



Molecular dynamics study of 2,2'-difurylmethane with n-propanol and n-butanol binary liquid mixtures

by

Otsile William Kgagodi

BSc General (Chemistry & Computer Science) (University of Botswana)

Department of Chemical and Forensic Sciences

College of Science

Botswana International University of Science and Technology

otsile.kgagodi@studentmail.biust.ac.bw, (+267) 71685697

A dissertation Submitted to the College of Science in Partial Fulfilment of the
Requirements for the Award of the Degree of Master of Science in Physical Chemistry

Supervisor: Dr. Foster Mbaiwa

Department of Chemical and Forensic Sciences

College of Science

mbaiwaf@biust.ac.bw

Signature:  Date: 21/07/2017

JULY, 2017

Declaration

I, Otsile William Kgagodi, declare that this dissertation is my original own work and that it has not been presented and will not be presented to any other university for a similar or any other degree award.

Signature: _____



Date: 21/07/2017

Copyright
by
Otsile William Kgagodi
2017

This dissertation is copyright material protected under the Berne Convention, the Copyright Act of 1999 and other international and national enactments, in that behalf, on intellectual property. It must not be reproduced by any means, in full or in part, except for short extracts in fair dealing; for researcher private study, critical scholarly review or discourse with an acknowledgement, without the written permission of the office of the Provost, on behalf of both the author and the Botswana International University of Science and Technology (BIUST).

© 2017 BIUST. All rights reserved

Certification

The undersigned certifies that he/she has read and hereby recommends for acceptance by the College of Science a dissertation/thesis titled: **Molecular dynamics study of 2,2'-difurylmethane with *n*-propanol and *n*-butanol binary liquid mixtures**, in fulfilment of the requirements for the degree of Master of Science in *Physical Chemistry* of the BIUST.

Dr. Foster Mbaiwa



(Supervisor)

Date: 21/07/2017

Acknowledgements

I would like to express my sincere gratitude to my advisor Dr. Foster Mbaiwa for the guidance, patience and advices he has given me during this work. His support and belief in me, kept me going where hope for success would have been easily lost. His knowledge, understanding and experience in the field of computational chemistry played a key role in the success of this dissertation.

I am grateful for the Financial support from the Botswana International University of Science and Technology (BIUST) in the form of scholarship, stipend etc.

I appreciate the love and support from my colleagues Kgosietsile Tshabang, Hawa Mukami, Obusitwe Makuku, Tumelo Tabane, Morlu Stevens and Nicholas Sehube. Our time together has been great.

I will forever be thankful to those who encouraged me to pursue and give it my all towards the completion of this dissertation: my family, my friends and most especially Ms. Nonfo S. Seope for generally supporting me with everything.

Sometimes I just look up (happy or not), smile and say, “I know that was you, God! Thanks!”

Dedication

This dissertation is dedicated to the late Daniel Kgagodi (*mi padre*) who has always supported and encouraged me to set higher targets, your memory lift my gaze and fills my heart.

Contents

Declaration	i
Certification.....	iii
Acknowledgements	iv
Dedication	v
List of Tables.....	ix
List of Figures	x
Abstract	xiv
1 Introduction.....	1
1.1 Liquid mixtures	1
1.2 Research problems and aims	3
1.2.1 Experimental studies	4
1.2.2 Simulation Studies	6
1.2.3 Specific aims and justification	8
1.3 Overview of dissertation	9
2 Computational Chemistry Methods	10
2.1 Introduction	10
2.2 Molecular dynamics	12
2.2.1 Force field in Molecular Dynamics	12
a. Bonded interactions	13
i. Bond stretching	13
ii. Valence angle bending	14
iii. Dihedral angle potential	14

b.	Non-bonded interactions.....	15
i.	Lennard-Jones interactions.....	15
ii.	Electrostatic interactions	16
2.2.2	Steps in Molecular Dynamics	17
2.2.3	Initial configuration of bulk systems	18
2.2.4	Periodic boundary conditions.....	21
2.2.5	Updating the initial configuration	22
2.2.6	Thermodynamic ensembles.....	22
a.	Micro-canonical ensemble (NVE).....	23
b.	Canonical ensemble (NVT)	23
c.	Isothermal–isobaric (NPT) ensemble	23
2.2.7	Temperature and pressure coupling	23
3	CASE STUDY 1: Molecular dynamics simulation study of <i>n</i> -propanol and 2,2'-difurylmethane binary liquid mixtures.....	25
	Introduction	25
3.1	Computational method	25
3.2	Results and Discussions	28
3.2.1	System equilibration	28
3.2.2	Thermodynamic properties	30
3.2.3	Structure of <i>n</i> -propanol/DFM binary mixture.....	33
a.	Site-site radial distribution functions.....	33
b.	Centre of mass radial distribution functions.....	38
c.	Coordination shell analysis.....	40
d.	Conformational analysis	44
3.3	Conclusions	48

4	CASE STUDY 2: Comparative molecular dynamics simulation study of 2,2'-difurylmethane with <i>n</i> -propanol and <i>n</i> -butanol liquid mixtures	50
	Introduction	50
4.1	Simulation details	51
4.2	Results and Discussions	51
4.2.1	Thermodynamic properties	52
4.2.2	Structural properties	54
a.	Atom-atom radial distributions	54
b.	Molecule-molecule center of mass radial distributions	57
c.	Dihedral angle distributions	64
4.3	Conclusions	67
5	Summary and conclusions	68
5.1	Possible future experiments	69
	References	70
	Appendices:	80
	Appendix A. Published paper(s)	80
	Appendix B. Single molecule coordinate files (.XYZ)	81

List of Tables

Table 3.1 Atomic charges and Lennard-Jones parameters for DFM and n-propanol. For DFM the atoms closest to the bridging carbon are regarded as inner atoms.	27
Table 3.2 Calculated and experimental (in parenthesis) thermodynamic properties for pure systems of n-propanol and DFM, density (ρ), enthalpy of vaporization (ΔH_{vap}), isothermal compressibility (kT) and molar volume (V_m).	30
Table 3.3 Coordination numbers calculated from molecule-molecule center of mass radial distribution functions of DFM/n-propanol mixtures and pure systems.	41
Table 3.4 Coordination numbers for site-site radial distribution functions of Difurylmethane/n-propanol mixtures and pure systems.	43
Table 3.5 The main structural differences of the five conformers of n-propanol	45
Table 4.1 Coordination numbers calculated from molecule-molecule center of mass radial distribution functions of DFM/n-butanol mixtures and pure systems. For comparison with DFM/n-propanol mixtures, see Table 3.3.	61
Table 4.2 Naming conventions for the conformers in Figures 4.13 and 4.14.....	67

List of Figures

Figure 1.1 Structure of 2,2'-difurylmethane.....	3
Figure 1.2 A plot of excess molar volumes for DFM with n-alkanols mixtures adapted from [9].	5
Figure 2.1 The connection between experiment, theory and computer simulations (adapted from[59]).....	11
Figure 2.2 Schematic view of (a) bond stretching, (b) valence angle bending and (c) dihedral angle interactions.	14
Figure 2.3 Non-bonded atoms separated by a defined distance.....	15
Figure 2.4 Lennard-Jones potential energy diagram showing the ε and σ parameters.....	16
Figure 2.5 Molecular dynamics flow chart	18
Figure 2.6 Structure of DFM with bond lengths at local energy minimum.....	19
Figure 2.7 Iterative process of geometry optimization	20
Figure 2.8 Initial configuration generated by packmol software and viewed using VMD.	20
Figure 2.9 Two-dimensional representation of periodic boundary condition.....	21
Figure 3.1 Molecular structures of DFM (left) and n-propanol (right).....	26
Figure 3.2 DFM/n-propanol (a) pressure and (b) temperature profiles as function of time for 0.5 mole fraction of DFM	27
Figure 3.3 Configurational energy profiles for pure n-propanol, DFM and mixed systems	29
Figure 3.4 System volume profiles for pure n-propanol, DFM and mixed systems.....	29
Figure 3.5 Calculated values for the densities of DFM/n-propanol mixtures as a function of DFM mole fraction (open red circles) and experimental densities[9] (closed black squares).	31

Figure 3.6 Calculated (open red circles) and experimental[9] (closed black squares) values for the excess molar volumes for DFM/ n-propanol mixtures as a function of DFM mole fraction.	32
Figure 3.7 Intermolecular Radial distribution functions for different sites (a) oxygen (OA)-hydrogen (HA) [n-propanol/n-propanol] (b) oxygen (OA)-oxygen (OA) [n-propanol/n-propanol] (c) oxygen (OF)-oxygen (OF) [DFM/DFM]	34
Figure 3.8 HA-OF Radial distribution functions for different DFM mole fractions.	35
Figure 3.9 HF/6-31G (d) lowest energy optimized geometry of DFM dimer.	36
Figure 3.10 HF/6-31G (d) lowest energy optimized geometry of DFM-propanol dimer...37	
Figure 3.11 Variation of the spatial distribution functions (SDFs) with DFM mole fraction. Red surfaces denote regions populated by oxygen atoms of DFM molecules. The isovalues were set to 0.88 for all mole fractions.....	38
Figure 3.12 Center of mass to center of mass radial distribution functions for different DFM mole fractions; (a) n-propanol/n-propanol (b) DFM/n-propanol and (c) DFM/DFM	39
Figure 3.13 Ratio of n-propanol molecules replacing each DFM molecule around DFM (black line with closed square symbols) and ratio of DFM molecules replacing each n-propanol molecule around n-propanol (red dashed line with open circle symbols)	42
Figure 3.14 Excess local mole fraction of n-propanol as a function of DFM mole fraction	44
Figure 3.15 Geometry structures of the five conformers: Tt, Tg, Gt, Gg ⁺ and Gg ⁻ of n-propanol.....	45
Figure 3.16 Dihedral angle distributions for C-C-C-O, C-C-O-H and H-C-O-H dihedral angles for n-propanol (where T represents Trans conformer and g ⁺ and g ⁻ represent gauche conformers of 60 ⁰ and -60 ⁰ respectively)	47
Figure 3.17 Dihedral angle distributions for H-C-C-H dihedral angle for n-propanol. Peaks offset by 50 units for clarity.	48
Figure 4.1 Comparison of experimental excess molar volumes for DFM/n-propanol and DFM/ n-butanol mixtures[9].....	50

