PREDICTION OF INTERFACIAL PROPERTY OF LIQUID SYSTEMS BY MULTISCALE MODELLING

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Dedicated to

My Parents.

Abstract

Binary immiscible liquid mixtures when mixes together tend to form an interface. to predict interfacial tension; it requires a detailed treatment of fundamental forces like Van der Waals, electrostatic interactions and hydrogen bonding among molecules. However in mesoscopic model all these detailed forces information result in the form of repulsive interaction parameters a_{ii} and $a_{jj.}$ In the present effort, the interfacial tension has been predicted based on different self-repulsive interaction parameters of each component for liquid-liquid system and also , interfacial tensions for different kinds of liquid-liquid systems at different temperatures are predicted using Dissipative Particle Dynamics (DPD). Isothermal compressibility of pure components is used to find the like-like repulsion parameter whereas the solubility parameter is used to evaluate the unlike interaction parameter. The temperature variation of isothermal compressibility and solubility parameter affects the interaction parameter and introduces the temperature effect into the system. The methodology is applied to water-alkane, water-aromatic and non-water systems and comparisons are made with experimental studies reported in the literature. The proposed formalism not only reproduces the temperature dependence of interfacial tension but also matches with the absolute values with reasonable accuracy.

Nomenclature

a_{ii} Self-repulsive interaction parameters of i bead

a_{jj} Self-repulsive interaction parameters of j bead

a_{ij} Repulsive interaction parameters between i & j

σ Fluctuation amplitude

ρ Dimensionless bead density

V_b Volume of bead

K_B Boltzmann constant

T Temperature

δ Solubility Parameter

K_T Isothermal compressibility

χ Flory Huggins parameter

R Gas constant

ΔG^C Combinatorial contribution in Gibbs energy

ΔS_{mix} Entropy of mixing

ΔG_{mix} Gibbs energy of mixing

ΔG^R Residual contribution in Gibbs energy

ΔS^C Combinatorial contribution in entropy of mixing

C Cohesive energy density

$\Delta_{vap}u$ Heat of vaporization

V_L Molar volume

f_i force on particle i

m_i Mass of particle i

a_i Acceleration of particle i Time

u^E Total energy of mixture

σ_{DPD} Stress in DPD units

P_{xx} Pressure force along x axis

w_D Weight function

v_{ij} Relative velocity

f_i^D Dissipative force

f_i^R Random force

f_i^C Conservative force

μ Chemical Potential

Γ Thermodynamic Factor

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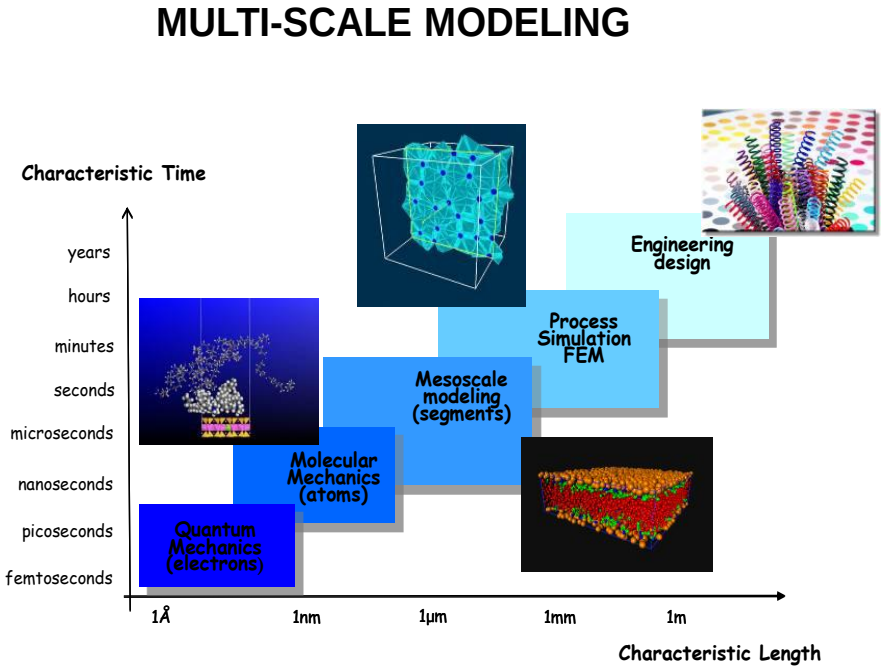
Chapter 1

Introduction

1.1 Multiscale modeling.

There have been rapid improvements in modeling of physical and chemical process at atomistic level over the past two decades mainly because of the increase in computer speed and memory, improved theoretical methods based in quantum or statistical mechanics etc. Multiscale modeling can effectively replace experiments and can give insight to various processes. Theory and modeling methods can be classified into four groups depending on the length and time scales to which they apply.

a) Electronic scale in which matter is made up of fundamental particles like electron and is described by quantum mechanics.
b) Molecular scale in which matter is made up of atoms which obeys laws of statistical mechanics.
c) Mesoscale in which matter is regarded as a cluster of atoms.
d) Continuum level in which matter is regarded as a continuum macroscopic laws like equations of continuity and momentum conservation can apply.



Ref:- COSMO-RS and process simulation: from physical properties to environmental impact ,by Maurizio Fermeglia & Sabrina Pricl 3

Fig 1.1 Multiscale Modelling

1.2 Prediction of thermo physical properties

Prediction of thermo physical properties like interfacial tension and diffusivity by different modeling methods is of great interest [1]. Both these properties are function of temperature an accurate prediction of temperature dependence is a challenging problem. Molecular level techniques have limited length and time scales. A proper mesoscale method can solve this problem to a great extent.

Dissipative Particle Dynamics (DPD) can be used for the prediction of interfacial tension. In broad sense, the term “interface” includes any boundary that separates two different phases. However, it is generally associated with the liquid-liquid case and interfacial tension is the force per unit length exerted on the interface between two immiscible liquids. In the past few decades, computer simulation methods such as molecular dynamics and Monte Carlo method have played a huge role in reducing the number of experiments [2,3]. However, it is not practically realizable to study a macroscopic system by detailed atomistic simulation due to the length and time scale involved. In recent years, Dissipative Particle Dynamics (DPD) introduced by Hoogerbruge and Koelman[4], has emerged as a popular coarse grained method.DPD enables us to reach length scale, where molecular level fluctuations are still important but at the same time inaccessible by atomistic simulation.

Chapter 2

Problem Definition

1) Prediction of various thermo physical properties (interfacial tension, diffusivity, solubility parameter etc) of liquids.
2) Formulate a general protocol for prediction of properties through meso-scale modeling.
3) Predict the temperature dependence of properties accurately.
4) Reduction of computational time by using coarse graining.

Chapter 3

Literature Review

3.1 Interfacial Tension

Interfacial tension is an important equilibrium property which strongly influences the dynamics of a multiphase system. Prediction of interfacial tension is of great interest in industrial applications like preparing emulsions, surfactants etc. There are some studies which predicts interfacial tension using dissipative particle dynamics In recent years, Dissipative Particle Dynamics model was successfully applied to study many important physical phenomena such as phase separation between immiscible liquids and polymer systems [5-6], morphology evaluation [7], reduction of interfacial tension through surfactants [8]. But all of them predicts interfacial tension for a few systems and could not provide a general protocol for prediction of variety of systems.

