse Grained Forcefield:

In this forcefield, parameters are provided for a group of atoms rather than for a single atom. Here, we don't have to parameterize the model each time for each atom

under consideration making it computationally fast and easy to use. CG model has been proved to be a powerful tool to study the dynamics of the system. So, it is widely used and preferred over traditional forcefields (like all atom and united atom).

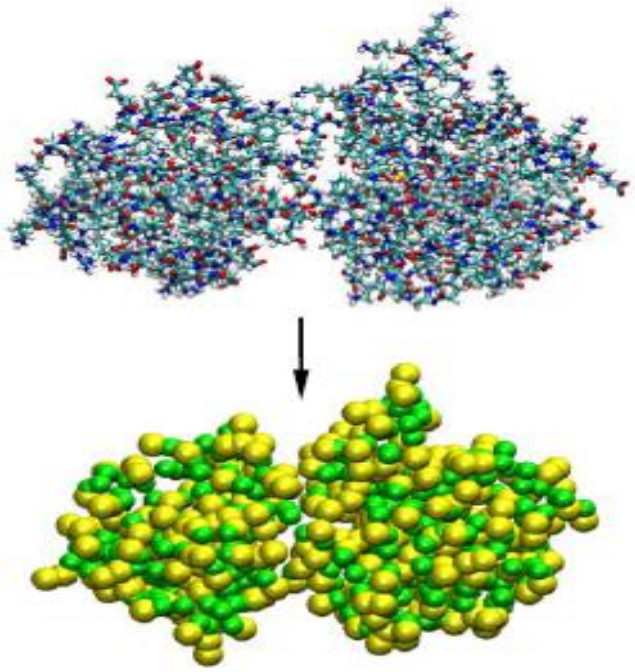

Fig 5: Group of atoms are parameterized in a Coarse Grained model unlike the traditional models

There are many forcefields present. Different forcefields designed for different purposes.

- AMBER (Assisted Model Building and Energy Refinement) - used for molecular dynamics simulation of proteins and DNA
- CHARMM (Chemistry at HARvard Molecular Mechanics) - used for molecular dynamics simulation of small and macromolecules
- ECEPP – first forcefield for polypeptide molecules
- UFF – General forcefield with parameters for full periodic table up to and including the actinoids.
- COMPASS – parameterized for variety of molecules in condensed phase.

Other forcefields are GROMOS, OPLS, TraPPE, COSMOS-NMR, ReaxFF, RWFF etc
Coarse grained forcefields are VAMM, MARTINI and Shinoda.

1.5.1 MARTINI FORCEFIELD:

MAPPING:

Martini model is based on 4:1 mapping i.e an average of 4 heavy atoms and associated hydrogens are represented as a single interaction centre. The 4:1 mapping is chosen as an

optimum between computational efficiency and chemical representability. Example, four water molecules together can be called a CG water bead. For ring structures, this 4:1 mapping becomes too coarse. So mapping is done with higher resolution for such structures.

Fig 6: Representation of mapping in Martini Forcefield

Based on the chemical nature of the underlying structure, CG beads are classified into different types. Martini model has four different particle types. They are:

- Polar (P)
- Non-Polar (N)
- Apolar (C)
- Charged (Q)

A polar particle has a net dipole which is the result of partial charges. A polar molecule has uneven distribution of electron density resulting from electronegativity differences being not so high. A non-polar molecule has no partial charges. The electron attracting power is same between the molecules resulting in even distribution of electron density. Apolar molecule has no electric polarity. A charged particle is fully positive or fully negative in charge. Due to high electronegativity difference, electron transfer takes place.

Owing to the nature of these four particle types, further classification is done. Polar and Apolar particles are classified based on the degree of polarity whereas Charged and Non-polar molecules are classified based on their hydrogen bonding capacity.

a) Based on hydrogen bonding capacity (Q, N):
   - d – donor
   - a – acceptor
   - da – both
   - o – none

   2 particle types classified further in 4 types gives a total of 8 particle types (4*2).

b) Based on degree of polarity (P, C):

Numbers from 1 to 5 rank the degree of polarity. Starting from 1 which indicates low polarity to 5 indicating high polarity. 2 particle types classified further into 5 types gives total of 10 particle types (5*2).

Together, there are **18 particle types.**

PARAMETERIZATION:

I. FOR NON-BONDED INTERACTIONS:

Non-bonded interactions involve vander waals (represented by Lennard Jones potential) and electrostatic forces (represented by Coulomb's law).

LJ POTENTIAL:

The Lennard Jones potential consists of two forces, attractive and repulsive forces. When two particles are at infinite distance, there is no interaction between them and energy between them can be considered to be zero. As the particles approach each other, attractive forces act between them and bring them more close to each other. At a particular distance of separation between the two particles σ, the intermolecular potential between them becomes zero. σ is called Vander Waals radius and gives information on how close two non-bonding particles can get. At distances less than σ, repulsive forces act. The 12-6 Lennard Jones potential is represented as

$$V_{LJ} = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

where V_{LJ} is the intermolecular potential between particles, ε is the well depth indicating how strongly the two particles can attract each other, r is the distance of separation between the two particles.

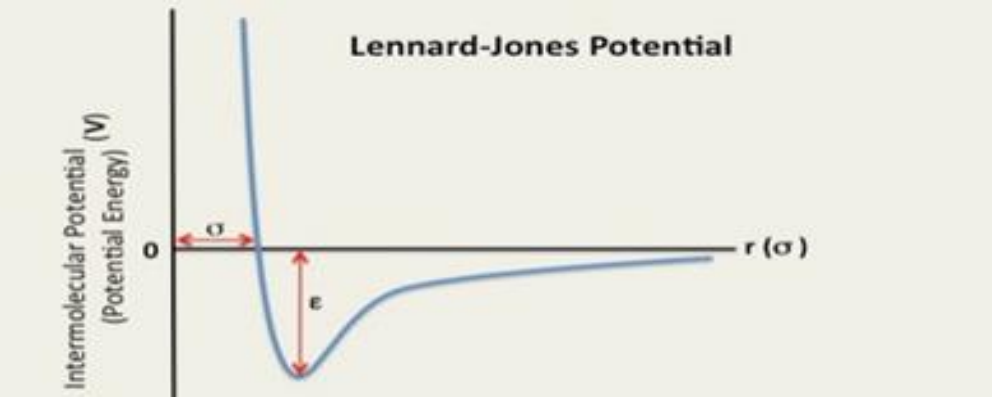

Fig 7: The graph of Intermolecular Potential with distance of separation between two particles

Parameters here to be found are ε, σ. They are found by comparing Coarse Grained simulations to atomistic simulations. It was found that the values of ε ranges from 5.6 KJ/mole

for interactions between strong polar groups to 2 KJ/mole for interactions between polar and apolar groups. The value of σ is 0.47nm for normal structures and is 0.43nm for ring like structures.

COULOMB'S LAW:

Coulomb's law describes the electrostatic interactions between electrically charged particles.

$$F_e = \frac{kq_1q_2}{r^2}$$

where k is the coulomb's constant, q_1, q_2 are charges and r is the distance between the charges.