Figure 4.2 (a) Pressure, (b) temperature, (c) configurational energy and (d) volume profiles for DFM/n-butanol ($x_1 = 0.5$) as a function of time.....	52
Figure 4.3 Calculated values (open blue circles) and experimental values[9] (closed black squares) for (a) the densities and (b) excess molar volumes of DFM/n-butanol mixtures as a function of DFM mole fraction.	53
Figure 4.4 Comparison between experimental and simulated excess molar volumes for DFM/n-propanol and DFM/n-butanol mixtures	54
Figure 4.5 Selected site to site radial distribution functions for n-butanol/n-butanol, n-propanol/n-propanol and DFM/DFM as well as DFM/alcohol calculated for DFM mole fractions of $x_1 = 0.1$ and 0.9	55
Figure 4.6 HF/6-31G (d) lowest energy optimized geometry of DFM/n-butanol dimer.	57
Figure 4.7 Center of mass radial distribution functions calculated for $x_1 = 0.1$ and 0.9 for (a) n-propanol/n-propanol and n-butanol/n-butanol (b) DFM-DFM in n-propanol and n-butanol environments and (c) DFM/n-propanol and DFM/n-butanol	59
Figure 4.8 HF/6-31G (d) lowest energy optimized geometry of DFM dimer showing the center of mass to center of mass interactions.....	60
Figure 4.9 The ratio of n-butanol (in green) and n-propanol (in black) molecules replacing each DFM molecule around DFM and the ratio of DFM molecules replacing each n-propanol (in red) and n-butanol (in blue) molecule around n-propanol (black line with closed square symbols).....	62
Figure 4.10 Excess local mole fractions of n-propanol (closed black squares) and n-butanol (red open circle) as a function of DFM mole fraction	63
Figure 4.11 Comparisons between dihedral angle distributions (C-C-C-O and C-C-O-H) for n-propanol and n-butanol.	64
Figure 4.12 C-C-C-C dihedral angle distributions for n-butanol for $x_1 = 0.1$ and 0.9	65
Figure 4.13 Images showing the most probable conformers of n-propanol for $x_1 = 0.9$..	66
Figure 4.14 Images depicting the most probable conformers of n-butanol for $x_1 = 0.9$...	66

Figure A.0.1 Excerpt from a published paper used with permission from © 2016 Elsevier
B.V. All rights reserved. 80

Abstract

Liquid-liquid mixtures are ubiquitous in many natural and industrial processes. Their excess thermodynamic properties are governed by the intermolecular interactions. As such, experimental techniques such as neutron and x-ray diffractions, or computational chemistry methods can be used to probe structure at atomic level. However, they are rather scarce and expensive. Our interest is on the binary liquid mixtures involving 2,2'-difurylmethane (DFM) and *n*-alcohol, which have been studied experimentally. For all the efforts in understanding these mixtures, there is still a need to probe molecular structure at microscopic level. Therefore, the aim of this dissertation is to gain information on the molecular level structure of DFM and *n*-propanol or *n*-butanol binary mixtures using computational chemistry methods. Molecular dynamics simulations have been performed using optimized potentials for liquid simulations all atom (OPLS AA) force field to study the thermodynamic properties and structural aspects of DFM with *n*-propanol and *n*-butanol binary mixtures. The results indicate that for both mixtures the computed and experimental thermodynamic properties are in close agreement. The calculated excess molar volumes show negative and positive deviations in lower and higher DFM mole fractions, respectively. DFM and *n*-propanol excess molar volumes assume the most negative values and tend to positive values at higher DFM mole fractions than DFM and *n*-butanol mixtures, which is in accord with the experimental trends. Radial distribution function and *ab initio* calculations indicate the presence of hydrogen bonding between one of the DFM oxygen atoms and acidic hydrogen of *n*-propanol or *n*-butanol. For both mixtures, the calculated coordination numbers reveal that there is better mixing in lower DFM mole fractions. However, DFM and *n*-propanol mixtures show better mixing than DFM and *n*-butanol. The dihedral angle distributions show evidence of hydrogen bonding as well as the effect of the alkyl chain. *n*-butanol seems to have an enhanced hydrogen bonding than *n*-propanol.

Chapter I

1 Introduction

1.1 Liquid mixtures

Liquid-liquid mixtures are a combination of two or more liquids that can be either heterogeneous or homogeneous. Heterogeneous liquid mixtures have their components and properties non-uniformly distributed throughout. Homogeneous liquid mixtures on the other hand have uniform distribution of components and properties[1].

A combination of components of like polarity often forms a homogenous mixture while those of unlike polarity form a heterogeneous mixture. Homogeneous liquid mixtures are usually referred to as solutions. Solutions can contain a random homogenous mixture of atoms, ions or molecules. The component in large quantity is referred to as a solvent while the other is a solute. A liquid mixture is called a binary mixture, ternary mixture or quaternary mixture when it contains two, three or four components respectively. Given sufficient time, the components in a homogeneous mixture are able to distribute themselves in a random manner.

In pure form, liquids are characterized by properties that are different from those of mixtures. This is attributed to the interactions occurring between like molecules as well as unlike molecules. As such, liquid mixtures play a significant role in scientifically and industrially important systems such as organic extraction, chemical synthesis, polymer chemistry and many more.

One of the earliest and important forms of chemistry in history is perfumery[2]. A perfume is a mixture of fragrant essential oils and solvents. Perfumes are used every day for personal care purposes, car fragrances, home fragrances and many more. The components responsible for the characteristic scent in a perfume can be synthesized or extracted from natural resources. Fragrances are a major income generator in the industry with applications in cosmetics, personal care, and even the food and beverage industry[2,3]. There are many

types of perfumes and the common ones are formulated with an alcohol-based or oil-based carrier. The carrier is the solvent that is intended to deliver fragrant essential oils (solute) to the skin. It evaporates when applied to the surface and what remain thereafter are the fragrant oils responsible for the particular perfume's characteristic scent. Evaporation, which is the process by which the molecules in liquid form vaporize, often depends on the intermolecular forces. The more the molecules form attractive forces the less the liquid evaporates.

Another interesting form of chemistry involving liquid mixtures is the petroleum industry. A mixture of volatile and inflammable liquid hydrocarbons known as gasoline is one of the most desired products in the petroleum industry. Gasoline is of great importance as a liquid transportation fuel[4]. It is most often produced by fractional distillation of crude oil containing different structures of hydrocarbons, primarily octane[4].

The quality of gasoline is quantified by the octane number. Octane rating or octane number is a measure of the resistance of gasoline and other fuels to detonation in spark ignition internal combustion engines. A fuel containing 100% iso-octane has an octane rating of 100. The higher the octane number, the more compression the fuel can withstand before detonating. Fuels that are less resistant to detonation have an octane rating less than 100. On the other hand, fuels that have more resistance to detonation have octane ratings greater than 100. However, due to the harmful effects of the usual additives tetra-ethyl lead (TEL) and methyl tert-butyl ether (MTBE) as octane enhancers in gasoline, the use of ethanol as an oxygenate and octane enhancer is common in countries like the United States[4,5]. Mixtures of unleaded gasoline and ethanol have higher octane levels, low exhaust emissions and reduce the dependence on oil[6]. However, the mixture composition has to be optimized to avoid changing fuel systems. Low volatility, low heating value and high enthalpy of vaporization of ethanol especially under cold conditions, has led to the preference of 10% anhydrous ethanol and 90 % gasoline by volume in most countries[6,7].

Combinations of various liquids at different compositions exhibit different properties. Therefore, characterizing each mixture component separately and then combining their effects allows the behavior of a mixture composition to be understood.

1.2 Research problems and aims

Our interest is on the study of volumetric properties for binary mixtures involving 2,2'-difurylmethane (DFM) with linear alcohols ($\text{CH}_3(\text{CH}_2)_n\text{OH}$ where $n = 0 - 6$) [8–10]. DFM (Figure 1.1) is a furan derivative that is assumed to exist mainly through dipole-dipole interactions in its pure liquid state[9]. It is used as a readily available replacement for diphenylmethanes in organic synthesis[11]. DFM also forms in significant amounts in the preparation of furfuryl alcohol resins[8]. In the food industry, DFM is of interest since it is present as a natural compound in beverages and food[12].

Linear alcohols consist of non-polar alkyl chain and the polar hydroxyl group. In liquid state, alcohols exist mainly through dipole-dipole interactions including hydrogen bonding, which leads to association[9,13]. This has found alcohols mostly used as solvents largely for organic substances. Essential oils, hydrocarbons, resins, sugars, most vegetable alkaloids, and pharmaceutical drugs such as acetanilide, phenacetin, and phenazone are some of the examples of substances that dissolve in alcohols.

An understanding of molecular interactions or the nature of interactions between DFM + n -alcohol binary mixtures is thus important to both the food industry and in synthesis chemistry. One of the relatively easy ways to study the interactions in liquid mixtures experimentally is via excess molar quantities of mixing such as excess molar volume. For

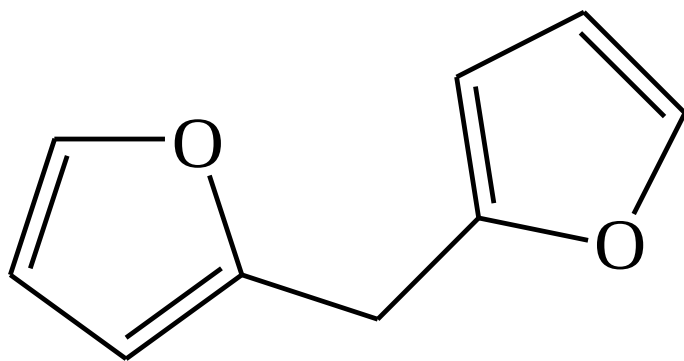


Figure 1.1 Structure of 2,2'-difurylmethane

binary mixtures, volume changes (contractions and expansions) can be obtained by measuring the density of the pure fluids and the density of mixtures at different

compositions. From determined densities, excess molar volumes can be calculated as follows:

$$V_m^e = V_m - V^{id} = \frac{M}{\rho} - \sum \left(\frac{x_i M_i}{\rho_i^*} \right) \quad (1.1)$$

where V_m is the measured molar volume, V^{id} is the ideal molar volume, M is the molar mass of the mixture, ρ is the density of the mixture, and x_i , M_i and ρ_i^* are the mole fraction, the molar mass as well as the density of the pure liquid component i respectively[9].

Excess molar volumes obtained are useful for understanding the interactions between the solute and solvent molecules occurring in the mixtures. For example, a mixture of ethanol and water, which is sometimes used to dissolve fragrance oils in perfumery, has a lower boiling point as compared to both components. If we were to study the volumetric effects of mixing 20 mL of pure ethanol with 20 mL of pure water, we would realize that the results are rather astonishing. The measured final volume of the mixture will not simply be the summation of pure liquid volume contributions. The final volume of the mixture may be more than 40 mL, which is a “positive deviation”, or less than 40 mL, which is a “negative deviation”. These differences in volumes are due to the different nature of intermolecular forces at various compositions. Hence, excess molar volumes are sources of information regarding intermolecular interactions between atomic and molecular species[8–10,14–19]. The dependence on temperature and composition is a strong indicator of significant effects resulting from intermolecular interactions[8,10,17,20–24]. The extent of either positive or negative deviation of excess properties sheds some light on the nature of the interactions involved.

1.2.1 Experimental studies

Mokate and Ddamba have investigated volumetric properties of DFM with methanol in a temperature range of 288.15-308.15K[8] and the volumetric properties of DFM with linear alcohols{C₁-C₆} at 298.15K[9] and later studied the effect of temperature on volumetric properties on these systems at 288.15-308.15K[10].

Their studies show that the alcohol chain lengths affect the magnitude of volume contraction and expansion. Mixtures of DFM and shorter chain *n*-alkanols (methanol and ethanol)

exhibit volume contraction, while mixtures with long chain alkanols (*n*-pentanol and *n*-hexanol) show volume expansion over the entire composition range. Mixtures with intermediate chain alkanols (*n*-propanol and *n*-butanol) display both volume contraction and volume expansion with higher mole fractions of DFM favoring volume expansion. Figure 1.2 shows all deviations for the mixtures studied.