DPD model was introduced by Hoggerbuge and Koelman [4] in1992. In DPD model all the detailed force information is taken care by the repulsive interaction parameter a_{ii} and $a_{ij.}$ In 1997 Groot et.al [9] introduced a relationship between the self-repulsive conservative force parameter a_{ii} and inverse of isothermal compressibility and also Groot et. al [9] formed a relation between repulsion parameter a_{ij} and Flory-Huggins parameter χ_{ij}. Here Groot et.al [9] made a basic assumption that $a_{ii}=a_{jj}$ which means the interaction between beads of i-i is equal to the interaction between beads of j-j. Maiti et.al [10] followed this method and predicted interfacial tension for a few number of systems. In 2007 Travis et al. [11] formed a new relation for calculating the interaction parameters by relating with Scatchard Hildebrand Regular Solution Theory (RST). He came up with a relation to get interaction parameter using solubility parameter and they eliminated the basic assumption of $a_{ii}=a_{jj.}$

3.2 Temperature Dependence of Interfacial Tension

Interfacial Tension is a function of temperature and accurate prediction of interfacial tension with temperature is a challenging problem. Though several researchers have studied the temperature dependence of interfacial tension experimentally, a general agreement on this is yet to be reached. Ataev [12] has measured the interfacial tension of water and hydrocarbons and found a positive coefficient of $\frac{d\sigma}{dT}$ which contradicts Antonov rule. Rafati *et al*. [13] have reported a linear decrease of interfacial tension with temperature for mixtures of ethylene glycol and aliphatic alcohols. A rather interesting observation comes from the works of Vázquez *et al*.[14] and Villers *et al*. [15] where the interfacial tension between water and lower alcohols is reported to be linearly decreasing with temperature and in case of higher alcohols, the existence of non-linearity is reported. In 2013 Mayoral et.al [16] have predicted the interfacial tension for water-cyclohexane and water-benzene system by adopting the parameterization method proposed in the seminal work of Groot et.al [9]. In this work they were able to match the slope of the straight line but the intercept values were in poor agreement. Our main objective is to predict the temperature dependence of interfacial tension by the method suggested by Goel et.al [17].

3.3 Diffusivity prediction

Mutual diffusion coefficient or cross diffusion coefficients is an important property which gives an idea about the miscibility of the system. There have been literatures in predicting diffusivity of liquids in polymer [18]. Liu et.al [19] has calculated Fick's diffusivities through molecular dynamics(MD) simulation for liquid-liquid systems. Fick's diffusivities are obtained from Maxwell Stefan (MS) diffusivities. Mutual diffusion experiments measure Fick's diffusion coefficients, while molecular simulation provides MS diffusivities. A thermodynamic factor is required to convert MS diffusivity into Fick's diffusivity. DPD can also give Fick's diffusivity but not as accurate as MD. Groot et.al [9] has given a equation to predict DPD diffusivity which shows that DPD diffusivity prediction will be an order of magnitude different.

Chapter 4

Methodology

4.1 Dissipative Particle Dynamics

Dissipative Particle Dynamics (DPD) is an off lattice, discrete particle method for modeling mesoscale systems. The Dissipative Particle Dynamics method was introduced by Hoogerbrugge and Koelman [4] in 1992. DPD model have the following advantages

- It exhibits hydrodynamic behavior.
- It has thermal fluctuations that can drive Brownian motion.
- It is cheap to simulate.

In the DPD approach, the forces due to individual solvent molecules is lumped together to yield effective friction and a fluctuating force between moving fluid elements. While this approach does not provide a correct atomistic description of the molecular motion, it has the advantage that it does reproduce the correct hydrodynamic behavior on long length and time scales.

Like standard molecular dynamics (MD) algorithm, DPD also involves the updation of positions and momenta of all the particles by numerically solving the equations of motion.

$$\frac{d\vec{r}_i}{dt} = \vec{v}; \frac{d\vec{p}_i}{dt} = \vec{f}_i$$

Where $\vec{x}_i$ is the position and $\vec{v}_i$ is the velocity of particle i and $\vec{F}_i$ is the force experienced by it due to its interaction with all other particles.

The difference is that, in addition to the conservative force $\vec{f}_{ij}^{\,C}$ acting between particles, the total force on a particle i now also contains a dissipative force $\vec{f}_{ij}^{\,D}$ and a random force $\vec{f}_{ij}^{\,R}$.

$$\vec{f}_i = \sum_{j \neq i} \vec{f}_{ij}^{\,C} + \vec{f}_{ij}^{\,D} + \vec{f}_{ij}^{\,R}$$

The conservative force $\vec{f}_{ij}^{\,C}$ can, be derived from a pair potential that acts between particles i and j.

$$\vec{f}_{ij}^{\,C} = a_{ij}\left(1 - \frac{r_{ij}}{r_c}\right)\frac{\vec{r}_{ij}}{r_{ij}} \qquad (r_{ij} < r_c)$$

$$\vec{f}_{ij}^{\,C} = 0 \qquad (r_{ij} \geq r_c)$$

Where a_{ij} is interaction parameter between i and j , $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j; r_{ij} = \left|\vec{r}_{ij}\right|$ and r_c is an interaction cut-off range parameter

The dissipative force corresponds to a frictional force that depends both on the positions and the relative velocities of the particles. The motion of the molecules within each bead dissipates energy and opposes relative motion of the beads.

$$\vec{f}_{ij}^{\,D} = -\gamma \omega_d(r_{ij})\left(\vec{r}_{ij} \cdot \vec{v}_{ij}\right)\vec{r}_{ij}$$

Where
- $\vec{v}_{ij} = \vec{v}_i - \vec{v}_j$ is the relative velocity
- γ is a friction coefficient
- ω_d is a distance dependent weight function that is zero for $r_{ij} > r_c$

The random motion of the molecules within each bead tends to exert a fluctuating force and it is of the form

$$\vec{f}_{ij}^{\,R} = -\sigma \omega_r(r_{ij})\theta_{ij}\vec{r}_{ij}$$

Where
- σ is a fluctuation amplitude
- ω_r is a distance dependent weight function that is zero for $r_{ij} > r_c$
- θ_{ij} is a Gaussian distributed random number with zero mean and unit variance

The strength of the dissipative force and random force cannot be chosen independently and is fixed by the fluctuation-dissipation theorem. These two components of the forces together act as the equivalent of thermostat in MD. So, the natural statistical ensemble in case of DPD is that of canonical ensemble. Following Groot et.al [9] the weight function takes the form

$$\omega_d = \left(1 - \frac{r_{ij}}{r_c}\right)$$

The dissipative and random are coupled through fluctuation-dissipation theorem [20].

$$\omega_d(r_{ij}) = \left[\omega_r(r_{ij})\right]^2$$

$$\sigma^2 = 2\gamma K_B T$$

Generally a value of 4.5 for frictional coefficient and Fluctuation amplitude value of 3 provides good results in literatures [9,10].

Dissipative particle dynamics model is used for large variety of applications.

- Simulating systems such as polymers, biopolymers, lipids, emulsions and surfactants.
- Complex fluids near interfaces: micro fluidics, slip of liquid flow past surfaces.
- Surfactants related applications including paints and coatings, emulsions, dispersions, bio and nanotechnology etc.