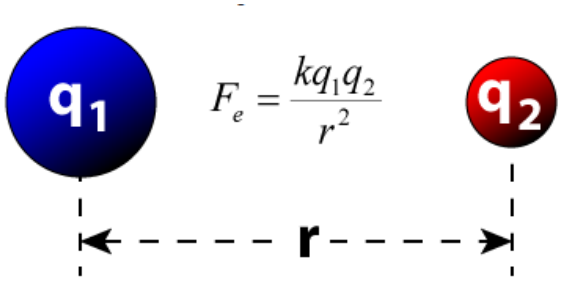

Fig 8: Diagrammatic Representation of Coulomb's law

The coulomb's constant k is given by

$$k = \frac{1}{4\pi\varepsilon_0\varepsilon}$$

where ε_0 is the permittivity of free space, ε is the relative permittivity of the material in which charges are present. Value of ε is derived by comparing the CG simulations to atomistic simulations and is found to lie between 1.3 to 2.5.

For non-bonded interactions, a shifted form of lennard jones potential and electrostatic interaction is used where both the interactions are made zero at a cut-off radius r_{cut}=1.2nm

II. FOR BONDED INTERACTIONS:

Parameterization is done in 2 ways. They are:

i. Using structural data of particles in a system like bond length, bond angle etc from atomistic simulations.
ii. Using CG simulations and comparing them to atomistic simulations.

Dependence on the 2nd method for parameterizing has increased over past years as it is a computationally fast and reliable technique.

In this method,

i. Interactions between centre of mass of corresponding coarse grained beads have to be studied
ii. CG simulation is run. After equilibrium is established, the distribution function is obtained. This distribution function is compared to the distribution function obtained from atomistic simulation.
iii. If satisfactory overlap of the distribution function is obtained, the values of parameters are calculated. If not, the simulations are repeated iteratively until the distribution functions are similar.
iv. The values of the present run of atomistic simulation are used as inputs for the next CG simulation
v. Once the distribution functions match, mathematical form of distribution function is taken from Statistical Mechanics and values of parameters needed are calculated.

LIMITATIONS:

Though it is one of the widely used model, Martini model too has many limitations. They are:

i. Model resolution and accuracy:

With the technique of 4:1 mapping used in the martini model, there are a few disadvantages with respect to few structures. Few properties of lipids like melting temperatures, bilayer stability and thickness depend strongly on the length of the acyl chain. Since the concept of mapping is used in this model, the length of the acyl chain is modified resulting in incorrect predictions of above properties of lipids. Similar limitation is seen in biomolecules such as sterols. Small changes in ring structures has large effect on its thermodynamics.

ii. Speed-up factor:

To have comparable time scales of both martini simulation and all atom simulation, a scaling factor of 4 is used which is called as scale-up factor. However, this value of 4 cannot be globally used. It depends on the type of molecule for which the simulation is carried. Alkanes have small speed-up factors compared to experiments or atomistic simulations. Alcohols have large speed-up factors.

iii. Thermodynamic properties:

Few thermodynamic properties are particularly affected due to the CG models. Martini forcefield is parameterized such that the values of free energies are reproduced well at the cost of reduction in number of degrees of freedom. This

indicates an incorrect temperature dependence of this forcefield. Though the free energy difference values are right, enthalpy and entropy values obtained from it are not accurate.

iv. The functional form of LJ potential:

Using 12-6 form of LJ potential is seen as not the best choice. The steep repulsion leads to few errors in CG simulations compared to atomistic simulations. Moreover, this form of LJ potential has limited fluid range. Martini water is prone to freezing even at room temperature. Another form of LJ potential may improve the relative stability of fluid phase.

CHAPTER 2

2.1 IONIC LIQUIDS:

An ionic liquid is a salt that melts without decomposing and vaporizing. It is a salt in the liquid state. They are made up of ions bonded by ionic bonds which are much stronger than the Vander Waals forces. As a result, these salts melt at higher temperatures than other solid molecules. Sodium Chloride is an ionic liquid that melts at $801^{O}C$ into liquid which contains sodium and chloride ions.

Following are a few examples of ionic liquids.

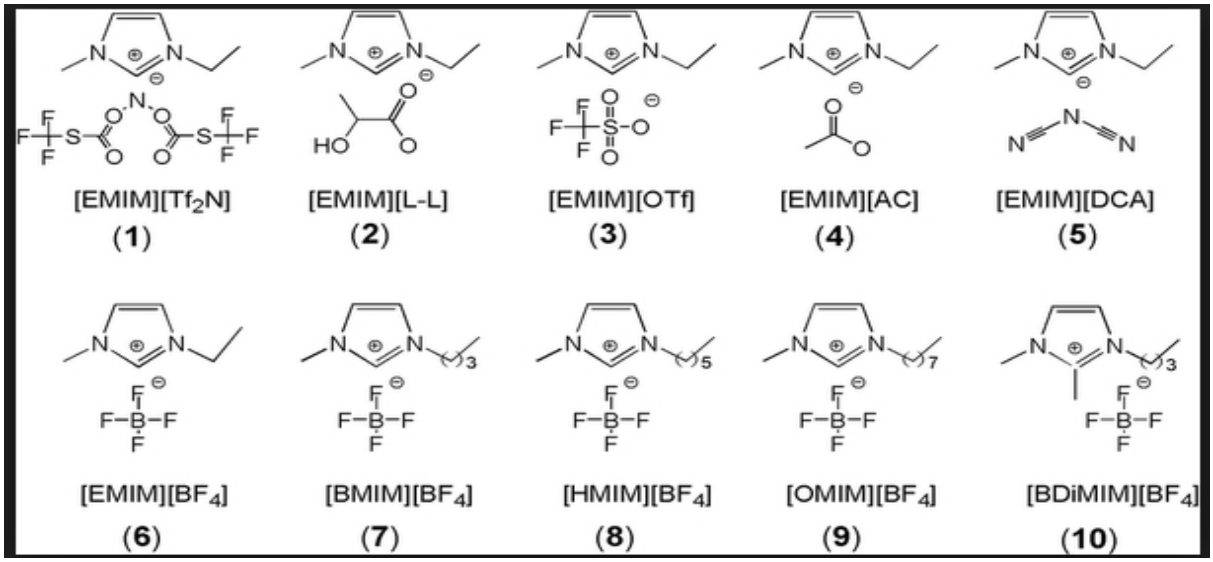

Fig 9: Examples of various ionic liquids

Ionic liquids exhibit properties like

- Thermal stability
- Low vapor pressure

- Electric conductivity
- Interesting solvent properties
- Biphasic systems possible
- Liquid crystalline structures
- High electroelasticity
- High heat capacity
- Non flammability

The applications of ionic liquids go into a large variety of industries like

- Lubricants and additives
- Electroelastic materials
- Analytics
- Solvents
- Liquid crystals
- Heat storage
- Electrolytes
- Separation

2.2 ELECTROSTATIC DPD:

Properties of normal liquids can be found using DPD simulations. However, the forcefield of DPD simulations does not account for electrostatic interactions of ionic liquids. This correction to the DPD forcefield is made using Ewald summation. Paul Peter Ewald introduced this Ewald summation technique for calculating electrostatic energies of ionic substances. In this method, electrostatic interactions are divided into two parts. One is the short-range interactions calculated in real space and the other is long-range interactions calculated in the fourier space. Advantage of this method is high accuracy and speed while computing long-range interactions. With these changes, the ELECTROSTATIC DPD was developed to measure the properties of ionic liquids.