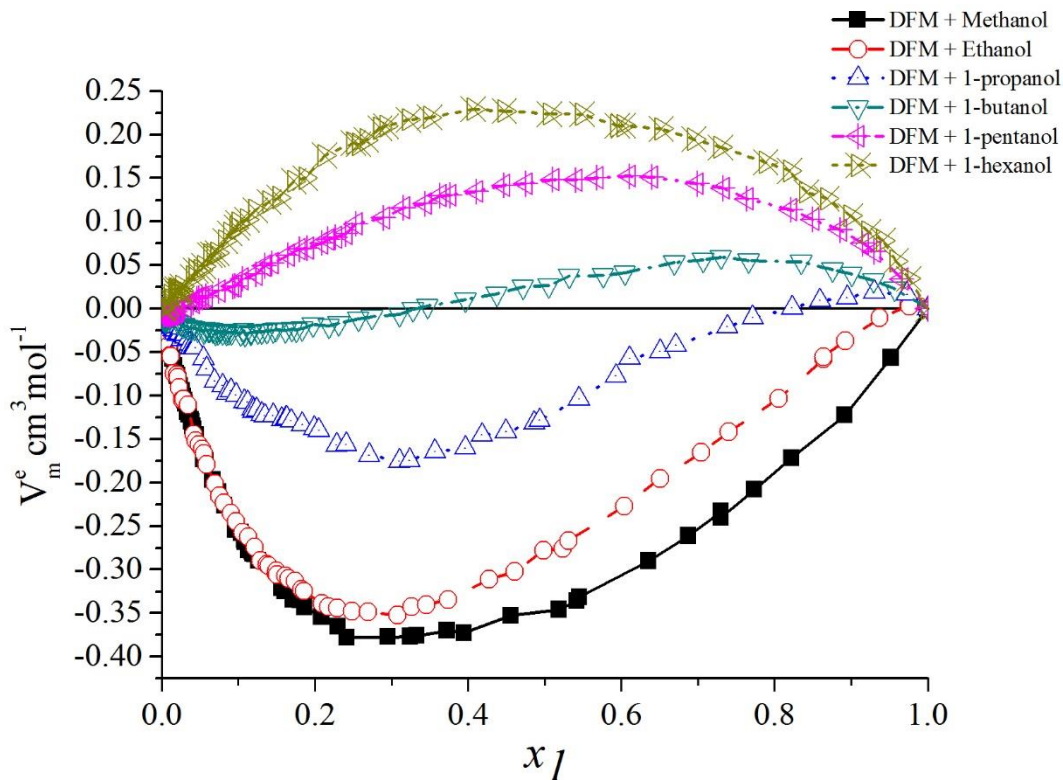


Figure 1.2 A plot of excess molar volumes for DFM with *n*-alkanols mixtures adapted from [9].

A number of experimental studies have been carried out on the volumetric properties of binary mixtures involving *n*-alcohol species. Examples of these include; (ethyl formate + 1-pentanol) system by Ghafeli and Aimas[22], (3-chloroaniline and 1-alkanols(C₆-C₁₀)) system by Rahul *et al*[25], (p-cresol with 1-alkanol(C₃-C₈)) system by Janardhanaiah *et al*[26], (1-alkanols with benzene) system by Sastry *et al*[15], (diethyl sulfoxide with methanol/ethanol) system by Ghazoyan and Markarian[27], (ethyl propionate with 1-pentanol or 1-hexanol) system by Verma *et al*[28], (acrylic esters with 1-hexanol) system by Patil *et al*[29], (dimethylacetamide with methanol) system by Peshwe *et al*[24], (acetonitrile + alcohol) systems by Grguric *et al*[30,31](2-(2-hexyloxyethoxy)ethanol with

n-alkanol) and (alkoxypropanol with *n*-alkanol) systems by Pal and Gaba[17][32], (1-alkanol with tri-*n*-butylamine) system by Oswal and Desai[33].

Amongst these systems, the experimental work performed by Grguric *et al*[30,31] resembles the mixtures involving *n*-propanol or *n*-butanol with DFM. Grguric *et al* studied excess molar volumes for mixtures of methanol or ethanol with acetonitrile by performing density measurements. Methanol with acetonitrile mixtures exhibited volume contractions over the entire composition range. Ethanol with acetonitrile showed volume expansion for lower ethanol mole fraction and volume contraction for higher ethanol mole fraction. The researchers have interpreted the results in terms of specific or non-specific interactions.

Despite considerable efforts to explain the origin of excess properties, there is still a need to probe molecular structure at microscopic level. As such, techniques like neutron and x-ray diffraction have been applied over the years to probe the atomic structure of complex liquid and liquid mixtures[34]. These techniques are suitable as complementary experimental methods to study the intramolecular and intermolecular microscopic structures of liquid mixtures[34–38]. However, they are rather scarce and expensive.

Studies reveal that pure alcohols have received an extensive research on structure using these techniques. Recently, the studies have extended to the binary mixtures involving alcohols and aqueous mixtures[36,39]. Structural information on complex liquids provides the means to characterize inter-atomic correlations. The most probable distances in the event of hydrogen bonding between O-O and O-H correlations, and even the coordination numbers, have been suggested by several authors[37,40].

1.2.2 Simulation Studies

Computational techniques such as molecular dynamics and Monte Carlo simulations can provide insights into the thermodynamic and structural properties of pure liquids and liquid mixtures[41–45]. One of the advantages of these simulation methods is the ability to tune parameters such as size, mass, moment of inertia and interaction potential independently, to understand the mechanisms of thermodynamic and structural properties microscopically. Over the years, the current systems of interest have not been studied theoretically. However,

pure alcohols and furan (which is a moiety of DFM) as well as their aqueous solutions have been investigated by several authors[42,46,47].

In 1984, Jorgensen *et al*[48] generated a set of intermolecular potential functions suitable for computer simulations of organic hydrocarbon fluids by fitting functions directly to experimental thermodynamic and structural data of liquid hydrocarbons. The close agreement of computed data with experimental values has led to extension of their procedures to liquid alcohols[46].

In 1986, Jorgensen[49] carried out Monte Carlo statistical thermodynamics simulations for liquid methanol, ethanol, 1-propanol, 2-propanol, and 2-methyl-2-propanol to study the thermodynamic and structural properties. The results showed great accord with experimental data. The force field (the functional form and parameter set used to define the intramolecular and intermolecular potentials) used by Jorgensen *et al* at the time is now what is known as Optimized Potential For Liquid Simulations-United Atom (OPLS-UA). For OPLS-UA, non-bonded interaction sites for hydrogen attached to heteroatom or carbons in aromatic rings and sites for all non-hydrogen atoms are treated explicitly, making OPLS-UA computationally attractive.

In 1996, Jorgensen *et al*[47] developed and tested the OPLS-all atom (AA) force field on conformational energetics and properties of different organic liquids. For OPLS-AA, all the hydrogen and non-hydrogen sites are explicitly defined. Hence, it is more computationally expensive than OPLS-UA. There is better agreement for OPLS-AA models with experimental results than OPLS-UA as has been reported. Many simulations on the investigations of alcohols using Jorgensen's OPLS have been carried out to study liquid alcohols[16,50–52].

DFM on the other hand has not been studied theoretically. However, furan, which is a moiety of DFM, and its aqueous solutions have been investigated using *ab initio* and force field based calculations[42,53]. In 1998, McDonald and Jorgensen[42] developed OPLS-AA force field for five membered heterocyclic compounds including pyrrole, pyrazole, imidazole, furan, isoxazole, and oxazole. They performed *ab initio* and force field calculations to parameterize the heterocycle compounds, and then carried out Monte Carlo simulations to determine their thermodynamic properties. There was good accord with

experimental data for most compounds, however, discrepancies were observed for oxazole and isoxazole. Nevertheless, OPLS-AA force fields have been applied and reparametrized for different compounds including macrocyclic polyketides and biaryl incorporating heterocycles compounds such as furan[43,54].

Thermodynamic properties of pure and liquid mixtures calculated from simulations are often in good agreement with experimental data[42,46,47]. The agreement justifies the deduction of the structure of liquids from molecular simulations.

1.2.3 Specific aims and justification

This work aims to investigate,

- The excess molar volumes of DFM/*n*-propanol and DFM/*n*-butanol binary mixtures using molecular dynamics simulations
- The effect of DFM mole fractions on *n*-propanol and *n*-butanol local compositions as well as their dihedral angle distributions
- How the local composition of DFM is affected by either *n*-propanol or *n*-butanol for various mole fractions.

Both DFM/*n*-propanol and DFM/*n*-butanol binary mixtures exhibit negative and positive deviations of the excess molar volumes over the whole composition range of DFM mole fractions. However, unlike DFM/*n*-propanol mixture, the DFM/*n*-butanol mixtures show mostly positive deviations with negative deviations mainly occurring at low DFM mole fractions (see Figure 1.2). The reason for the differences in the extent of volume changes may be tracked back to the dominance between strong intermolecular attractive and repulsive forces. The observed similarities in the trends of experimentally measured excess molar volumes mean that in the respective mixtures, contributions to the overall structure are somewhat similar. However, DFM/*n*-butanol system is expected to be more structured due to additional methyl groups. It is for this reason that an investigation on DFM/*n*-butanol mixture be performed and compared with DFM/*n*-propanol systems. Both *n*-propanol and *n*-butanol molecules in pure liquids, form molecular clusters through strong hydrogen

bonding, however, the presence of an extra $-\text{CH}_2$ group in *n*-butanol presents the possibility of more conformers than *n*-propanol.

We argue that the intermolecular interactions between like or unlike species in these mixtures are governed by shape, size and structural arrangements of molecules. For this reason, it is also worth taking a closer look at *n*-propanol and *n*-butanol coordination numbers and dihedral angle distributions to ascertain which is the most stable conformer for various mole fraction of DFM typically dominates.

1.3 Overview of dissertation

In this dissertation, we aim to combine *ab initio* calculations and molecular dynamics simulations to investigate thermodynamic properties and the structural aspects of [2,2'-difurylmethane (DFM) + (*n*-propanol or *n*-butanol)] binary mixtures. The focus on these mixtures is influenced by the fact that, in the binary liquid mixtures of DFM and homologous series of *n*-alcohol ($\text{C}_1\text{-C}_6$), only *n*-propanol and *n*-butanol show both negative and positive deviations over the entire composition range.

The next Chapter deals with the details of computational methods including the force field and molecular dynamics in relation to this work. For the force fields, we give details based on the OPLS AA force field. In Chapter III, molecular dynamics is performed for pure and mixed systems of DFM and *n*-propanol. Chapter III presents the thermodynamic properties and structural aspects of DFM and *n*-propanol systems. Chapter IV compares the thermodynamic properties and structural aspects of DFM/*n*-butanol with DFM/*n*-propanol mixtures. The summary of the findings from this dissertation and possible future experiments are given in Chapter V.