4.2 Molecular Dynamics

Molecular Dynamics simulation is a technique for computing the equilibrium and transport properties of a classical many-body system [2] . The essence of molecular modeling resides in the connection between the macroscopic world and the microscopic world provided by the theory of statistical mechanics. The atoms and molecules are allowed to interact for a period of time, giving a view of the motion of the atoms. In the most common version, the trajectories of atoms and molecules are determined by numerically solving the Newton's equations of motion for a system of interacting particles, where forces between the particles and potential energy are defined by molecular mechanics force fields.

The molecular dynamics simulation method is based on Newton's second law or the equation of motion, F=ma, where F is the force exerted on the particle, m is its mass and a is its acceleration. From knowledge of the force on each atom, it is possible to determine the acceleration of each atom in the system. Integration of the equations of motion then yields a trajectory that describes the positions, velocities and accelerations of the particles as they vary with time. From this trajectory, the average values of properties can be determined. There are large numbers of commercial force field available such as OPLS, Trappe, UFF, CHARMM, AMBER, GROMOS, Dreiding, COMPASS etc.

$$F_i = m_i a_i$$

$$F_i = m_i \frac{\partial^2 r_i}{\partial t^2}$$

Where F_i is the force on particle i, m_i is mass of particle i,a_i is acceleration on particle i, and t represent time.

Numerous numerical algorithms have been developed for integrating the equations of motion. Some are listed below.

1) Verlet algorithm
2) Leap-frog algorithm

3) Velocity Verlet

4) Beeman’s algorithm

Thermostats are available to add and remove energy and mainly to control temperature of the system in the canonical ensemble. The thermostat is used to control temperature fluctuations such as velocity rescaling, the Nose-Hoover thermostat, Nosé-Hoover chains, the Berendsen thermostat, the Andersen thermostat etc. Similarly A variety of barostats are available to control the pressure of the system in the NPT ensemble such as Parrinello, Anderson, and Berendsen barostat.

At present, the atomistic simulation simulates smaller system of few atoms and covers smaller time scales in the range of nanoseconds. The greatest challenge for using atomistic simulation is the computational cost. However, increasing capacity of computing power will be able to tackle such issues.

Chapter 5

Liquid Models

5.1 Regular Solution Theory

Regular solution is defined as solution where the components mix with no excess entropy provided that there is no volume change of mixing. Scatchard and Hildebrand proposed a parameter Cohesive Energy Density (C) for the improvement of the theory. The parameter C is defined as

$$C = \frac{\Delta_{vap} u}{v^L}$$

Where the energy of complete vaporization is, is the molar volume of the liquid, C is the cohesive energy density. The cohesive energy density is defined as amount of energy needed to remove unit volume of molecule

The energy of a binary liquid mixture can be expressed as a quadratic function of volume fraction.

$$-(u_{liq} - u_{ideal\,gas})_{mix} = \frac{c_{11} v_1^{\,2} x_1^{\,2} + 2c_{12} v_1 v_2 x_1 x_2 + c_{22} v_2^{\,2} x_2^{\,2}}{x_1 v_1 + x_2 v_2}$$

This can be written in terms of volume fractions ϕ_1 and ϕ_2 as

$$-(u_{liq} - u_{ideal\,gas})_{mix} = (x_1 v_1 + x_2 v_2)(c_{11}\phi_1^{\,2} + 2c_{12}\phi_1\phi_2 + c_{22}\phi_2^{\,2})$$

c_{12} is taken as the geometric mean between c_{11} and c_{22}

$$c_{12} = \sqrt{c_{11} c_{22}}$$

$$-(u_{liq} - u_{ideal\,gas})_{mix} = (x_1 v_1 + x_2 v_2)\phi_1\phi_2(\delta_1 - \delta_2)^2$$

Where δ_1,δ_2 are the Hildebrand solubility parameters which is nothing but the square root of cohesive energy density [21]. Hansen proposed a 3D solubility parameter [22].

5.2 Flory-Huggins Theory

The Flory Huggins theory is based on a lattice approach. The regular solution theory, applied to molecules of similar sizes where as Flory-Huggins theory applied to molecules having difference in their volume like polymer solutions. The Gibbs energy of mixing consists of enthalpy and entropy contributions. Entropy contributed cannot be neglected. There are two terms (1) Combinatorial contribution ΔG^C (2) Residual contribution ΔG^R.

$$\Delta G_{mix} = \Delta G^C + \Delta G^R$$

Flory and Huggins also showed that if the amorphous polymer and the solvent mix without any energetic effect (AThermal behavior) the change in Gibbs energy and entropy of mixing are given by.

$$\Delta G^C/RT = \Delta S^C/R = -(N_1 \ln\phi_1 + N_2 \ln\phi_2)$$

The residual term will depend on the interactions between solvent molecules and polymer segments, and also on the composition of the system.

$$\Delta G_{mix}/RT = (N_1 \ln\phi_1 + N_2 \ln\phi_2) + \chi\phi_1\phi_2(N_1 + N_2).$$

$$\chi = V(\delta_1 - \delta_2)^2/RT$$

Where χ is known as Flory Huggins parameter, R is gas constant, T is Temperature, and δ is Hildebrand solubility parameter. The Flory Huggins parameter χ is responsible for the energy of the mixing for polymer and solvent molecules.

Chapter 6

Prediction of liquid properties

6.1 Prediction of Interfacial Tension

When two immiscible liquids are mixed together they will not mix with each other and will form an interface as thin as possible. At interface, there are unresolved forces between different liquids, which cause tension at the boundary. The interfacial tension can be rightly predicted by considering the unresolved forces involved at interface. As mentioned by Maiti et. al.[10] interfacial tension can be computed by integrating the difference between normal and tangential stresses across the interface (normal to the x-direction). In order to create x-normal interfaces it is common practice to increase the system extent in the x-direction. This simple alteration makes a x-normal interface have a smaller surface area, which leads to a lower free energy.

$$\sigma_{DPD} = \int \left[\bar{p}_{xx}(\bar{x}) - \frac{1}{2}\left(\bar{p}_{yy}(\bar{x}) + \bar{p}_{zz}(\bar{x})\right) \right] d\bar{x}$$

$$\sigma_{real} = \frac{k_B T}{r_c * r_c} \sigma_{DPD}$$

6.1.1 Calculating DPD interaction parameter

To find the interaction parameters between the beads a combined approach of Groot et.al [9] and Travis *et al* is[11] been used. However, the assumption of equality of like-like interaction parameter ($a_{11} = a_{22}$) taken by Groot et al [9] is omitted. The isothermal compressibility of each component to calculate the repulsion parameter between similar beads and use solubility parameters to calculate the repulsion parameter between dissimilar beads.

The like-like repulsion parameter a_{ii} is obtained by using the relation,

$$a_{ii} = \left[\kappa_i^{-1}\left(N_{m,i} - 1\right)/2\alpha\rho_i\right]k_B T,\ i = 1,2$$

Where $N_{m,i}$ is the degree of coarse graining for species i, α is a numerical constant, ρ_i is the number density of species i and κ_i^{-1} is the dimensionless isothermal compressibility of the species which is related to the physical isothermal compressibility $\kappa_{T,i}$ as $\kappa^{-1} = 1/\rho k_B T \kappa_{T,i}$.ρ,being the number density of the molecules.

The interaction parameter between different types of beads, a_{12} ,is obtained using the relation

$$\left(\delta_1 - \delta_2\right)^2 = -r_c^4 \alpha\left[\rho_1^2 a_{11} + \rho_2^2 a_{22} - 2\rho_1\rho_2 a_{12}\right]$$

Where δ_i is the solubility parameter of pure component i, r_c is the cut-off radius and a_{ij} is the interaction parameter between component i and j.