CHAPTER 3

PROBLEM DEFINITION – 1:

Predicting Liquid-Liquid Equilibrium(LLE) of a system through interfacial tension using DPD simulations.

3.1 APPROACH:

In order to predict LLE of a liquid-liquid system, we consider the approach of calculating interfacial tension values at different temperatures and compositions using DPD simulations and analyzing their values to capture the co-existence points. The procedure for calculating interfacial tension values is as follows:

- Select a particular liquid-liquid system.
- Find values of isothermal compressibility, solubility parameter at required temperatures.
- Calculate values of interaction parameters using the below formulae

$$a_{AA} = a_{BB} = \frac{K^{-1} - 1}{2\alpha\rho k_B T}$$

$$a_{AB} = \frac{\frac{(\delta_A - \delta_B)^2}{0.9} + a_{AA} + a_{BB}}{2}$$

- Input these values into DPD module of Materials Studio. Run the simulation
- Dimensionless interfacial tension is obtained as output of the simulation
- Convert it into dimensional interfacial tension.

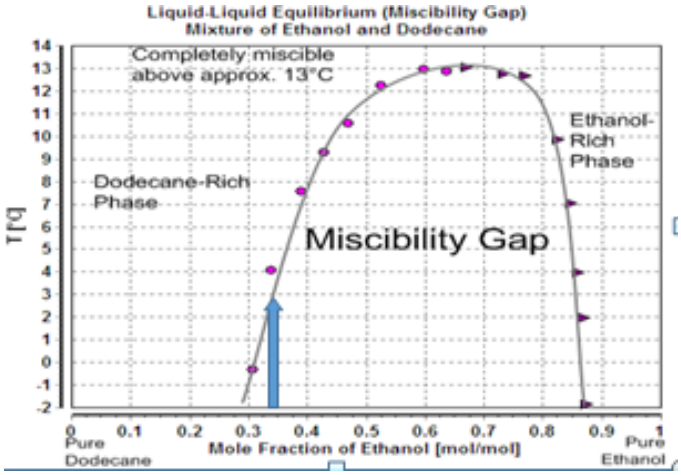

Fig 10: LLE curve of Ethanol-Dodecane system

In an LLE graph of a liquid-liquid system, the area under the curve represents the immiscible zone where interfacial tension values are high whereas area outside the curve is the miscible zone where interfacial tension values are low. So when we proceed from one region to another region at constant composition predicting interfacial tension values, if we observe an abrupt change in its value, then we can say that we have captured a co-existence point. This is the logic to be used in this problem.

3.2 WORK IMPLEMENTED:

We have selected Water-Tetrahydrofuran system which has both upper and lower consolute temperature.

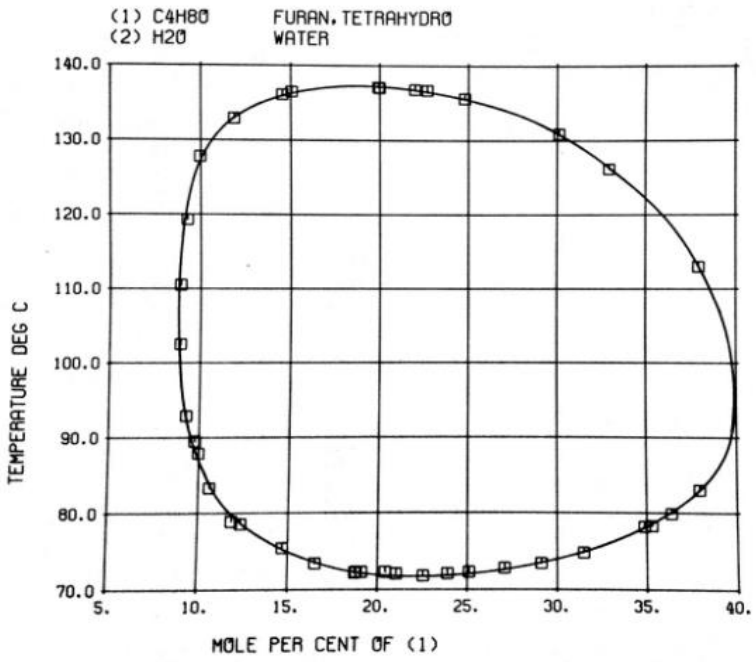

Fig 11: Liquid-Liquid equilibrium curve of Water-Tetrahydrofuran system

We have selected four points in the above graph at which the simulations are to be done [(0.3,120), (0.3,138), (0.3,70), (0.3,80)]. Inputs needed are isothermal compressibility and solubility parameter values of water and THF. Isothermal compressibility values for water and THF are available in literature. There are no reported values of solubility parameter at these temperatures for THF and water. So we have to run MD simulations for both the liquids at the required temperatures.

The results of few MD simulations are as follows:

- For water, at temperature = 353 K (80^{O}C),

  Total number of water molecules = 300

Table 3: Temperature Standard Deviation for various times of simulation

TOTAL TIME OF SIMULATION (ps)	TEMPERATURE STANDARD DEVIATION (K)
0-200	15.314
200-400	11.332
400-600	11.148
600-800	11.092

The solubility parameter value obtained from the simulation was 43.533 $MPa^{1/2}$.

- For water, at temperature = 393 K ($120^{O}C$),

  Total number of water molecules = 300

Table 4: Temperature standard deviation for various times of simulation

TOTAL TIME OF SIMULATION (ps)	TEMPERATURE STANDARD DEVIATION (K)
0-200	15.669
200-400	11.724
400-600	11.486
600-800	11.176

The solubility parameter value obtained from the simulation was 42.837 $MPa^{1/2}$.

The desired temperature standard deviation is 4K. All above standard deviations are quite high. As a result, the numbers of molecules for a simulation are increased.

- For water at temperature = 353K,

  Total number of molecules = 400

Table 5: Temperature standard deviation for various times of simulation

TOTAL TIME OF SIMULATION (ps)	TEMPERATURE STANDARD DEVIATION (K)
0-200	8.239
200-400	8.053
400-600	7.985

- For total molecules of THF = 300,

  Solubility parameter at 353K = 15.58 $MPa^{1/2}$ (Temperature standard deviation = 15.297K)

  Solubility parameter at 393K = 14.82$MPa^{1/2}$ (Temperature standard deviation = 11.312K)

In none of the above cases did the temperature standard deviation reduce below 4K. Also, solubility parameter that is found through Materials Studio is Hildebrand Solubility Parameter. For simple molecules (whose Hansen and Hildebrand SP are almost equal), we can choose to run MD simulations for getting SP value. For example, Benzene has Hildebrand SP as 18.5$MPa^{1/2}$ and Hansen SP as 18.6$MPa^{1/2}$, Octane has Hildebrand SP as 15.54$MPa^{1/2}$ and Hansen SP as 15.5$MPa^{1/2}$. But for THF, the Hildebrand SP is 18.6$MPa^{1/2}$ and Hansen SP is 19.4$MPa^{1/2}$. So

the point that could be inferred from above MD simulations of THF is that we cannot rely on the results of these simulations as the output is in terms of Hildebrand SP. There is a need to find a way so that simulations can be run to give Hansen SP.