Chapter II

2 Computational Chemistry Methods

2.1 Introduction

A general description of the methods applied will be given in this Chapter. Detailed methods of individual computational experiments will be presented in the relevant Chapters. Chemistry is an experimental science that aims to study structure, composition and properties of matter. Computational chemistry is one area of research in chemistry that has emerged and can be used as a complementary method to experiment with the benefit of predicting properties that are difficult or impossible to measure experimentally[55,56]. It uses computational techniques to model the real-world particles (atoms, ions or molecules) in the form of mathematical approximations based on *quantum* and *classical mechanics*[57,58].

Quantum chemistry deals with the behavior of molecules as well as the electrons, subatomic particles and nucleus. It is basically a collection of methods that solve the *Schrodinger equation* which says, given the number and type of particles in the system and knowing the way they interact, the total energy of the system can be obtained by solving a quite complicated partial differential equation[57]. These methods include *ab initio* calculations such as Hartree-Fock (HF), Müller-Plesset perturbation theory (MP) and configuration interaction calculations (CI) and semi-empirical calculations like complete neglect of differential overlap (CNDO), modified intermediate neglect of differential overlap (MINDO) and Pariser-Parr-Pople method (PPP)[56].

Classical mechanics describe the motion of particles using Newton's laws of motion to determine past and future particle positions under the influence of a system of forces[58]. Nuclei are treated as point particles and the electrons are approximated as one potential energy surface. Computationally, classical mechanics methods are less expensive than quantum chemistry methods; however, the latter have higher accuracy.

Computational chemistry simulations serve as a valuable bridge between actual experiment and theory (Figure 2.1) [59]. Real experiments can be performed to obtain experimental measurements, and then models are developed to mimic the system of interest. Given a specific model, the microscopic behavior of molecular motions of system components can be mimicked using mathematical approximations and performing simulations. The exact results from simulations for a specific model are then compared with results from theory to determine the accuracy and validity of the approximations in the theory. The accuracy of a given model can be checked by comparing experimental and simulation results. An accurate model is capable of reproducing properties of a class of compounds. Therefore, researchers can predict properties of new compounds before actual synthesis or simulate conditions difficult to achieve experimentally[59].

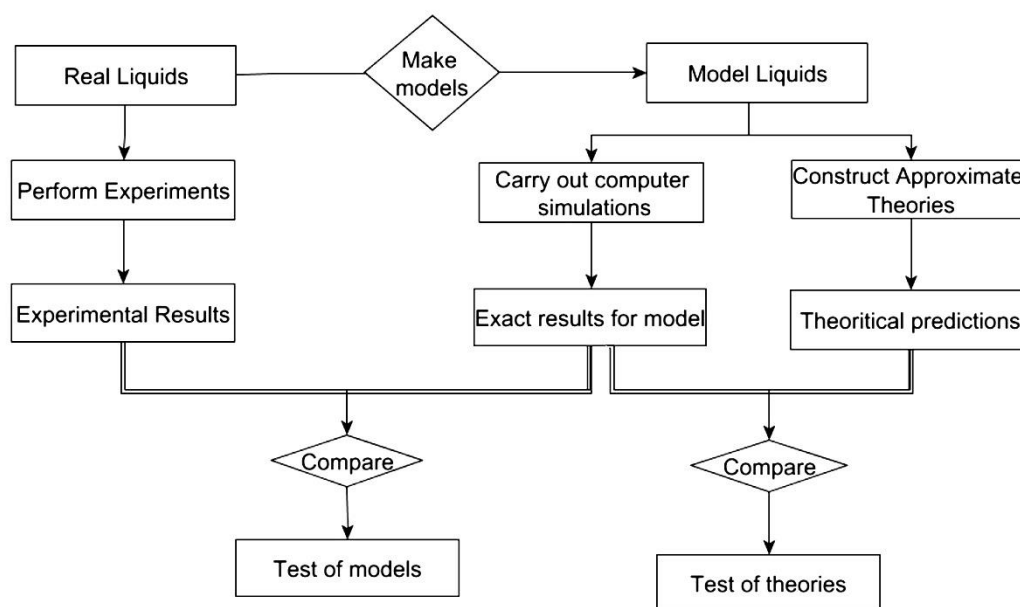


Figure 2.1 The connection between experiment, theory and computer simulations (adapted from[59])

In computational chemistry, the two main methods used at atomic level modeling (no explicit treatment of electrons) are molecular dynamics and Monte Carlo[57,60]. Simulations of liquid mixtures using these techniques began several decades ago and are widely used to investigate structure and dynamics of fluids for different conditions[59]. Monte Carlo simulations generate molecular configurations by making random changes to the positions of the atoms in a system whereas molecular dynamics simulations solve

Newton's equations of motion for a system of N interacting particles, by a stepwise algorithm.

2.2 Molecular dynamics

Molecular Dynamics simulations mimic how atoms and molecules move in time while rotating and colliding with each other by numerically integrating Newton's equations of motion. As such, momentum, position, and orientation of each particle with respect to time can be described[55,59]. The force experienced by an atom i is given by

$$\mathbf{F}_i = m_i \frac{\partial^2 \mathbf{r}_i}{\partial t^2} \quad (2.1)$$

where $\mathbf{F}_i$, is the force acting on atom i , m_i and $\mathbf{r}_i$ are the mass and position vector of atom i .

The basic principle to molecular dynamics simulations is the representation of the energy (potential) of components as a function of their atomic coordinates. At equilibrium, low energy state regions of potential energy function (U) are expected to be populated. The forces on individual atoms are related to the gradient (equation 2.2) of this function, hence the term "force field"[59].

$$\mathbf{F}_i = -\frac{\partial U}{\partial \mathbf{r}_i} \quad (2.2)$$

The accuracy of molecular dynamics depends mainly on the choice of *force field* employed amongst other parameters such as timesteps, Δt , as well as temperature and pressure relaxation times. Thermodynamic properties at given pressure and temperature can be obtained once proper potential function and parameters for atoms composing molecules are provided.

2.2.1 Force field in Molecular Dynamics

Combinations of mathematical equations and concomitant parameters used to evaluate the energy of molecules as a function of atomic coordinates is referred to as force field[59]. Force fields of inorganic or organic compounds require a physical description (equation 2.3) of potentials (U_{tot}) which describes bonded and non-bonded interactions,

$$U_{tot} = U_{bonded} + U_{non-bonded} \quad (2.3)$$

where U_{bonded} is the interaction energy due to bond stretching, bond angle bending and torsions whereas $U_{non-bonded}$ is the interaction energy between two distinct atoms due to electrostatic and coulombic forces. In this work OPLS-AA [42,47,54] force field is employed, and therefore the force field functions and parameters will be discussed in terms of OPLS-AA.

As mentioned in Chapter I OPLS force field parameters for both all atom and united atom calculations that can be mixed were developed by Jorgensen *et al*[47]. OPLS initially was parameterized for bio-molecular systems and organic liquids. The parameters were optimized to fit experimental densities and heats of vaporization of liquids as well as gas-phase torsional profiles. The force field has been updated and independent modifications to the force field have been developed elsewhere[43,61,62].

a. *Bonded interactions*

Bonded interactions include bond stretching (1-2 interactions), angle bending (1-3 interactions) and dihedral angle (1-4 interactions) interactions based on a fixed list of atoms. The atoms are physically linked to each other as shown in Figure 2.2. This may be seen as an analogy of balls connected by a spring that obeys Hooke's law.

Bonded interactions potentials are given by

$$U_{bonded} = U_{bond} + U_{angle} + U_{dihedral} \quad (2.4)$$

where U_{bond} , U_{angle} and $U_{dihedral}$ are bond stretching, bond angle bending and dihedral angle potentials, respectively.

i. *Bond stretching*

The bond stretching potential between two covalently bonded atoms of type 1 and 2 is represented by a harmonic potential

$$U_{bond(r_{12})} = \frac{K_b}{2} (r_{12} - r_0)^2 \quad (2.5)$$

where K_b is the force constant, r_0 is equilibrium separation and r_{12} is the distance between atoms type 1 and 2.

ii. *Valence angle bending*

The bond angle bending interaction potential between atoms 1, 2 and 3 is also described by a harmonic potential

$$U_{angle(r_{123})} = \frac{K_\theta}{2} (\theta_{123} - \theta_0)^2 \quad (2.6)$$

where K_θ is the force constant, θ_0 and θ_{123} are the equilibrium angle between and the angle between atoms 1, 2 and 3, respectively.

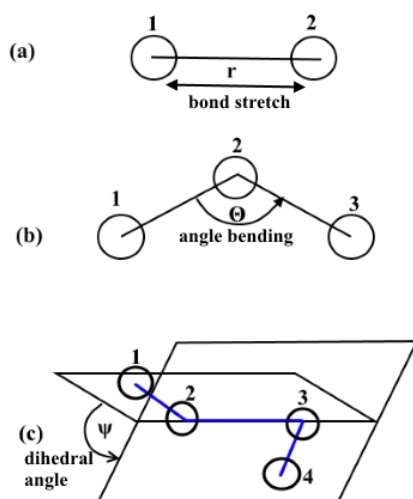


Figure 2.2 Schematic view of (a) bond stretching, (b) valence angle bending and (c) dihedral angle interactions.

iii. *Dihedral angle potential*

The dihedral angle potentials also known as torsional potentials describe the interaction arising from torsional forces in molecules.

$$U_{(\varnothing)} = \frac{V_1}{2} [1 + \cos(\varnothing + f_1)] + \frac{V_2}{2} [1 - \cos(2\varnothing + f_2)] + \frac{V_3}{2} [1 + \cos(3\varnothing + f_3)] \quad (2.7)$$

where $\varnothing$ is the dihedral angle, V_1 , V_2 and V_3 are the coefficients in the Fourier series, and f_1 , f_2 and f_3 are phase angles.

b. *Non-bonded interactions*

Non-bonded interactions in OPLS-AA include the Coulombic and Lennard-Jones interactions (equation 2.8) which are used for intermolecular and intramolecular non-bonded atoms separated by at least three bonds. From Figure 2.2, this means that atoms 1 and 4 experience intramolecular non-bonded interactions. These non-bonded interactions are evaluated based on a list of non-bonded atoms within a defined radius (Figure 2.3)

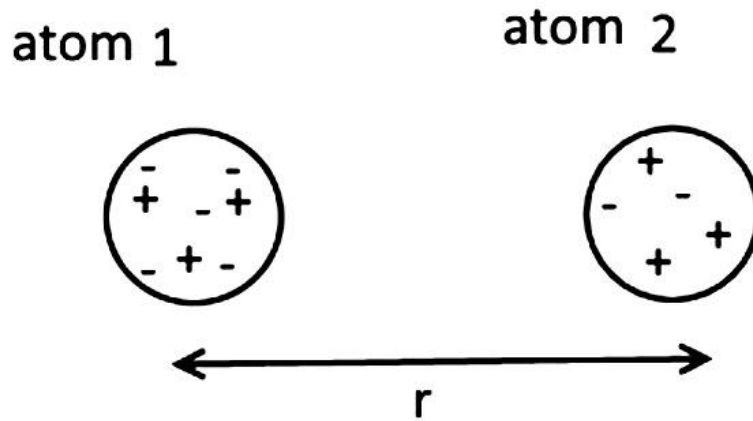


Figure 2.3 Non-bonded atoms separated by a defined distance

$$U_{non-bonded} = U_{LJ} + U_C \quad (2.8)$$

where U_{LJ} and U_C are the Lennard-Jones and Coulomb potentials, respectively.

i. *Lennard-Jones interactions*

The van der Waals interaction, which is the energy describing the repulsion and attraction between non-bonded atoms for the system are handled by the Lennard-Jones potentials U_{LJ} according to equation 2.9

$$U_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (2.9)$$

where ε_{ij} and σ_{ij} are Lennard-Jones potential parameters, and r_{ij} is the distance between atom i and j . Figure 2.4 shows the Lennard-Jones potential energy diagram for atoms separated by distance r . ε represents the well depth, which is a measure of how strongly the two atoms are attracted to each other and σ is associated with the distance at which the potential energy between the two atoms is zero. At this distance, the non-bonding atoms cannot come closer any further. Lennard-Jones potential parameters between same species, ε_{ii} and σ_{ii} are usually derived by empirical or semi-empirical methods[63].