The coarse grain model is based on averaging of molecular volume and interaction among molecules. For water and Benzene, coarse grain model W[5][1]B[1][1] is been chosen. The reason behind choosing W[5][1]B[1][1] coarse grain model is due to the size and individuality of benzene structure. Here W[5][1] indicates one water bead consist of five water molecule and B[1][1] indicates one benzene bead of one benzene molecule. The benzene molecule is aromatic compound having a ring structure, which cannot be cut or broken. Therefore, it has to be taken as a single molecule bead. The molecular volume of five water molecules becomes 150 $A°^3$ and one benzene molecule is $148A°^3$. So the average molecular volume of bead is kept $149A°^3$.Based on this bead volume, we calculated the a_{12} repulsive interaction parameters.

6.2 Prediction of temperature dependence of interfacial tension

6.2.1 By calculating DPD mutual interaction parameter through solubility parameter

Goel et.al [17] predicted interfacial tension of 45 systems using a combined approach of Groot et.al [9] and Travis et.al. [11] The same method has been followed for finding the interaction parameters. The temperature effect in the system can only be introduced through the interaction parameters. We must have the information of isothermal compressibility of individual components at different temperatures to estimate the like-like interaction parameter. Similarly, we must have the solubility parameters for both the components at different temperatures to calculate the unlike repulsion parameter. Mayoral et.al [16] has done a temperature dependence study using DPD. Experimental values of interfacial tension at different temperatures in taken from literatures [23-25].

6.2.2 By calculating DPD mutual interaction parameter through Flory-Huggins parameter

Groot et.al [9] formulated a method to find unlike interaction parameters using Flory-Huggins interaction parameter and is been followed by Maiti et.al [10].

$$a_{ij} = a_{ii} + 3.27\,\chi_{ij}$$

They assumed the like like interaction parameters to be equal. In this work the assumption of like like interaction parameters is been removed and the following equation is been used for calculating the unlike interaction parameter.

$$a_{ii}* = a_{ii} + 3.27\,\chi_{ij}$$

$$a_{jj}* = a_{jj} + 3.27\,\chi_{ij}$$

$$a_{ij} = \frac{a_{ii}* + a_{jj}*}{2}$$

We calculated Mutual interaction parameter by using a_{ii} and a_{jj} individually and average the values to get a_{ij}

6.3 Prediction of mutual diffusion coefficient

To describe diffusive mass transport in liquid mixtures, generalized Fick's law and the Maxwell Stefan theory are often used. For describing multicomponent diffusion in liquids, the Maxwell Stefan (MS) approach is often advocated. The key point of this approach is that the driving force for diffusion of component i (i.e., the chemical potential gradient $\Delta\mu_i$) is balanced by a friction force, resulting in the following equation.

$$\frac{-1}{RT}\nabla\mu_i = \sum_{j=1,\, j\neq i}^{n} \frac{x_j(u_i - u_j)}{D_{ij}}$$

in which R and Tare the gas constant and absolute temperature ,respectively. The friction force between components i and j is proportional to the difference in average velocities of the components, $(u_i\text{-}u_j)$. As generalized Fick's law and the MS theory describe the same physical process, it is possible to relate the corresponding transport coefficients. The mutual diffusion coefficient, D_{12}^{Fick}, can be written as a product of a thermodynamic factor, **Γ**, and the Maxwell-Stefan diffusion coefficient, D_{12}^{MS}.

$$D_{12}^{Fick} = \Gamma D_{12}^{MS}$$

Thermodynamic factor Γij is defined by

$$\Gamma_{ij} = \delta_{ij} + x_i\left(\frac{\partial \ln \gamma_i}{\partial x_j}\right)_{T,p,\Sigma}$$

δ_{ij} is the Kronecker delta, and γ_i is the activity coefficient of component i. The symbol $\sum$ Is used to indicate that the differentiation is carried out while keeping constant the mole fractions of all other species except the n-th.

Wilson activity coefficient model is used for calculation in this work.

It is given by

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

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

Where Λ_{12} and Λ_{21} are Wilson parameters which are taken from literatures [26].

6.4 Simulation details

The simulations are carried out using the DPD module of Material Studio suite 6.0 [27]. All the inputs to the solver are provided in dimensionless units. Dimensionless number density $\rho^* = 3$ is used in the simulation, so that we can use the DPD equation of state. The strength of dissipative and random forces is kept at 4.5 and 3, respectively in order to maintain the temperature at $k_B T = 1$. Dimensionless time step, i.e., $\Delta t^* = 0.02$ was used during the simulation. Velocity-Verlet algorithm is used for numerically solving the equation of motion, with slight modification to account for the velocity dependent drag force in the DPD model. 6000 DPD particles were used in the simulation and the dimension of the simulation domain were $L_x^* = 20,\ L_y^* = L_z^* = 10$. Periodic boundary conditions were imposed in all direction

Similarly, Molecular Dynamics simulations were carried out on Material Studio 6.0 using Forcite module [28] of Accelrys. Periodic cells are constructed with 25A° sides by using amorphous cell construction module. After construction, the system has been energy minimized and geometry optimized. A time step of one femtosecond was used. The equilibration period of 50 picoseconds (NVT dynamics) was used followed by production run (NPT dynamics) for 150 picoseconds. Also COMPASS forcefield [29] is used for interatomic interactions in molecular dynamic simulations. All the results are analyzed with the help of Forcite analysis.

Chapter 7

Results and Discussions

7.1 Prediction of interfacial tension with DPD model

In this chapter, we would like to discuss briefly about result obtained by DPD simulations. To validate new approach for determining self-repulsive interaction parameters. We have validated the interfacial tension for different liquid-liquid system with published experimental data. It includes different polar and nonpolar molecules with different chemical structure and properties.

Table 7.1 Interfacial tension for Partially Miscible Mixtures

System	Coarse Graining Model	Predicted Interfacial Tension at 25°C dyn/cm	Interfacial tension experimental (Temp.) dyn/cm
Water-Tridecane	W[7][1]TD[1][2]	55.55	51.14(25°C)
Water-Tetradecane	W[2][1]TR[1][7]	54.49	51.55(25°C)
EG-Heptane	EG[1][1]H[1][2]	19.44	16.02(20°C)
Glycerol-Heptane	G[2][1]H[1][1]	35.6	31.07(20°C)
Glycerol-Nonane	G[2][1]N[1][1]	28.85	30.53(20°C)
DMSO-Decane	DM[3][1]D[1][1]	9.07	9.20(23°C)
FM –Decane	FM[2][1]D[1][3]	29.77	28.33(23^0C)
Water-Pentadecane	W[2][1]PD[1][7]	52.76	51.2(25°C)

EG: Ethylene Glycol, FM: Formamide, DMSO: Dimethyl sulfoxide

- In older studies, coarse graining was handled only for few liquid-liquid systems and these studies only include the prediction of the interfacial tension for few water & alkane system. In our approach, we tend to build a protocol for different liquid-liquid systems based on their specific underlying chemistry and physics.
- Also, a preferred beading was found to match a particular experimental data.
- The main advantage of this approach is to reduce a simplified assumption $a_{ii}=a_{jj}$ and to predict the interfacial tension for large number of system.
- The unit for interfacial tension is in dyn/cm.
- In some of the cases, due to the unavailability of experimental data for interfacial tension at specific temperature, we have predicted interfacial tension at 25°C. As an example. Glycerol- Heptane system, we have predicted interfacial tension at 25°C with a value of 35.6, but the experimental value 31.07 is available at 20°C. As temperature increases, the interfacial tension tends to decrease.
- Here Ethylene glycol is modeled as single molecule in a single bead due to its characteristics of having intra hydrogen bonding among its molecule. For this specific reason, we must use a single molecule of Ethylene glycol in a bead.
- In case of Glycerol, DMSO, Formamide molecules, their nature have intermolecular hydrogen bonding among themselves, which results in 2-3 molecules in a bead.