CHAPTER 4:

PROBLEM DEFINITION – 2:

To predict Liquid-Liquid Equilibrium using DPD interaction parameters.

4.1 INTRODUCTION:

At low pressures, all gases are mutually soluble in each other in all proportions. The same is not always true with liquids. For a binary liquid mixture over certain ranges of temperature and composition, the liquids split and exist as two liquid phases with different compositions. At thermodynamic equilibrium, this is called Liquid – Liquid Equilibrium (LLE). At other ranges of temperature and compositions, the liquids are miscible in each other.

For example, the phase diagram i.e temperature – compositions graph of Ethanol – Dodecane system consists of two regions. The area under the curve is the immiscible region. In the range of the temperature and composition below the curve, the two liquids do not mix with each other and exist as two separate liquid phases. The arrow mark in the graph indicates the miscibility gap for a particular composition of Ethanol. Outside the curve, the two liquids become miscible in each other.

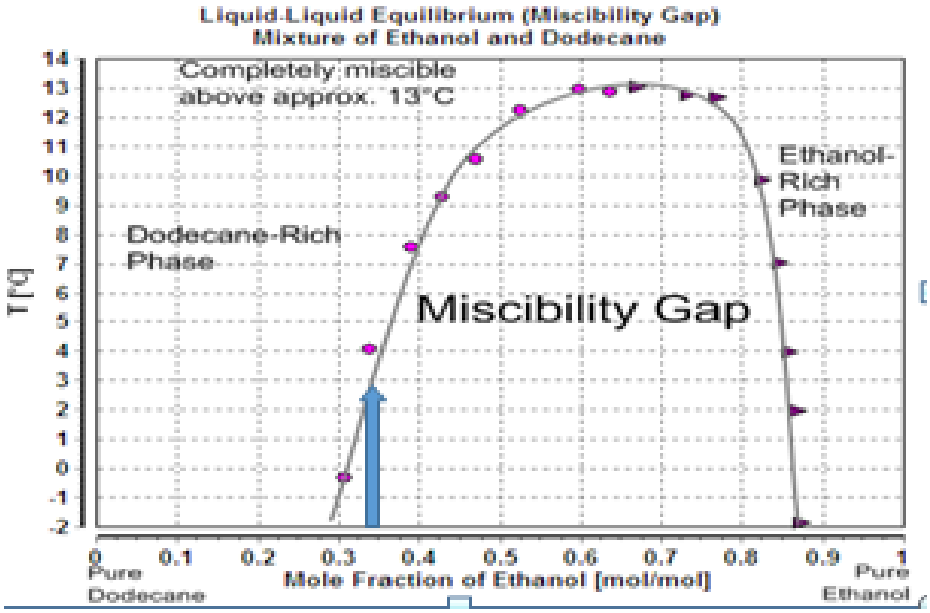

Fig 12: Phase diagram of Ethanol – Dodecane system

Certain liquid mixtures exhibit a complete closed curve in the phase diagram unlike the one seen in the above graph.

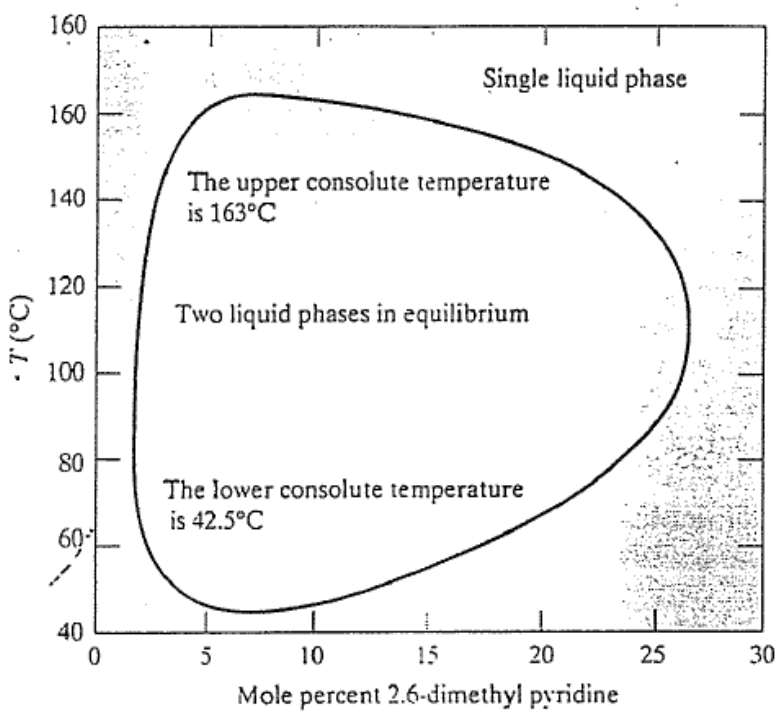

Fig 13: Phase diagram of 2,6 – dimethyl pyridine and water

The highest point of temperature of the curve is called the Upper Consolute Temperature or Upper Critical Solution Temperature (UCST) and the lowest point of temperature of the curve is called the Lower Consolute Temperature of the Lower Critical Solution Temperature (LCST). For the temperatures and compositions lying within this closed curve, two liquid phases are seen. For any other temperature above the UCST and below the LCST, a single miscible liquid phase is seen.

Starting point of all phase equilibrium calculations is

$$x_i^I \gamma_i^I f_i^I = x_i^{II} \gamma_i^{II} f_i^{II} \qquad (16)$$

where x_i is the mole fraction of the ith component, γ_i is the activity coefficient of the ith component and f_i is the fugacity of the ith component in a liquid system.

Thermodynamic requirement for any phase equilibrium is that composition of all species in both phases should be such that the below relation is satisfied.

$$f_i^I(T, P, x^I) = f_i^{II}(T, P, x^{II})$$

Equation (16) reduces to

$$x_i^I \gamma_i^I f_i(T,P) = x_i^{II} \gamma_i^{II} f_i(T,P)$$

where i = 1, 2, 3 ….upto n components present in the system.

Since the fugacity on both the sides of the equation is same, the above equation reduces further to

$$x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \quad (17)$$

where i = 1,2,3 and so on upto n components present in the system

Also, sum of mole fractions of all components in a single phase is 1.

$$\sum_{i=1}^{n} x_i^I = 1 \text{ and } \sum_{i=1}^{n} x_i^{II} = 1 \quad (18)$$

Equation (17) and (18) are generally used to solve a LLE phase diagram problem. The values of activity coefficient are calculated using activity coefficient models given by the expression of excess Gibbs free energy. Any expression of Gibbs free energy must obey the Gibbs-Duhem Equation.