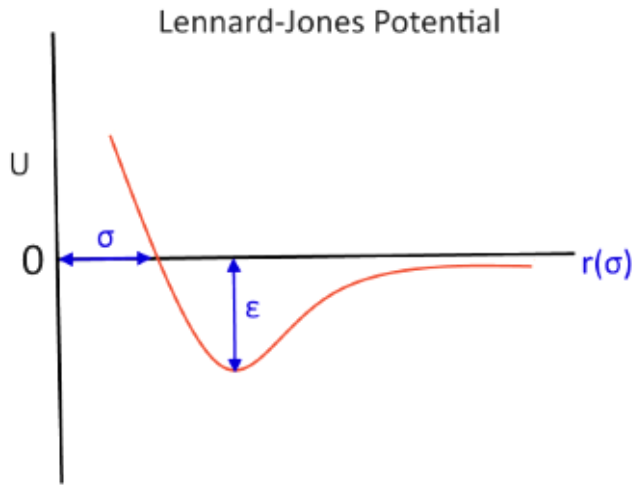


Figure 2.4 Lennard-Jones potential energy diagram showing the ε and σ parameters

In OPLS-AA the geometric mixing rules are applied for the Lennard-Jones potential parameters [47].

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad \text{and} \quad \sigma_{ij} = \sqrt{\sigma_i \sigma_j} \quad (2.10)$$

ii. Electrostatic interactions

The Coulombic interaction U_C between two charged atoms exist due to an uneven internal distribution of electrons, which leads to positively and negatively charged parts in a molecule, is given by

$$U_C = \frac{1}{4\pi\epsilon_0} \frac{q_i q_j e^2}{r_{ij}} \quad (2.11)$$

where q_i and q_j are the charges on atom i and j and ϵ_0 is the dielectric constant.

2.2.2 Steps in Molecular Dynamics

In a typical molecular dynamics calculation, many copies of a *geometry-optimized molecule* are created to make a reasonable initial configuration representing a real system (gas, liquid or solid). Simulation conditions such as thermodynamic ensemble, pressure, temperature and force field parameters representing the physical thermodynamic properties of interest are setup. The system has to undergo a process of energy minimization to adjust the structure by random distribution of molecules to reduce steric clashes. As time elapses, the velocities and the positions are calculated and updated at specified time intervals (timesteps). If the forces on the atoms are too high and both the temperature and pressure are unrealistic, the velocities are rescaled until the required conditions are achieved. The rescaling step is iterated until the kinetic and potential energies are equal. The process is referred to as system equilibration. Once the system has equilibrated, the following trajectories can be used to determine system properties such as thermodynamic properties. Figure 2.5 shows the steps in molecular dynamics[59]. It must be pointed out that the molecular dynamics code normally depends on external methods for the generation of initial configurations.

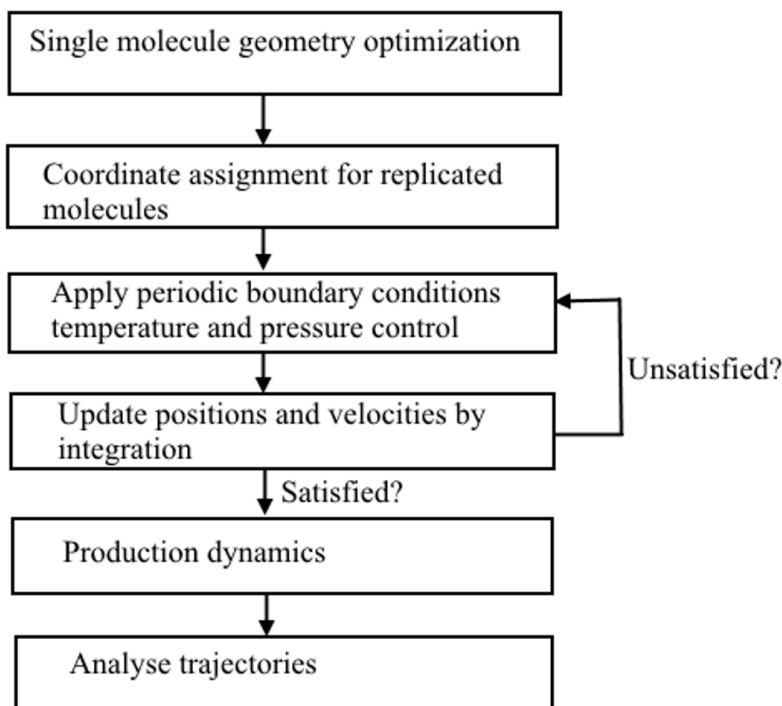


Figure 2.5 Molecular dynamics flow chart

2.2.3 Initial configuration of bulk systems

Setting up an initial configuration representing bulk systems requires that each individual system component be geometry optimized. For small molecules, the usual procedure is to get a minimum energy configuration of single molecule from single crystal x-ray diffraction or *ab initio* methods. The process of finding an orientation of atoms in space such that the net inter-atomic force on each atom is close to zero is called geometry optimization[64–66]. This process may be achieved by having an orientation that represents a local or global energy minimum. Local or global energy minimum may be thought of as energy as a function of atomic positions, $U(\mathbf{r})$, where the derivative of energy with respect to position (equation 2.2) is a zero vector.

An optimized geometry of a single molecule must have bond lengths and bond angles that reduce the forces pulling atoms together or pushing them apart. Figure 2.6 shows the bond lengths of a structure of DFM molecule that has reached global energy minimum. (See Appendix B for xyz coordinates of the molecules).

As a result, the optimized structure should resemble a molecule, as it exists in nature. By developing a computational model that provides an approximate $U(r)$ of correct geometry, an iterative optimization procedure such as the one in Figure 2.7 may be followed. There are many codes that can be used for geometry optimization, some of these include Gaussian[67] and General Atomic and Molecular Electronic Structure System (GAMESS-US)[68]. With an optimized single molecule, many copies are created to resemble a realistic model such as liquids.

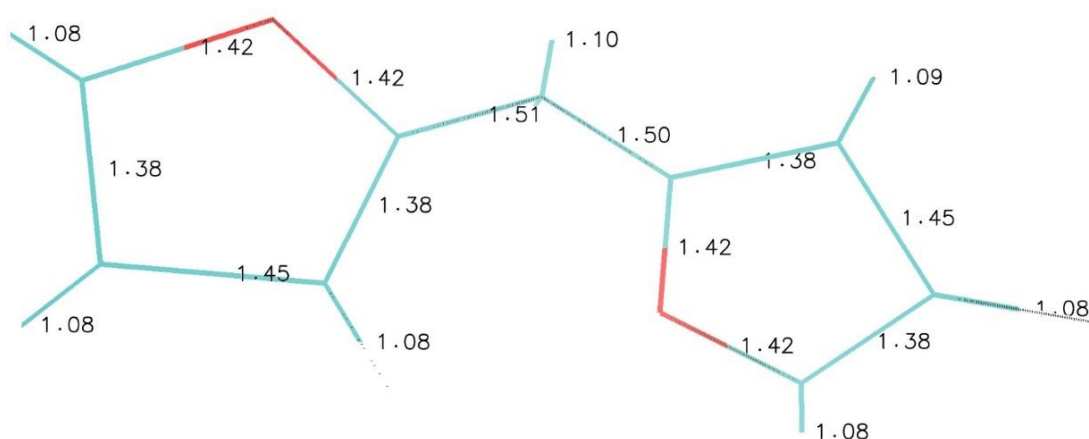


Figure 2.6 Structure of DFM with bond lengths at local energy minimum

This is the initial configuration required to initiate the simulation. N particles in a system need a starting configuration that is reasonably close to a realistic physical occurrence at the desired conditions. This requires the energy distribution of the molecules to be adjusted to achieve the desired conditions. If the proximity of the atoms in an initial configuration is too small, the excessive potentials which over speed the particles might cause temperature-scaling disruption for some reasonable integration time step. This may be overcome by using an experimentally determined configuration from X-ray diffraction methods that give 3-dimensional structure especially for solids.

Another option is to use computer codes such as molConfig[69] and Packmol[70,71] to make the desired number of copies of the optimized single molecules. In this way, constraints can be introduced, for example, to avoid atoms from different molecules coming unphysically close together. In this work, Packmol software was utilized to obtain an arbitrary initial configuration. Figure 2.8 shows the initial configuration of atoms from two different molecules in cubical box.