7.2 Prediction of temperature dependence of interfacial tension

7.2.1 By calculating DPD mutual interaction parameter through solubility parameter

We have evaluated interfacial tension for different types of systems and made the comparison between the present method, method suggested by Mayoral *et al* [16] and the experimental data available in the literature. All the systems are studied at 50:50 composition of DPD particles and within a temperature range of 25°C – 60°C. The various systems undertaken for study are divided into different categories as shown in Table 7.2.1

Table 7.2.1 Classification of different systems studied

1. Water-alkane systems	Water-Heptane, Water-Octane
2. Water-aromatics systems	Water-Benzene, Water-Toluene
3. Other systems	Water-Cyclohexane, Ethylene glycol-Tetradecane

WATER-ALKANE SYSTEMS:

In Figure 7.2.1 and 7.2.2 we have shown the temperature dependence of interfacial tension of water-heptane and water-octane systems obtained from present DPD simulation along with the earlier experimental results. The temperature range considered for this study is from 25°C – 60°C, same as that considered in the experimental studies. It can be seen that our simulation results are in close match with the experiments. As expected, interfacial tension decreases almost linearly with temperature

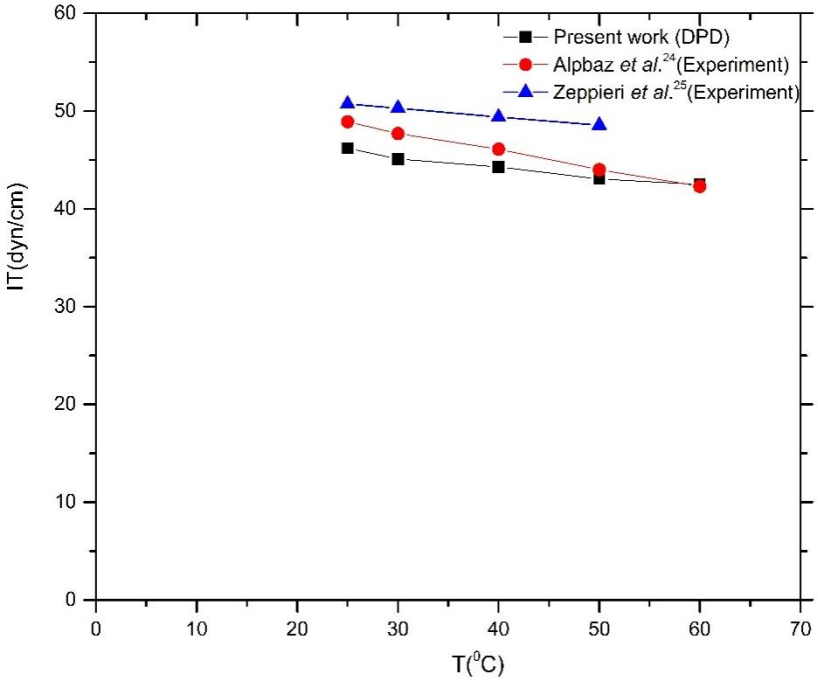


Fig.7.2.1 Temperature dependence of interfacial tension for water-heptane system.

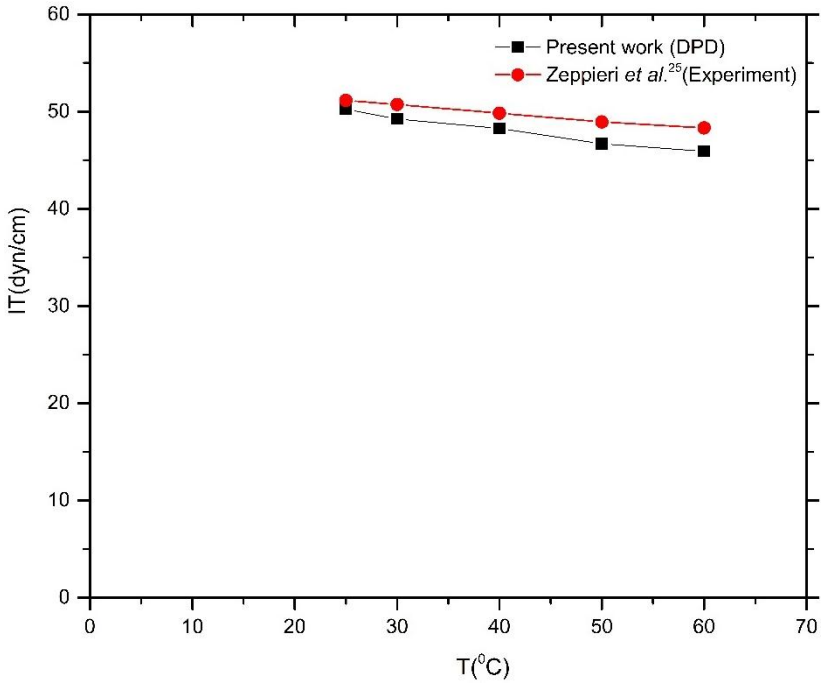


Fig.7.2.2 Temperature dependence of interfacial tension for water-octane system.

WATER-AROMATICS SYSTEMS:

Figure 7.2.3 and 7.2.4 shows the comparison of DPD prediction of interfacial tension with that of experimental measurements for water-benzene and water toluene systems. For water-benzene system, we have also made comparison with earlier DPD work of Mayoral *et al*.[16] in which they have matched the slope of the linear relationship but not the absolute values. Like the earlier case, simulations done by the present effort have good agreements with the experimental findings.

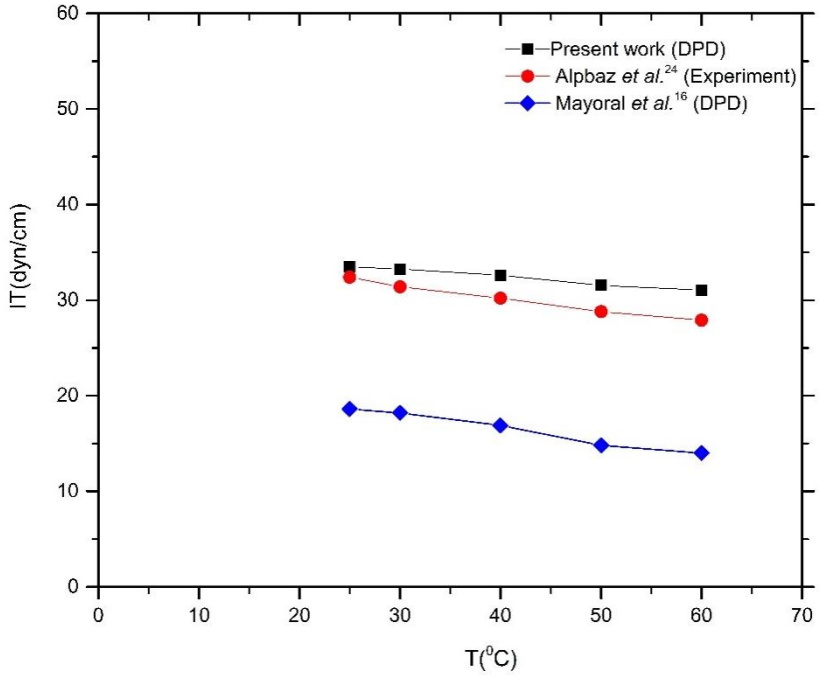


Fig.7.2.3 Temperature dependence of interfacial tension for water-benzene system.