There are a number of activity coefficient models present. They are

- **One-constant Margules Activity Coefficient Model:**

  It is a simple thermodynamic model introduced by Max Margules in the year 1895. The expression of Gibbs free energy is

  $$G^{ex} = Ax_1x_2$$

  where G^{ex} is the excess Gibbs free energy, A is a constant, x_1 and x_2 are mole fractions.

  The expression for activity coefficient from Gibbs free energy is obtained by the following relation

  $$\ln \gamma_i = \frac{\partial \left(\frac{NG^{ex}}{RT}\right)}{\partial N_i}$$

  Therefore, Margules Model in terms of activity coefficients is

  $$RT\ ln\ \gamma_1 = Ax_2^2$$

  $$RT\ ln\ \gamma_2 = Ax_1^2$$

  The one constant margules model is symmetric in terms of mole fractions and activity coefficients when plotted as a function of concentration are mirror images of each other.

The Margules model in terms of activity coefficient at infinite dilution is

$$\text{As } \gamma_1 \to \infty, \mathrm{x}_1 \to 0 \text{ and } \mathrm{x}_2 \to 1$$

$$\text{As } \gamma_2 \to \infty, \mathrm{x}_1 \to 1 \text{ and } \mathrm{x}_2 \to 0$$

$$\ln \gamma_1^{\infty} = \ln \gamma_2^{\infty} = \frac{A}{RT}$$

- **Two-constant Margules Activity Coefficient Model:**

$$RT \ln \gamma_1 = \alpha_1 x_2^2 + \beta_1 x_2^3$$

$$RT \ln \gamma_2 = \alpha_2 x_1^2 + \beta_2 x_1^3$$

where $\alpha_i = A + 3(-1)^{i+1}B$ and $\beta_i = 4(-1)^i B$, i = 1 and 2 for a binary liquid mixture.

Unlike the one-constant Margules Model, the two-constant Margules model is not symmetric in terms of mole fractions and activity coefficients are not mirror images when plotted against concentration.

- **Van-Laar equation:**

This model was developed by Johannes Van Laar in 1910-1913. The equation is derived from the Vander Waals equation.

$$\ln \gamma_1 = \frac{\alpha}{\left[1 + \frac{\alpha x_1}{\beta x_2}\right]^2}$$

$$\ln \gamma_2 = \frac{\beta}{\left[1 + \frac{\beta x_2}{\alpha x_1}\right]^2}$$

The values of α and β are found by fitting the experimental activity coefficient data to these equations. Alternatively, if values of corresponding activity coefficients at a particular composition are known, the values of parameters can be found.

Van-Laar model in terms of activity coefficient at infinite dilution is

$$\ln \gamma_1^{\infty} = \alpha \, , \ln \gamma_2^{\infty} = \beta$$

- **Wilson equation:**

  It is a two-parameter model introduced by Wilson. The expression of Gibbs Free Energy is given by

$$\frac{G^{ex}}{RT} = -x_1 ln(x_1 + x_2\Lambda_{12}) - x_2 ln(x_2 + x_1\Lambda_{21})$$

  The activity coefficients are

$$\ln \gamma_1 = -ln(x_1 + x_2\Lambda_{12}) + x_2\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right]$$

$$\ln \gamma_2 = -ln(x_2 + x_1\Lambda_{21}) - x_1\left[\frac{\Lambda_{12}}{x_1 + x_2\Lambda_{12}} - \frac{\Lambda_{21}}{x_1\Lambda_{21} + x_2}\right]$$

  The activity coefficients at infinite dilution are

$$\ln \gamma_1^{\infty} = -\ln \Lambda_{12} + 1 - \Lambda_{12}$$

$$\ln \gamma_2^{\infty} = -\ln \Lambda_{21} + 1 - \Lambda_{21}$$

- **NRTL equation:**

  This is a three parameter model. The expression of Gibbs free energy is

$$\frac{G^{ex}}{RT} = x_1 x_2\left(\frac{\tau_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau_{12}G_{12}}{x_2 + x_1G_{12}}\right)$$

  where $\ln G_{12} = -\alpha\tau_{12}$ and $\ln G_{21} = -\alpha\tau_{21}$

  The expressions for activity coefficients are as follows

$$\ln \gamma_1 = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right]$$

$$\ln \gamma_2 = x_1^2\left[\tau_{12}\left(\frac{G_{12}}{x_2 + x_1G_{12}}\right)^2 + \frac{\tau_{21}G_{21}}{(x_1 + x_2G_{21})^2}\right]$$

  And

$$\ln \gamma_1^{\infty} = \tau_{21} + \tau_{12}G_{12}$$

$$\ln \gamma_2^{\infty} = \tau_{12} + \tau_{21}G_{21}$$

Other activity coefficient models are Flory-Huggins equation, UNIQUAC equation, UNIFAC equation etc.

All the above equations have parameters whose values are found by curve fitting method. The experimental activity coefficient values are compared with the above equations and values of parameters are found. This method is time consuming and there exists different values of parameters for different temperatures for different liquid systems. To avoid this kind of parameter estimation, a model whose parameters are estimated in a defined way is to be developed.

One such model was developed using the DPD interactions parameters (a_{11}, a_{22} and a_{12}). There are standard formulae present which are used to calculate these parameters unlike the other activity coefficient models. In addition, the model satisfies the Gibbs-Duhem equation and as $x_1 \rightarrow 1\ (i.e\ x_2 \rightarrow 0)$, the expression of Gibbs free energy $G^{ex} \rightarrow 0$. Also as $x_2 \rightarrow 1\ (i.e\ x_1 \rightarrow 0)$, the expression of Gibbs free energy $G^{ex} \rightarrow 0$.

The expression of the Gibbs free energy is

$$\frac{G^{ex}}{RT} = A_{11}x_1^3x_2 + A_{22}x_1x_2^3 - A_{12}x_1^2x_2^2$$

where A_{11}, A_{22} and A_{12} are scaled interaction parameters. The interaction parameters in DPD are defined for a group of atoms i.e beads. To consider atom-atom interactions in this equation, the DPD interactions parameters cannot be taken directly. Therefore, we use scaled parameters in the above equation.

$$A_{11} = \alpha_1 a_{11}, A_{22} = \alpha_2 a_{22} \text{ and } A_{12} = \alpha_3 a_{12}$$

This new equation in terms of activity coefficients is

$$\ln \gamma_1 = 3a_{11}x_1^2x_2^2 + a_{22}(x_2^4 - 2x_1x_2^3) - a_{12}(2x_1x_2^3 - x_1^2x_2^2)$$

$$\ln \gamma_2 = a_{11}(x_1^4 - 2x_1^3x_2) + 3a_{22}x_1^2x_2^2 - a_{12}(2x_1^3x_2 - x_1^2x_2^2)$$

The aim is to predict LLE of binary systems using the above equations.

4.2 APPROACH:

- A MATLAB code is written to find the co-existence points of a simple binary liquid-liquid system using any of the conventional activity coefficient models.
- To validate the code, its results are checked for another binary liquid-liquid system.
- An error function is formulated and the scaling factors α_1, α_2 and α_3 are found.
- The new model is now ready to predict the LLE curve of liquid systems.

4.3 WORK IMPLEMENTED:

STEP 1: An example of isobutane-furfural system is considered. Its co-existence points are to be calculated using Van-Laar equation. The values of parameters α and β are given. A MATLAB code was written for the same.