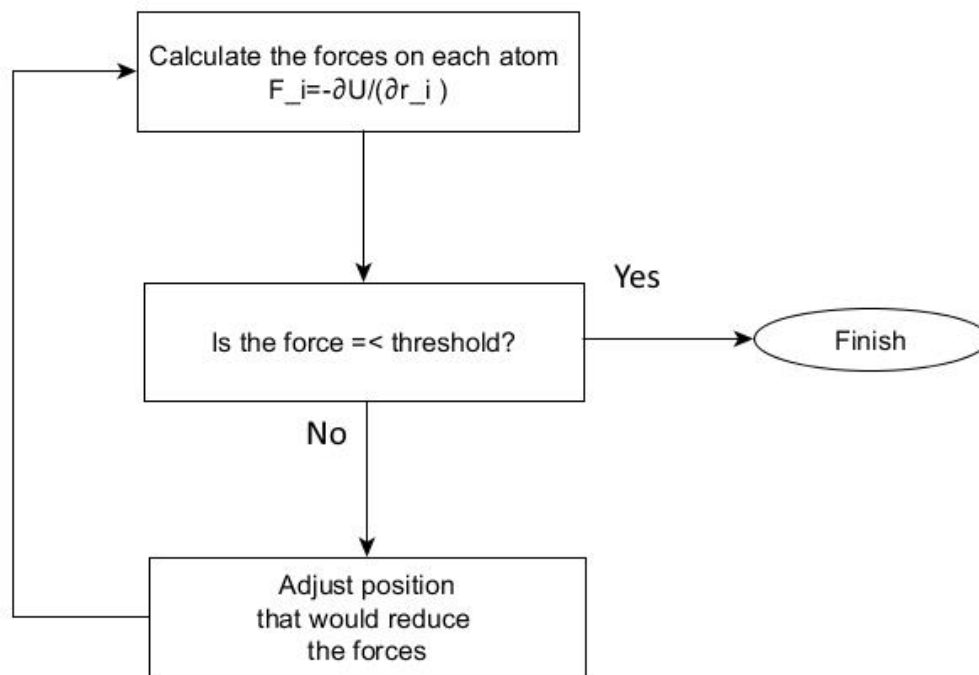


Figure 2.7 Iterative process of geometry optimization

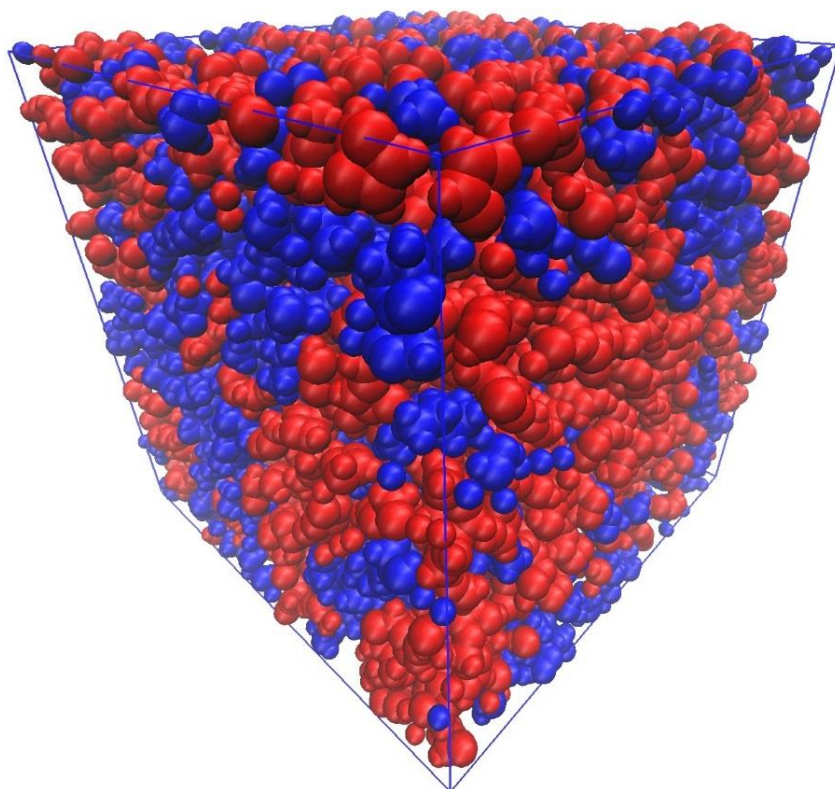


Figure 2.8 Initial configuration generated by packmol software and viewed using VMD.

2.2.4 Periodic boundary conditions

For the simulation of bulk properties (system with no free surfaces), it is conventional to use the periodic boundary condition. In periodic boundary conditions for example, an infinite lattice is formed by the replicated cubical simulation box throughout space (Figure 2.9). As the simulation progresses and a movement of an atom in the middle box takes place, its periodic image in all the other boxes moves with the precise orientation. Thus, as an atom leaves the central box, a copy of it will enter through the opposite face. The number of atoms in the central box and the entire system is conserved, thus atoms cannot be lost or created.

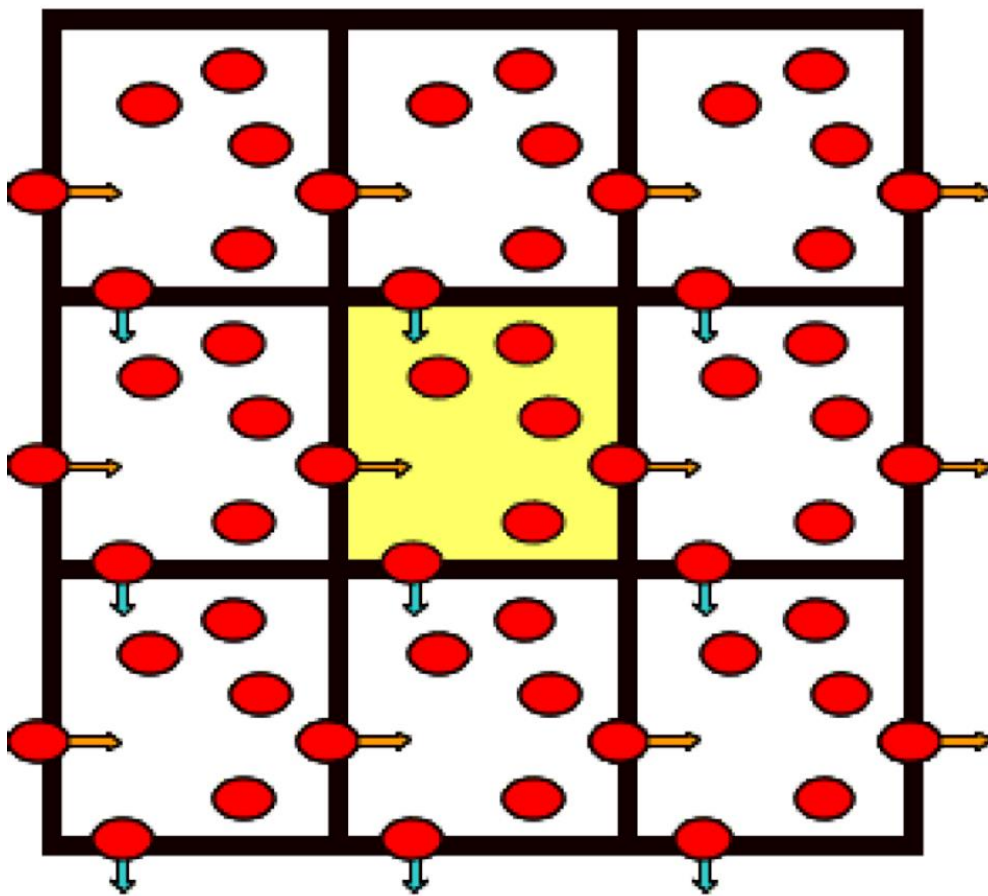


Figure 2.9 Two-dimensional representation of periodic boundary condition

Applying periodic boundary condition minimizes the edge effects in a finite system.

2.2.5 Updating the initial configuration

For particles to move around the initial configurations are altered and this is usually the first step performed by molecular simulation packages. DL_POLY Classic[72] is one of the packages designed to perform molecular dynamics simulations of molecular systems, it solves Newton's equations of motion using the Verlet algorithm which is itself based on Taylor series expansion. Verlet algorithms contained in DL_POLY Classic code are Verlet leapfrog and velocity Verlet algorithms. In this dissertation, the leapfrog algorithm is used to integrate the equations of motion.

In the leapfrog algorithm, the values of force (F) and position (r) at time t are established while the velocities (v) are half a timestep behind $\left(t - \frac{\Delta t}{2}\right)$. For the arbitrary structure, by integrating the force (equation 2.1), the velocities and positions are updated. The first step is to determine the v ,

$$v = \frac{dr_i}{dt} \quad (2.12)$$

then use new v to update the positions

$$v\left(t + \frac{\Delta t}{2}\right) = v\left(t - \frac{\Delta t}{2}\right) + \frac{F(t)}{m}\Delta t \quad (2.13)$$

$$r\left(t + \frac{\Delta t}{2}\right) = r(t) + v\left(t + \frac{\Delta t}{2}\right)\Delta t \quad (2.14)$$

The velocity at time t is obtained from the averaged velocities half a timestep before and after time t

$$v(t) = \frac{1}{2}\left[v\left(t - \frac{\Delta t}{2}\right) + v\left(t + \frac{\Delta t}{2}\right)\right] \quad (2.15)$$

This is important for properties that depend simultaneously on position and velocity.

2.2.6 Thermodynamic ensembles

As the system is updated at various time steps, the conditions have to resemble those of a real physical state. Therefore, molecular dynamics can be performed under different scenarios that resemble thermodynamic conditions in closed and open systems. In these

systems, some variables may be allowed to remain constant while others fluctuate. A combination of constant variables is known as thermodynamic ensemble and it governs the outcome of the results.

a. *Micro-canonical ensemble (NVE)*

In the micro-canonical (NVE) ensemble, the system is isolated and the number of moles (N), volume (V) and energy (E) remain constant. The total energy is conserved by an exchange of potential and kinetic energy. However, there is always a slight drift in energy due to rounding and truncation errors during the integration process.

b. *Canonical ensemble (NVT)*

The amount of substance (N), volume (V) and temperature (T) are kept constant in the canonical ensemble (NVT). The endothermic and exothermic energy processes are exchanged with a thermostat.

c. *Isothermal–isobaric (NPT) ensemble*

In the isothermal-isobaric (NPT) ensemble, the number of particles (N), pressure (P) and temperature (T) are conserved. The volume of the system is allowed to fluctuate over a sufficiently long simulation and once the equilibrium is reached, it is possible to determine the density of the system. This ensemble requires a thermostat and a barostat to maintain temperature and pressure respectively. We use this ensemble in our work.

2.2.7 Temperature and pressure coupling

Temperature control plays a crucial role in molecular dynamics simulations for various situations such as constant temperature or constant pressure simulations. Scaling procedures may be used to optimize the molecular system towards the desired temperature. DL POLY Classic applies three different thermal reservoir methods: Nosé-Hoover, Berendsen, and Gaussian constraints.

A brief description of the Nosé-Hoover method, which was used for this work, is given here using the canonical representation. The Newton's equations of motion are modified as follows:

$$\frac{d^2 r_i(t)}{dt^2} = \frac{F_i}{m_i} - \xi \frac{dr_i(t)}{dt} \quad (2.16)$$

wherefore the thermal reservoir parameter ξ , the equations of motion are expressed with target temperature T_0 and instantaneous temperature T .

$$\frac{d\xi}{dt} = \frac{1}{Q} (T - T_0) \quad (2.17)$$

The parameter Q is obtained by

$$Q = \frac{\tau_T^2 T_0}{4\pi^2} \quad (2.18)$$

where τ is a time constant parameter. The modification of the Newton's equations of motion requires also the modification of the leapfrog integration as follows

$$\xi\left(t + \frac{\Delta t}{2}\right) = \xi\left(t - \frac{\Delta t}{2}\right) + \frac{1}{Q} (T - T_0) \Delta t \quad (2.19)$$

$$\xi(t) = \frac{1}{2} \left[\xi\left(t - \frac{\Delta t}{2}\right) + \xi\left(t + \frac{\Delta t}{2}\right) \right] \quad (2.20)$$

$$v\left(t + \frac{\Delta t}{2}\right) = v\left(t - \frac{\Delta t}{2}\right) + \left[\frac{F_i}{m_i} - \xi \frac{dr_i(t)}{dt} \right] \Delta t \quad (2.21)$$

Just like temperature coupling, pressure coupling can be implemented by Nosé-Hoover method.