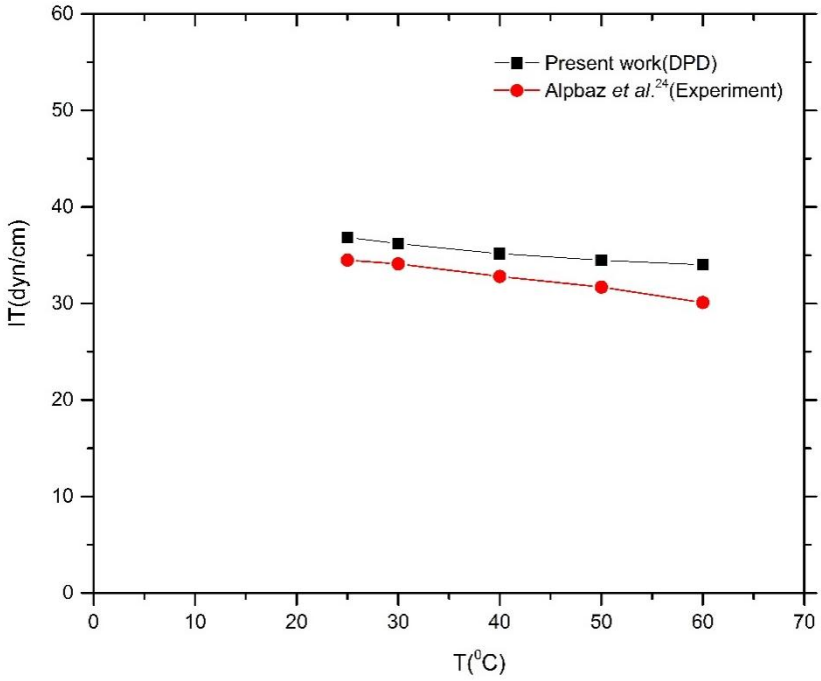


Fig.7.2.4 Temperature dependence of interfacial tension for water-toluene system.

OTHER SYSTEMS:

We have investigated the case of water-cyclohexane system, which has also been studied by Mayoral *et al*. [16] 3and the comparison of both the results with experiments is shown in Figure 7.2.5. It can be observed that results of present study are more close to the experimental data whereas Mayoral and co-workers [16] have only matched the slope. In order to test the range of applicability of our present formalism, we wanted to simulate different kinds of systems. But the lack of experimental values of interfacial tension limits the number of cases. However, we did try for one non-water system i.e. ethylene glycol-tetradecane, for which we found the required experimental values and the comparison is presented in Fig. 7.2.6. It can be observed that there is a slight increase in the value of interfacial tension with temperature in the experiments as reported by Inaba *et al*.[23] The slight increase in the experimental values may be within the experimental error and interfacial tension of this system can be considered as temperature independent.

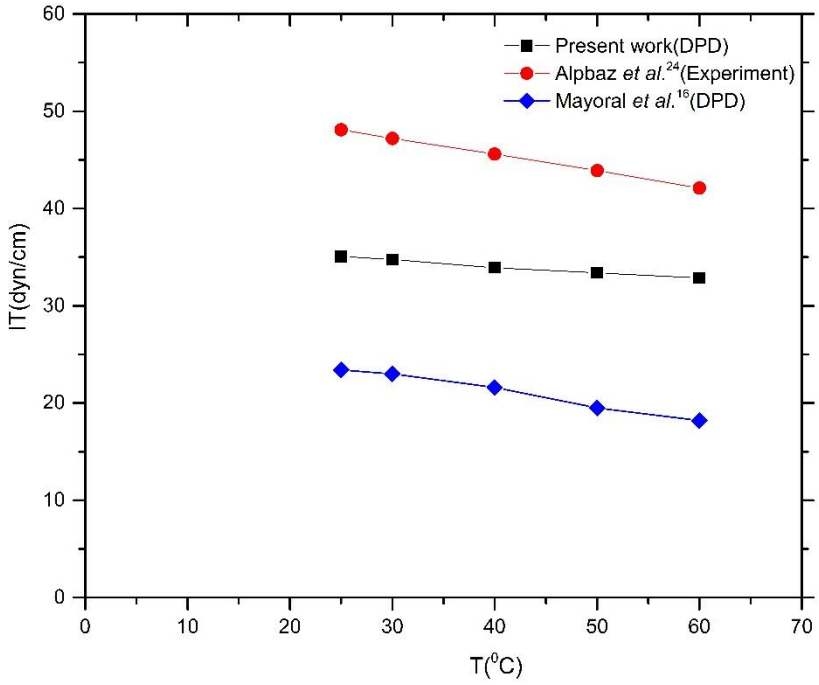


Fig.7.2.5 Temperature dependence of interfacial tension for water-cyclohexane system.

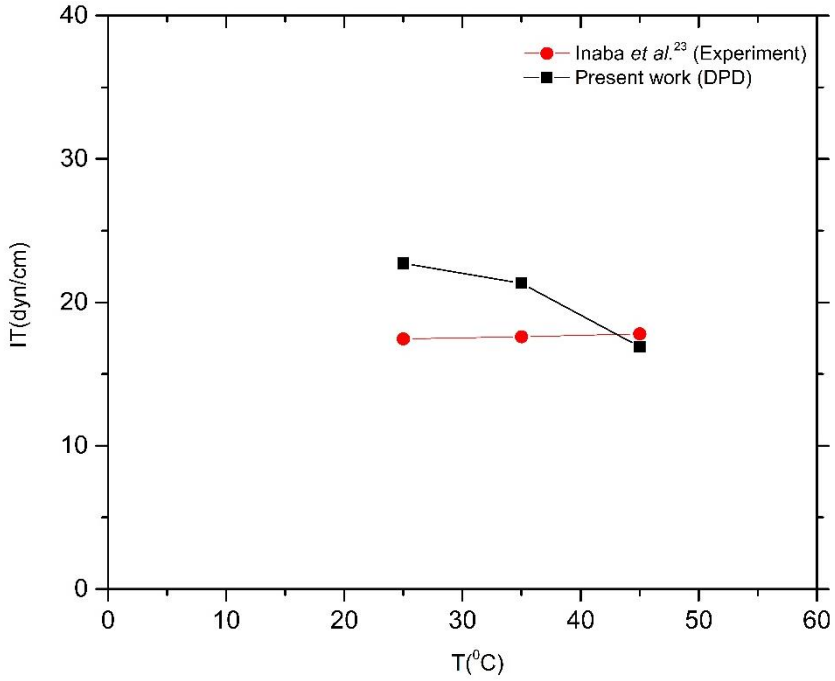


Fig.7.2.6 Temperature dependence of interfacial tension for ethylene glycol-tetra decane system.