The four equations used to solve the above problem are

$$x_1^I \gamma_1^I = x_1^{II} \gamma_1^{II} \tag{19}$$

$$x_2^I \gamma_2^I = x_2^{II} \gamma_2^{II} \tag{20}$$

$$x_1^I + x_2^I = 1 \tag{21}$$

$$x_1^{II} + x_2^{II} = 1 \tag{22}$$

Substituting equations (21) and (22) in equations (19) and (20), we get

$$x_1^I \, exp\left\{\frac{\alpha}{\left[1+\frac{\alpha x_1^I}{\beta\left(1-x_1^I\right)}\right]^2}\right\} = x_1^{II} \, exp\left\{\frac{\alpha}{\left[1+\frac{\alpha x_1^{II}}{\beta\left(1-x_1^{II}\right)}\right]^2}\right\} \tag{23}$$

$$x_2^I \, exp\left\{\frac{\beta}{\left[1+\frac{\beta x_2^I}{\alpha\left(1-x_2^I\right)}\right]^2}\right\} = x_2^{II} \, exp\left\{\frac{\beta}{\left[1+\frac{\beta x_2^{II}}{\alpha\left(1-x_2^{II}\right)}\right]^2}\right\} \tag{24}$$

The algorithm is as follows:

- A guess value for x_1^I is taken.
- Substitute x_1^I in equation (23). Then value of x_1^{II} is found.
- Using value of x_1^I, value of x_2^I is found from equation (21)
- Substitute x_2^I in equation (24). Then value of x_2^{II} is found.
- Finally, check if equation (22) is satisfied. If satisfied, the value of x_1^I is correct and co-existence points on LLE curve are found. If not, guess another value of x_1^I and follow the above steps.

A MATLAB code was written using fminunc function using initial points. The answers matched with those in the textbook. To get rid of initial points, another code was written. The value of x_1^I is put in loop ranging from 0 to 1 with a step size of 0.001. There are two objective functions in this approach. One to calculate x_1^{II} and the other to calculate x_2^{II}. The first objective function to be minimized is the absolute value of equation (23). The minimum value of objective function is noted for values of x_1^{II} between 0 and 0.1, 0.1 and 0.2, 0.2 and 0.3 and so on upto 0.9 and 1. All minimum values of objective function are stored, compared with each other and the minimum

value among them is selected and stored along with the value of x_1^{II}. Value of x_2^I is found from equation (21). Then the second objective function to be minimized is the absolute value of equation (24). The same procedure is to be followed as done for finding x_1^{II} to get x_2^{II}. Equation (22) is used to validate the values found. If equation (21) is not satisfied, the next guess value of x_1^I is considered and above procedure is repeated.

The values obtained from code are as follows. The values of α and β at 310K is available in textbook whereas its values at other two temperatures is taken from the graph of activity coefficients available in Dortmund Databank.

Table 6: Data obtained from code compared to aspen data at different temperatures for isobutane-furfural system.

			ASPEN DATA				CODE DATA			
TEMP	**ALPHA**	**BETA**	**x11**	**x12**	**x21**	**x22**	**x11**	**x12**	**x21**	**x22**
310 K	2.62	3.02	0.938	0.208	0.06	0.79	0.9284	0.1128	0.0716	0.8872
324 K	2.51	2.83	0.15	0.878	0.85	0.122	0.1336	0.9072	0.8664	0.0928
338 K	2.4	2.64	0.1	0.82	0.9	0.18	0.1603	0.8779	0.84	0.1221

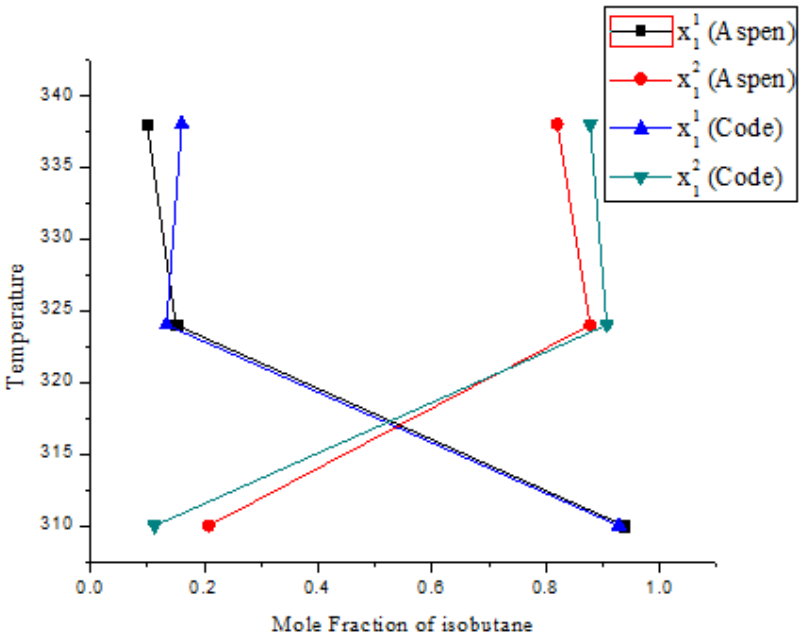

Fig 14: Mole fraction of isobutene at different temperature obtained from code compared to the aspen data.

STEP 2: The code is checked using water-benzene system for validation.

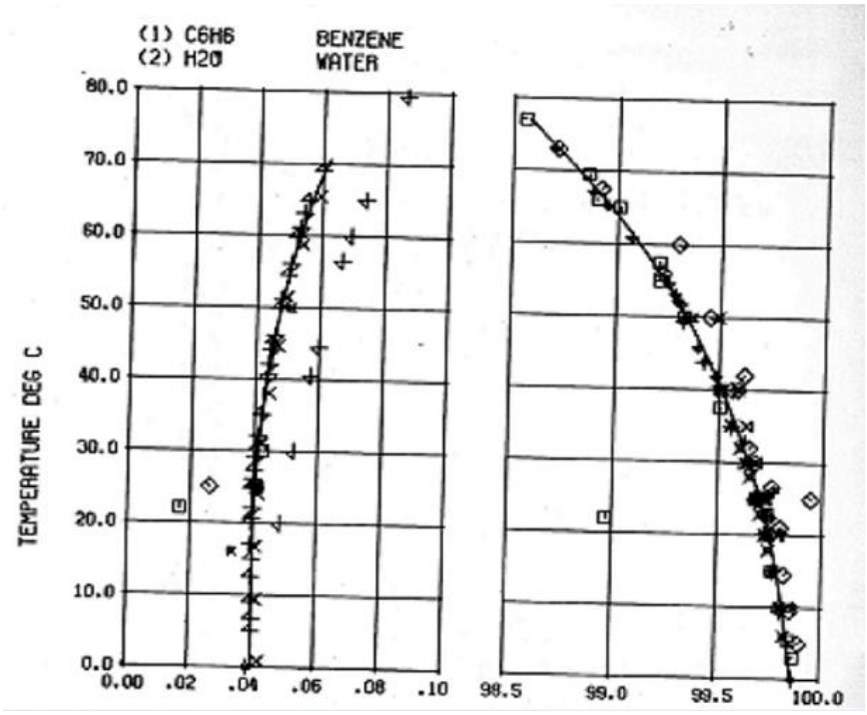

Fig 15: LLE phase diagram of Water-Benzene system

Before proceeding, we need to have values of α and β for water-benzene system at different temperatures. The values found in the literature for this system did not give right values of mole fractions. So, two approaches were followed. One, the above code was run with one loop for values of α and another loop for values of β. For different values of α and β, the code was run and final condition of equation 4 is checked and the appropriate values of α, β and mole fractions were stored. The best combination is selected.