Chapter III

3 CASE STUDY 1: Molecular dynamics simulation study of *n*-propanol and 2,2'-difurylmethane binary liquid mixtures

Introduction

In this Chapter, *ab initio* calculations and molecular dynamics simulation are combined to investigate thermodynamic properties and the structural aspects of [DFM/*n*-propanol] binary mixtures. The results indicate that there is a link between excess molar volume and local compositions of these liquid mixtures. Coordination numbers and excess local mole fractions from calculated radial distribution functions were used to probe the local structures. Clustering due to weak hydrogen bonding has been evidenced between DFM oxygen and *n*-propanol acidic hydrogen. Dihedral distributions also reveal the most stable conformers of *n*-propanol for various mole fractions of DFM.

3.1 Computational method

For *n*-propanol, the OPLS-AA force field developed by Jorgensen[47] was used. OPLS-AA was described in detail from Chapter II. The latest version of the force field, OPLS-2005, was used[73]. The OPLS-AA force field parameters of DFM were derived from the furan OPLS-AA (furan) and -CH₂- group of alkanes. As in reference[42] the furan moieties of the DFM were constrained to be planar. Partial charges are the hyperbolic-restrained electrostatic potential (RESP –A1) charges obtained by a two stage fit to the HF/6-31G(d)

Adapted with permission from Otsile William Kgagodi and Foster Mbaiwa, *Journal of Molecular Liquids*, Volume 227, February 2017, Pages 366-372. © 2016 Elsevier B.V. All rights reserved.

molecular electrostatic potential[74]. The charges as well as Lennard-Jones parameters for DFM and *n*-propanol are given in Table 3.1. Figure 3.1 shows atomic labels for both DFM and *n*-propanol molecules. *Ab initio* molecular geometries of *n*-propanol, DFM and DFM/*n*-propanol dimers were optimized at the Hartree-Fock theory with the 6-31G (d) basis set using GAMESS-US program[68,75]. Frequency calculations were performed on the optimized geometry to ensure that it corresponds to a minimum and not a transition state. Initial configurations of the mixtures were generated using Packmol[76]. For all mixtures, 1000 molecules (DFM + *n*-propanol) with a distance tolerance of 2.0 Å (which is the minimum distance between pairs of atoms of different molecules) were initially placed in a cubic box of (60 * 60 * 60) Å³.

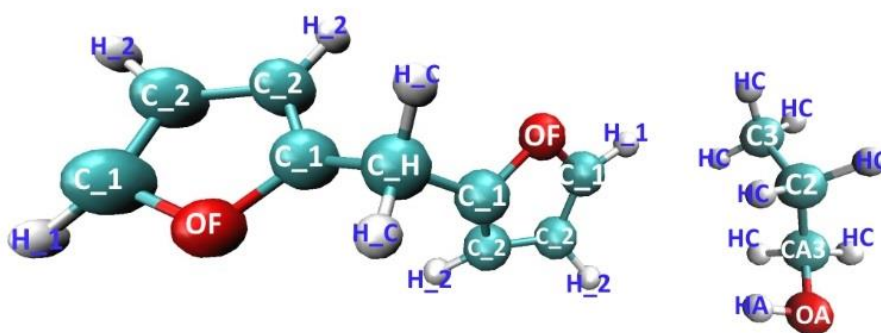


Figure 3.1 Molecular structures of DFM (left) and *n*-propanol (right)

Molecular Dynamics simulations were performed for pure systems and mixtures of DFM/*n*-propanol using DL_POLY Classic code[72]. The dynamics were calculated for mixtures of mole fraction compositions of DFM ranging from 0.0 to 1.0 at 0.1 step sizes. Isothermal-isobaric ensemble dynamics were performed at 1 atm and 298.15 K (see Figure 3.2 for the pressure and temperature profiles) by applying Nose-Hoover thermostat and barostat with relaxation times of 0.1 ps and 0.5 ps, respectively. Verlet leapfrog algorithm with a timestep of 1.0 fs was used for the integration of Newton's equations in all calculations.

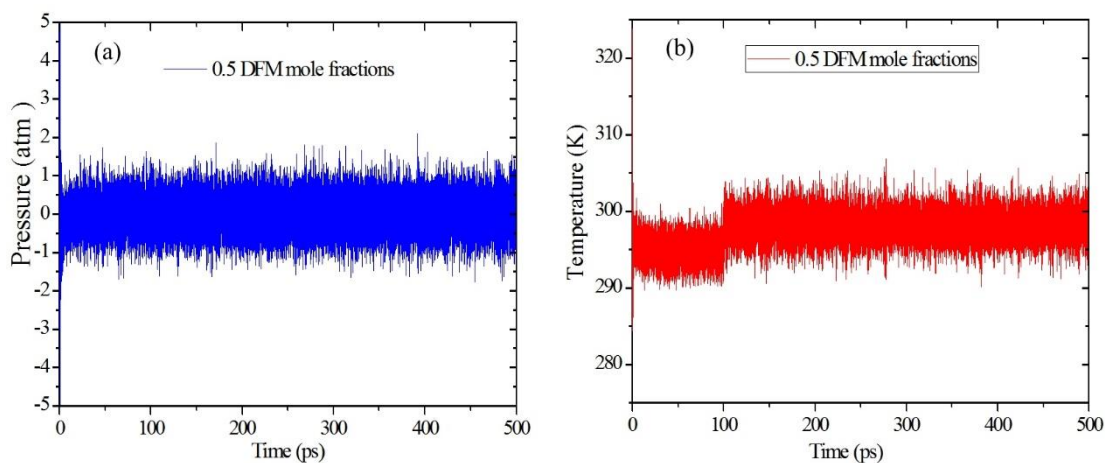


Figure 3.2 DFM/n-propanol (a) pressure and (b) temperature profiles as function of time for 0.5 mole fraction of DFM

Table 3.1 Atomic charges and Lennard-Jones parameters for DFM and n-propanol. For DFM the atoms closest to the bridging carbon are regarded as inner atoms.

Atom	Charge q	$\sigma(\text{\AA})$	$\epsilon(\text{kcal mol}^{-1})$
<i>n-propanol</i>			
HC	0.06000	2.9580	0.0445
C3	-0.18000	3.5000	0.0660
C2	-0.12000	3.5000	0.0660
CA3	0.14500	3.5000	0.0660
OA	-0.68300	3.3045	0.1059
HA	0.41800	0.0000	0.0000
<i>2,2'-difurylmethane</i>			
H_2(outer)	0.179192	2.4200	0.0300
H_2(inner)	0.176809	2.4200	0.0300
H_1	0.170415	2.4200	0.0300
C_2(outer)	-0.245424	3.5000	0.0700
C_2(inner)	-0.234468	3.5500	0.0700
C_1(inner)	0.218161	3.5000	0.0700
C_1(outer)	-0.054550	3.5500	0.0700
C_H	-0.299168	3.5000	0.0660
H_C	0.135245	2.5000	0.0300
O_F	-0.195796	2.9000	0.1400

For all mixtures, each system was equilibrated for 100 ps, which was sufficient to establish equilibrium values for the energies and volumes. The statistics were sampled over 400 ps of production runs. A cut-off distance of 1.2 nm was applied for both the van der Waals interactions and electrostatic interactions, which were evaluated using the smooth particle-mesh-ewald technique[77].

3.2 Results and Discussions

3.2.1 System equilibration

Most experimental observations are performed at constant temperature and pressure, therefore in molecular simulations the isothermal-isobaric ensemble proceeds with the objective of mimicking such conditions. An initial configuration of a system of N -particles of which constant external pressure is imposed, the system volume fluctuates to achieve a volume that would maintain a mechanical equilibrium between external and internal pressure. If the external and internal pressures are unbalanced, it means the configurational energies are unrealistic. Configuration energies are usually too high at this point and therefore, the system requires a method of energy minimization to relax. By monitoring both the system volume and configurational energies, a conclusion can be made that indeed the system has equilibrated. The point at which the system volume and configurational energies start to level off signifies the closeness to an equilibrated system. Figures 3.3 and 3.4 show the configurational energy and system volume profiles for pure and mixed systems of *n*-propanol and DFM.

From Figure 3.3 the point at which the configurational energy profiles start to flatten is observed at about 50 ps. However, the system was allowed to undergo further energy minimization for 80 ps to ascertain that indeed the system has fully equilibrated. Figure 3.4 shows that the system volume profiles start to flatten at around 50 ps, which is in accord with the configurational energy profiles. As the composition of DFM is increased, the volume size increases, however it does not affect the point at which the system starts to equilibrate. With equilibrated systems, the thermodynamics properties can now be evaluated.

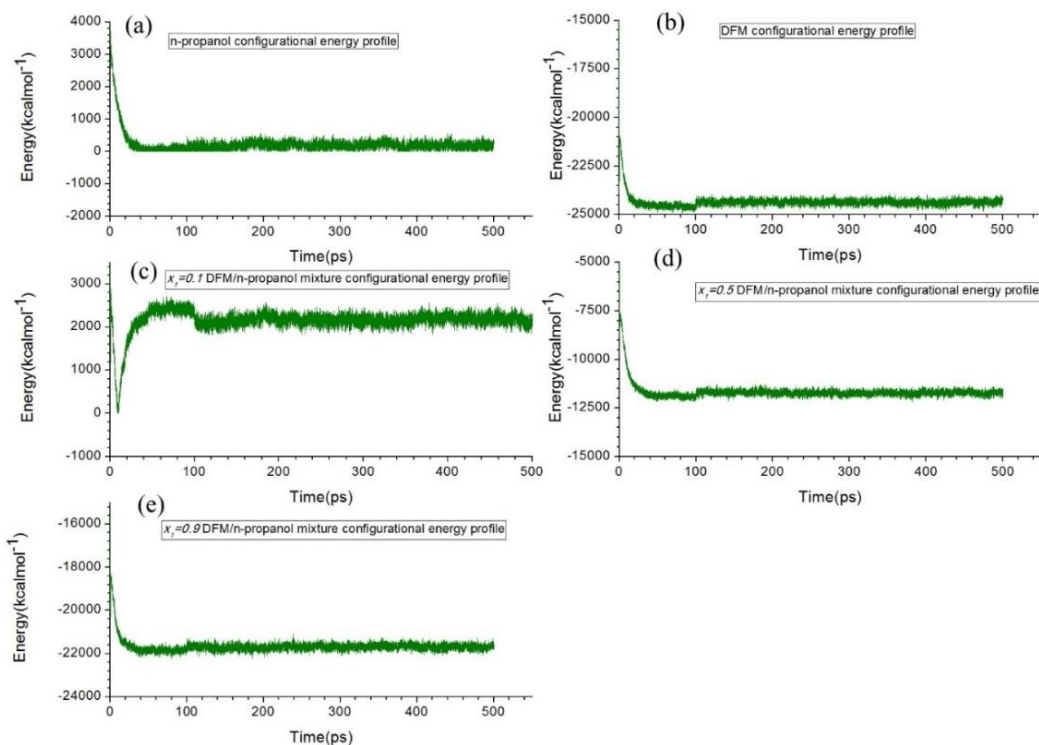


Figure 3.3 Configurational energy profiles for pure n-propanol, DFM and mixed systems