For each of the cases studied, the values of the intercept and the slope of a best fitted straight line are shown in Table II and comparisons are made with earlier experimental and DPD results. For water-heptane system, it can be seen that the reported slope is different in two experimental studies [24,25] and our results are more close to the more recent result reported by Zeppieri et al [25]. In case of water-octane system, both the intercept and slope are in good agreement with those of experiment.

Table 7.2.2 Temperature Dependence of systems

System	Experiment	DPD simulation (Mayoral et al.)	DPD simulations (present work)
Water-heptane	σ= 52.7-0.171T σ= 52.9-0.089T		σ= 48.45-0.103T
Water-octane	σ= 53.22-0.084T		σ= 53.12-0.102T
Water-benzene	σ=36.0-0.139T	σ=(22.4±0.3)-(0.147±0.007)T	σ=35.39-0.073T
Water-toluene	σ=37.7-0.123T		σ=38.64-0.083T
Water-cyclohexane	σ=52-0.161T	σ=(27.76±0.3)-(0.161±0.005)T	σ=36.62-0.064T
Ethyleneglycol-tetradecane	σ=17+0.017T		σ=30.5-0.291T

7.2.2 By calculating DPD mutual interaction parameter through Flory-Huggins parameter

By following Goel et.al [17] which calculates DPD parameter from solubility parameter we were able to match the accurate values of interfacial tension but not the slope so we calculated DPD interaction parameter through Flory-Huggins parameter and predicted the interfacial tension Flory-Huggins parameter will vary with temperature. Fig 7.2.7 shows the variation F-H parameter with temperature for water-heptane system.

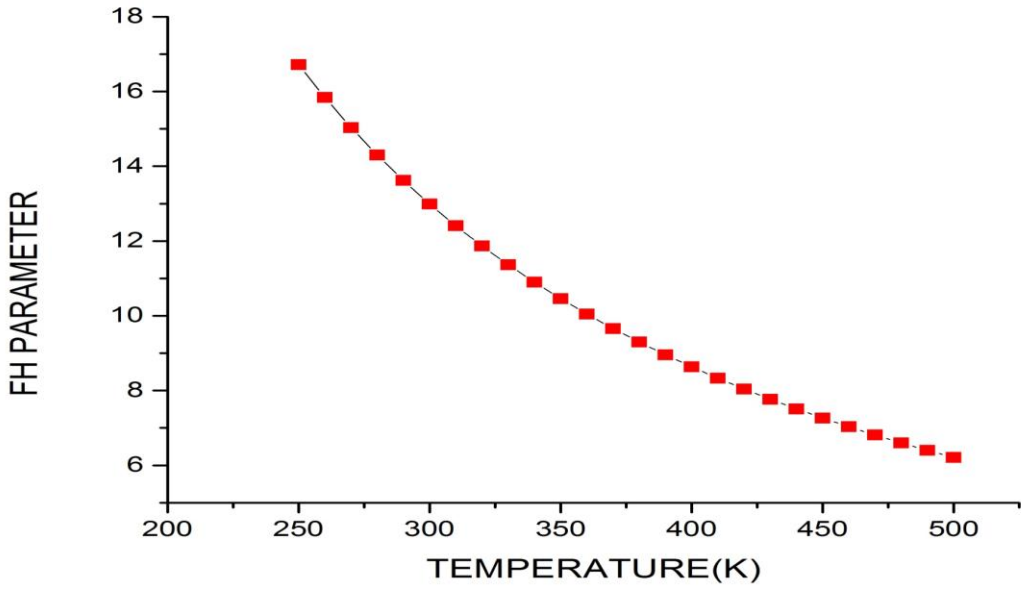


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Fig 7.2.7 variation F-H parameter with temperature for water-heptane system

Fig 7.2.8 and 7.2.9 shows the comparison of interfacial tension predicted for water-heptane and water-octane by both methods.

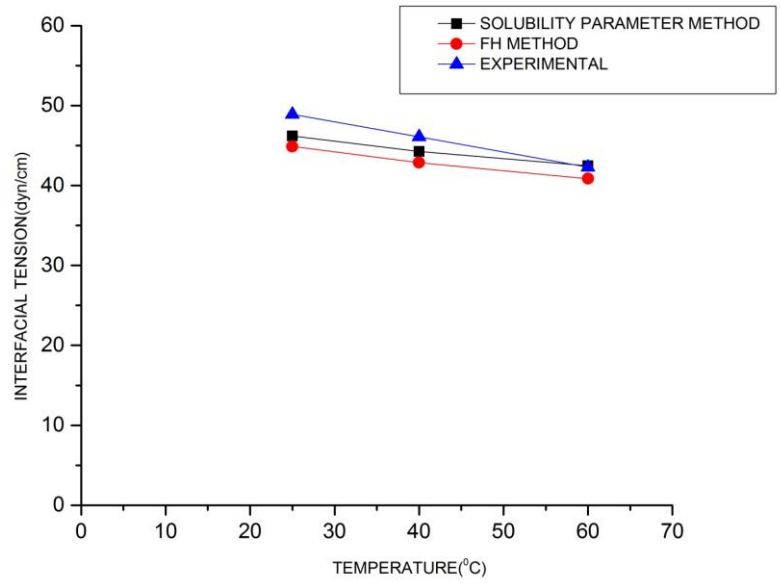

Fig 7.2.8 Water- Heptane System FH Method

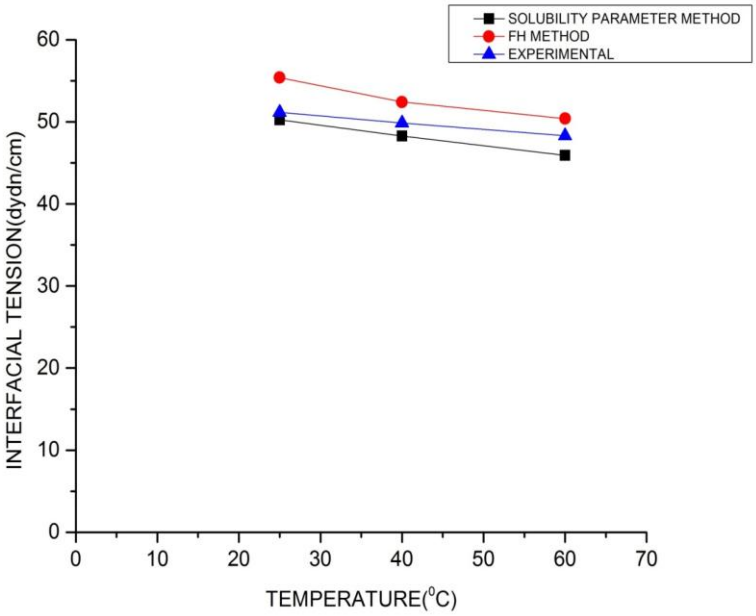

Fig 7.2.9 Water- Octane System FH Method

Calculating interaction parameter using solubility parameter is more accurate than using Flory-Huggins method. But for the case of water- heptanes system slope can be slightly modified by using FH method.

For the case of other liquid systems like Water- Benzene system the FH parameter method is not accurate. Fig 7.2.9 shows the case of Water-Benzene system.