Table 7: Data comparison of Water-Benzene system obtained from code

			GRAPH DATA				**CODE DATA**				
TEMP	**ALPHA**	**BETA**	**x11**	**x12**	**x21**	**x22**	**x11**	**x12**	**x21**	**x22**	**x12+x22**
293 K	7.824	4.542	0.0004	0.9975	0.9996	0.0025	0.0004	0.9889	0.9996	0.0113	1.0002
308 K	7.771	4.155	0.00042	0.996	0.99958	0.004	0.00042	0.9831	0.9996	0.0169	1
323 K	7.599	4.208	0.0005	0.9938	0.9995	0.0062	0.0005	0.9839	0.9995	0.016	0.9999
333 K	7.567	5.072	0.00052	0.9912	0.99948	0.0087	0.00052	0.9935	0.9995	0.0065	1

The points taken above lie on one half of the phase diagram. Another approach involves building a contour for different values of α and β using the MATLAB code and analyzing areas where the objective function is minimum. Accordingly, the values of the parameters are noted. Now, points on the two curves of the graph are taken and values are much accurate compared to the previous approach.

Table 8: Data comparison of Water-Benzene system obtained from contour construction in the code

			GRAPH DATA				CODE DATA				
TEMP	**ALPHA**	**BETA**	**x11**	**x12**	**x21**	**x22**	**x11**	**x12**	**x21**	**x22**	**x12+x22**
293 K	7.829	5.63	0.0004	0.9975	0.9996	0.0025	0.0004	0.9962	0.9996	0.0037	0.9999
323 K	7.606	5.116	0.0005	0.9938	0.9995	0.0062	0.0005	0.9937	0.9995	0.0063	1
343 K	7.421	4.426	0.0006	0.988	0.9994	0.012	0.0006	0.9781	0.9994	0.0128	0.9999
333 K	6.596	4.67	0.99	0.00056	0.01	0.99943	0.99	0.0014	0.01	0.9987	1.0001
313 K	6.654	5.34	0.995	0.00054	0.005	0.99946	0.995	0.0013	0.005	0.9989	1.0002

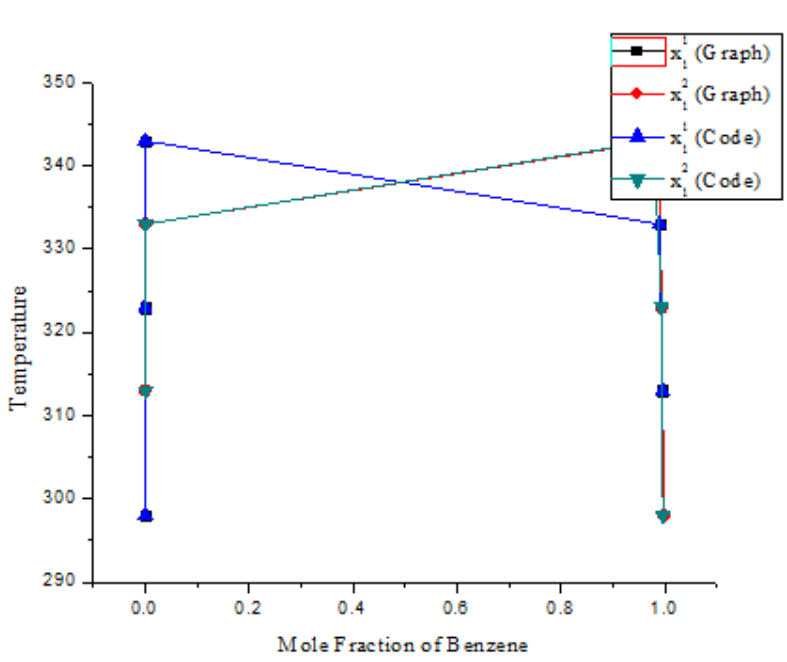

Fig 15: Mole Fraction of Benzene at different temperatures obtained from code compared to graph data.

Therefore, the code is validated

STEP 3: The values of scaling factors are to be found to calculate the scaled interaction parameters using which the new activity coefficient model will be ready to test for any liquid system.

Two methods Differential Evolution and Genetic Algorithm were used to find the scaling factors.

Using Differential Evolution, the code first was tested using the example considered in step 1. The DE stepsize was taken as 0.6 and the crossover probability as 0.4. The results did not match the experimental data.

Through Genetic Algorithm, the Optimization Toolbox in MATLAB was used to find the scaling factors. 5 points on the graph were taken. When Genetic Algorithm was applied at each point on the curve, universality in the scaling factors was seen. This indicates that one set of scaling factors can be used for all points on the curve for a particular liquid-liquid system to find the co-existence points.

The objective function is

$$\sum_{i=1}^{n} (\ln \gamma_{VL} - \ln \gamma_{NF})^2$$

where γ_{VL} is the activity coefficient of Van Laar model, γ_{NF} is the activity coefficient of New Formula.

Table 9: The scaling factors of Water-Benzene system at different temperatures.

TEMP	**x11**	**x12**	$\boldsymbol{\alpha_1}$	$\boldsymbol{\alpha_2}$	$\boldsymbol{\alpha_3}$
298 K	0.0004	0.9962	-0.291	0.13	0.273
323 K	0.0005	0.9937	-0.22	0.162	0.257
343 K	0.0006	0.9871	-0.276	0.187	0.345
333 K	0.99	0.0014	-0.223	0.157	0.265
313 K	0.995	0.0013	-0.255	0.13	0.294

4.4 RESULTS:

From here, the basic idea was to first use evolutionary technique to find the local minima and then use the classical technique to find the global minima. A number of GA runs were done for each point and the corresponding sets of scaling factors were collected to calculate scaled interaction parameters. These are used to find the co-existence points. The set of scaling factors which gives the nearest possible answer was chosen.

Table 10: The co-existence points of Water-Benzene system calculated for different temperatures using the new expression of Gibbs Free Energy.

	SCALING FACTORS			**UNSCALED PARAMETERS**			**SCALED PARAMETERS**			**GRAPH DATA**		**CODE DATA**	
TEMP	$\boldsymbol{\alpha_1}$	$\boldsymbol{\alpha_2}$	$\boldsymbol{\alpha_3}$	$\mathbf{a_{11}}$	$\mathbf{a_{22}}$	$\mathbf{a_{12}}$	$\mathbf{A_{11}}$	$\mathbf{A_{22}}$	$\mathbf{A_{12}}$	$\mathbf{x_{12}}$	$\mathbf{x_{22}}$	$\mathbf{x_{12}}$	$\mathbf{x_{22}}$
298 K	0.001	0.132	0.996	24.71	60.35	94.69	0.02471	7.9662	94.3112	0.9962	0.0037	0.9945	0.1053
323 K	0.001	0.162	0.847	23.98	47.02	76.34	0.02398	7.6172	64.659	0.9937	0.0063	0.992	0.1079
343 K	0.001	0.164	0.891	22.26	39.87	63.74	0.02226	6.5386	37.734	0.9871	0.0128	0.9854	0.1144
333 K	0.001	0.158	0.79	23.11	42.43	73.16	0.02311	6.7039	30.361	0.0014	0.9987	0.0031	0.897
313 K	0.001	0.16	0.824	24.63	52.03	82.06	0.02463	8.3248	73.115	0.0013	0.9989	0.003	0.8973

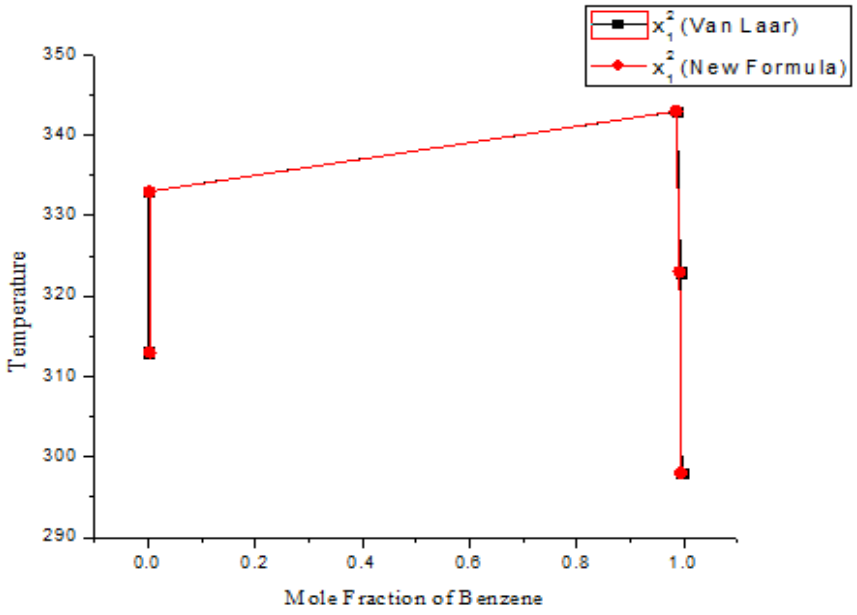

Fig 16: Mole Fractions of Benzene calculated from New Formula is compared to Van Laar values.

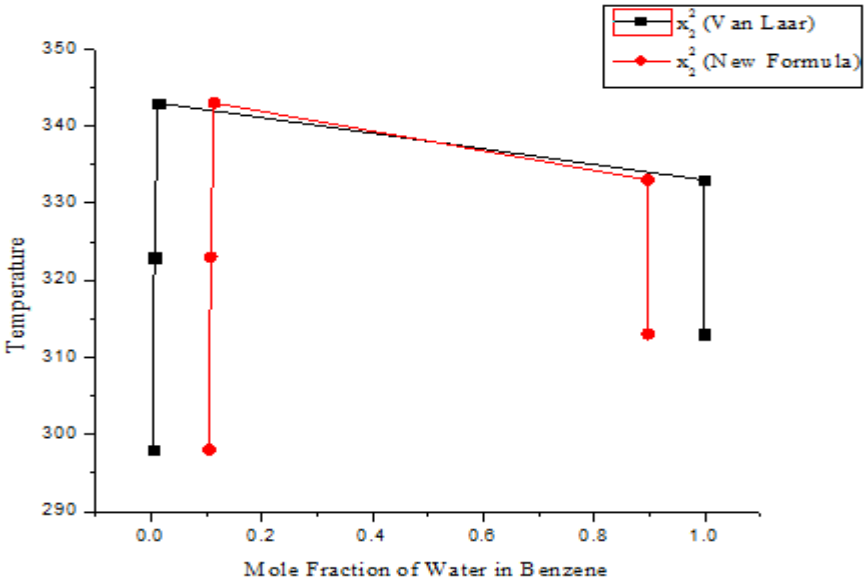

Fig 17: Mole Fractions of Water calculated from New Formula is compared to Van Laar values.

REFERENCES:

1. Dissipative Particle Dynamics: Bridging the gap between Atomistic and Mesoscopic Simulations by Robert D. Groot and Patrick B. Warren, J. Chem. Phys., Vol. 107, No. 11, 15 September 1997.
2. Understanding Molecular Simulations by Frenkel and Smith
3. Bead-bead interaction parameters in DPD: relation to bead-size, solubility parameter and surface tension by Amitesh Maiti and Simon McGrother,
4. The Martini Force Field: Coarse Grained Model for Biomolecular Simulations by Siewert J. Marrink et al, J. Phys. Chem. B, Vol. 111, No. 27, 2007
5. Perspective on the Martini model by Siewert J. Marrink and D. Peter Tieleman, Chem. Soc. Rev., 2013,42, 6801
6. Atomistic Simulation of the Thermodynamic and Transport Properties of Ionic Liquids by Edward J. Maginn, American Chemical Society, VOL. 40, NO. 11, 2007
7. Molecular simulation of ionic liquids: current status and future opportunities by E J Maginn, J. Phys.: Condens. Matter 21 (2009) 373101
8. Electrostatic interactions in DPD using Ewald Sums by Gonzalez Melchor et al, J. Chem. Phys. 125, 224107, 2006
9. Study of interfacial tension between an organic solvent and aqueous electrolyte solutions using electrostatic dissipative particle dynamics simulations E. Mayoral1 and E. Nahmad-Achar, J. Chem. Phys. 137, 194701 (2012)
10. Prediction of Ionic Liquids Properties through Molecular Dynamics Simulations by Marta L. S. Batista, Joao A. P. Coutinho and Jose R. B. Gomes, Current Physical Chemistry, 2013, Vol. 3, No. 3
11. Direct determination of Monte Carlo phase coexistence properties of fluids by simulation in a new ensemble Athanassios Z. Panagiotopoulos, Molecular Physics, 2002, vol.100, No I, 237-246.
12. Binary Mixtures of n-Butane, Isobutane, and 1-Butene with Furfural, Vapor-liquid equilibria and thermodynamic properties, T. S. Mertes and A. P. Colburn, Industrial and Engineering Chemistry, Vol. 39, No. 6
13. Chemical, Biochemical and Engineering Thermodynamics by Stanley I. Sandler
14. On the simulation of vapor–liquid equilibria for alkanes by Shyamal K. Nath, Fernando A. Escobedo, and Juan J. de Pablo, The Journal of Chemical Physics 108, 9905 (1998)
15. Vapor-liquid Equilibria in Methane-Hydrocarbon Systems by Nicholas W. Prodany and Brymer Williams, Journal of Chemical and Engineering Data, Vol. 16, No. 1, 1971
16. Numerical Methods for Engineers by S. K. Guptha