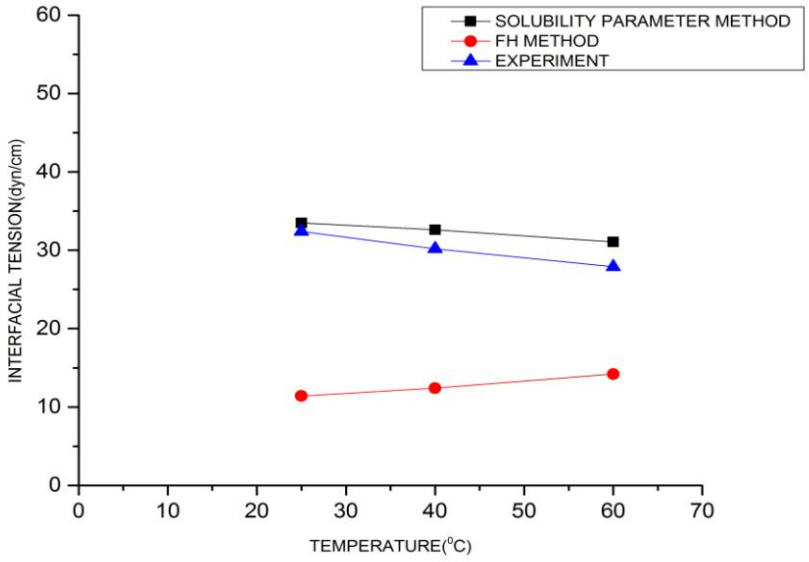

Fig.7.2.10 Water-Benzene System FH Method

7.3 Mutual Diffusion coefficient prediction

Mutual diffusion coefficient is predicted by using both Molecular Dynamics and DPD. Molecular Dynamics simulation will give a good result for diffusion coefficient. Whereas DPD fails to predict diffusivity exactly. Table 7.3.1 and 7.3.2 shows the comparison of diffusion coefficients of benzene-cyclo hexane system for different compositions by using both MD and DPD and compared with experimental result [30].

Table 7.3.1 Diffusion coefficients of benzene-cyclohexane system

MOLE FRACTION OF CYCLO HEXANE	MS DIFFUSIVITY*10^9(m^2/s)	THERMODYNAMIC FACTOR	FICKS DIFFUSIVITY *10^9(m^2/s)	EXPT*10^9 (m^2/s)	% ERROR	STANDARAD DEVIATION
0.2	2.06	0.88	1.81	1.9	4.7	3.8
0.4	1.8	0.87	1.57	1.8	10.5	2.92
0.6	1.9	0.857	1.63	1.7	4.1	3.14
0.8	1.9	0.84	1.62	1.8	10	3.23

Table 7.3.2 Diffusion coefficients using DPD

MOLE FRACTION OF CYCLO HEXANE	MD DIFFUSIVITY*10^9(m^2/s)	DPD DIFFUSIVITY*10^8(m^2/s)	EXPT. *10^9(m^2/s)
0.2	1.81	2.22	1.9
0.4	1.57	2.04	1.8
0.6	1.63	2.2	1.7
0.8	1.62	2.1	1.8

7.4 Properties of individual components

Table 7.4.1 shows the properties of individual components such as density, isothermal compressibility, and solubility parameters of an individual component taken from various references [31-35] .

Component	Density (g/cm^3)	Molecular volume ($A°^3$)	Isothermal Compressibility ($*10^{-10}$ Pa) (Temp)	Solubility Parameter $(J/cm^3)^{1/2}$
Water	1	30	4.59	47.9
Formamide	1.134	66	4.11	36.65
Pentane	0.626	191.39	21.8	14.4
Heptane	0.6795	244.87	14.4	15.2
Octane	0.703	269.82	12.8	15.4
Nonane	0.718	296.4	11.8	15.6
DMSO	1.10	117.94	5.25	26.7
Dodecane	0.750	378	9.88	15.9
Decane	0.730	323.62	10.9	15.7
Hexane	0.650	218	16.8	14.9
Benzene	0.876	148	9.66	18.41
Glycerol	1.26	121.24	2.19	34.12
o xylene	0.88	200.34	8.11	18
m xylene	0.86	205	8.62	17.9
p xylene	0.86	205	8.59	17.9
Ethyl benzene	0.866	203.46	8.65	17.9
Toluene	0.866	176.68	9.12	18.3
Bromo benzene	1.495	174.38	6.68 (20°C)	19.94
Iodo Benzene	1.831	185.02	5.82	20.45
Chloroform	1.483	133.67	10.30 (20°C)	18.9
Ethylene glycol	1.11	92.5	3.40	33.70
Undecane	0.740	350.7	10.30	15.8
Tridecane	0.756	404.8	9.48	16.0
Chlorobenzene	1.10	112.56	7.71	19.61

The values of density, isothermal compressibility, solubility parameter and molar volume of pure components from literatures [36-40] used for finding the interaction parameters for temperature dependence of interfacial tension are listed in Table 7.4.2

Table 7.4.2 Properties of components at different temperatures

Component	Temperature (K)	Density (g/cm^3)	Isothermal Compressibility ($*10^{-10}$ Pa)	Solubility Parameter $(J/cm^3)^{1/2}$	Molar Volume ($A°^3$)
Water	298	0.997	4.59	46.84	30.8
	313	0.992	4.42	46.06	31.2
	333	0.983	4.45	44.88	31.69
Benzene	298	0.876	9.66	19.24	145.77
	313	0.856	10.9	18.78	148.48
	333	0.834	12.8	18.12	152.74
Toluene	298	0.861	9.11	18.3	177.32
	313	0.847	10.2	18.0	180.68
	333	0.828	11.8	17.4	184.29
Heptane	298	0.679	14.4	15.3	244.87
	313	0.666	16.4	14.96	249.72
	333	0.649	19.6	14.5	256.18
Octane	298	0.698	12.8	15.5	271.59
	313	0.686	14.5	15.19	276.29

	333	0.669	17.1	14.7	283.33
Cyclohexane	298	0.773	11.2	16.82	181.27
	313	0.759	12.8	16.35	184.54
	333	0.740	15.2	15.96	188.1
Ethylene Glycol	298	1.11	3.61	33.7*	92.5
	308	1.105	3.74	31.89*	93.1
	318	1.1	3.92	30.08*	93.6
Tetradecane	298	0.759	9.13	15.8	433.12
	308	0.752	9.73	15.6	437.15
	318	0.745	10.4	15.39	441.2

* properties found by using molecular dynamics

Chapter 8

Conclusions

In this study, we suggested an a combine method of Groot et.al and Travis et.al to find the DPD interaction parameter. The assumption of equal self-conservative repulsive parameters $a_{ii}=a_{jj}$ is not used and we calculated them individually .With this method We have validated interfacial tension for large number of immiscible and partially miscible systems. This method works nicely for the prediction of temperature dependence of interfacial tension. We have studied six different types of system for temperature dependence. We tried to predict the temperature dependence more accurately using FH parameter and found out that for some systems it is giving better results but in general Goel et.al method will give a nice prediction for interfacial tension for a variety of systems.

Chapter 9

Scientific Contribution

Journals

Estimation of interfacial tension for immiscible and partially miscible liquid systems by Dissipative Particle Dynamics. Himanshu Goel, Rakesh Chandran P, Kishalay Mitra, Saptarshi Majumdar, Partha Ray, Chemical Physics Letters 600 (2014) 62–67

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