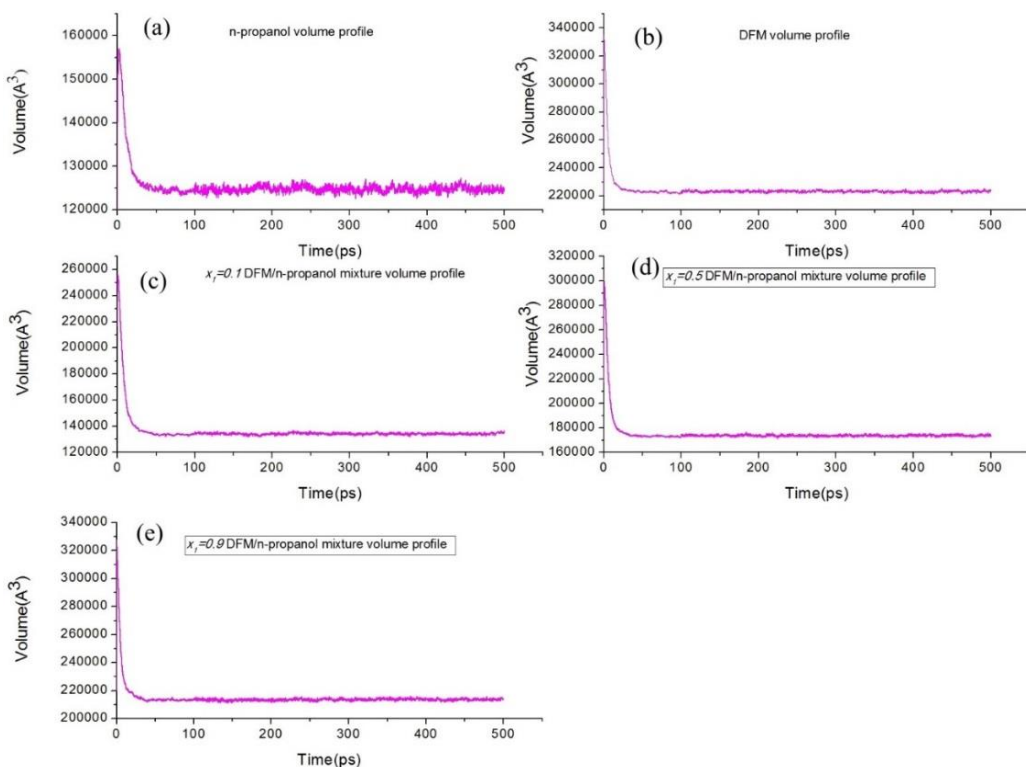


Figure 3.4 System volume profiles for pure n-propanol, DFM and mixed systems

3.2.2 Thermodynamic properties

In this section, first we present results for simulated thermodynamic properties of pure (*n*-propanol and DFM) as well as those of the mixtures. Calculated and experimental thermodynamic properties are listed in Table 3.2 for comparison. Densities of the systems were calculated directly from the total mass of simulated molecules and average equilibrium volume. In both cases, deviation from the experimental densities and molar volume is less than 2 %.

The enthalpy of vaporization (ΔH_{vap}) for pure systems were computed according to equation 3.1

$$\Delta H_{vap} = \frac{-(E_{coul} + E_{vdw})}{N} + RT \quad (3.1)$$

where E_{coul} and E_{vdw} are respectively the coulombic and Van der Waal's energies of the system, R is the gas constant, T is temperature and N is the total number of molecules.

Table 3.2 Calculated and experimental (in parenthesis) thermodynamic properties for pure systems of n-propanol and DFM, density (ρ), enthalpy of vaporization (ΔH_{vap}), isothermal compressibility (k_T) and molar volume (V_m).

Property	<i>n</i> -propanol	2, 2'-difurylmethane
ρ (g cm ⁻³)	0.79968 (0.79954) ^a	1.1021 (1.0909) ^a
ΔH_{vap} (kJ mol ⁻¹)	45.35 (47.45) ^b	162.59
k_T (atm ⁻¹) x10 ⁶	93.10 (101.57) ^c	50.81 (62.51) ^d
V_m (cm ³ mol ⁻¹)	75.15 (75.16) ^a	134.44 (135.82) ^d

^a Reference [9], ^b Reference [46] ^c Reference [78] ^d Reference [19]

In comparison with literature values[46,47,78], the simulated enthalpy of vaporization for pure *n*-propanol is very close with a difference of less than 5%. The isothermal

compressibility k_T for pure systems were computed from the simulation fluctuations according to equation 3.2,

$$k_T = \frac{\delta V^2}{V k_B T} \quad (3.2)$$

where δV^2 is volume fluctuation, V is the system's average volume and k_B is the Boltzmann constant. The k_T compares well with other literature values for *n*-propanol[46,78]. For DFM the reported k_T agrees reasonably well with the calculated values. It must be pointed out however that the reported data are not direct experimental measurements. The isothermal compressibility was obtained via the Flory theory of solutions[19].

Densities for the entire composition range were also computed and compared with experimental data as shown in Figure 3.5. In general, simulated densities agree well with the experimental densities for all compositions. However, as the mole fraction of DFM is increased the deviation increases, but overall trend is the same. With increasing mole fraction (x_1) of DFM there is an increase in density for the mixtures since DFM is denser than *n*-propanol.

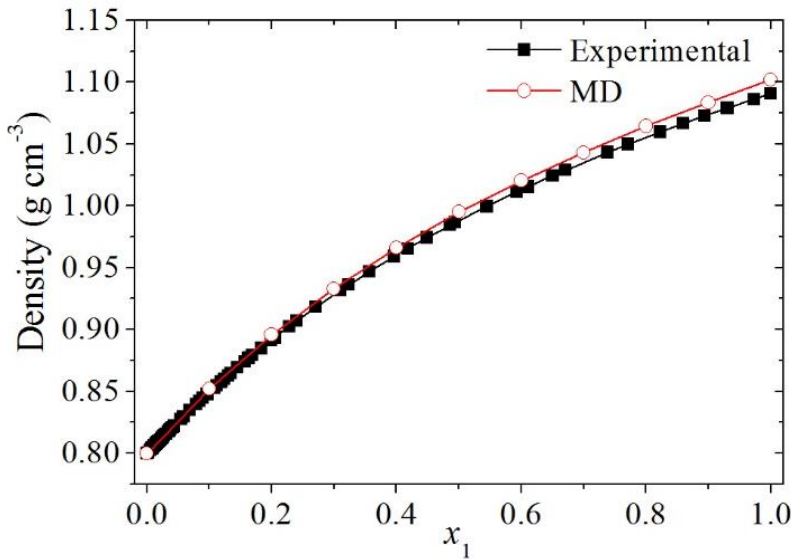


Figure 3.5 Calculated values for the densities of DFM/*n*-propanol mixtures as a function of DFM mole fraction (open red circles) and experimental densities[9] (closed black squares).

From the calculated densities, excess molar volumes, V_m^e , were calculated according to equation 1.1. Simulated and experimental excess molar volumes for the entire composition range as a function of DFM mole fraction are presented in Figure 3.6. The experimental and calculated values V_m^e show significant differences in magnitude. This is not surprising given that excess thermodynamic properties are very sensitive parameters, a small change in calculated density can lead to a relatively large change in excess volume. However, the general trend of the experimental V_m^e is well captured by the theoretically derived curve. The excess molar volumes assume both negative and positive values with minima at $x_1 = 0.2$ and $x_1 \approx 0.3$ for calculated and experimental values respectively. A maximum is observed for $x_1 \approx 0.9$ in both cases. Thus, the simulated results reproduce both the negative and positive deviations in V_m^e . In the next section, we focus on the structural aspects of this mixture.

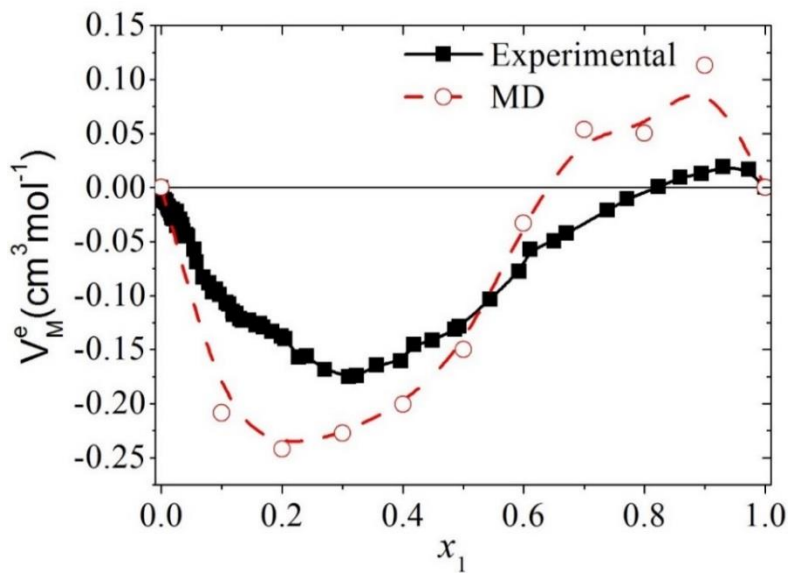


Figure 3.6 Calculated (open red circles) and experimental[9] (closed black squares) values for the excess molar volumes for DFM/ *n*-propanol mixtures as a function of DFM mole fraction.

3.2.3 Structure of *n*-propanol/DFM binary mixture

Radial distribution functions (RDFs) are useful in studying intermolecular structure and interactions in bulk systems[40,52,79–81]. The RDF $g_{ij}(r)$ between particles of type i and j can be defined as follows:

$$g_{ij}(r) = \frac{\langle \rho_j(r) \rangle_{local}}{\langle \rho_j \rangle_{bulk}} \quad (3.3)$$

where $\langle \rho_j(r) \rangle$ is the number density of particles of type j at a radius r around particle i and $\langle \rho_j \rangle_{bulk}$ is the number density of particles of type j averaged over all spheres around particle i . $g_{ij}(r)$ defines the probability of finding a particle j at a radius r from particle i . When $r \rightarrow 0$ then $g_{ij}(r) = 0$ and when $r \rightarrow \infty$ then $g_{ij}(r) = 1$. RDFs computed at different compositions of the binary mixtures were used to investigate the structures. Site-site and center of mass RDFs were calculated from the simulation results collected over 400 ps production runs. For the interpretation of the RDFs, see Figure 3.1 for the atomic descriptions for DFM and *n*-propanol.

a. *Site-site radial distribution functions*

Selected site-to-site radial distribution functions (ssRDFs) are shown in Figures 3.7 and 3.8. For the sake of clarity, the RDF's are for $x_1 = 0, 0.1, 0.5, 0.9$ and 1. The RDF's of HA-OA and OA-OA for *n*-propanol are a characteristic of hydrogen bonding and are consistent with those previously reported[40,46,47]. The peak heights show high sensitivity to changes in x_1 . As x_1 increases the peak heights increase, indicating that the local structure is maintained for various x_1 . This behavior has been attributed to the tight clusters formed by alcohols through hydrogen bonding[16].

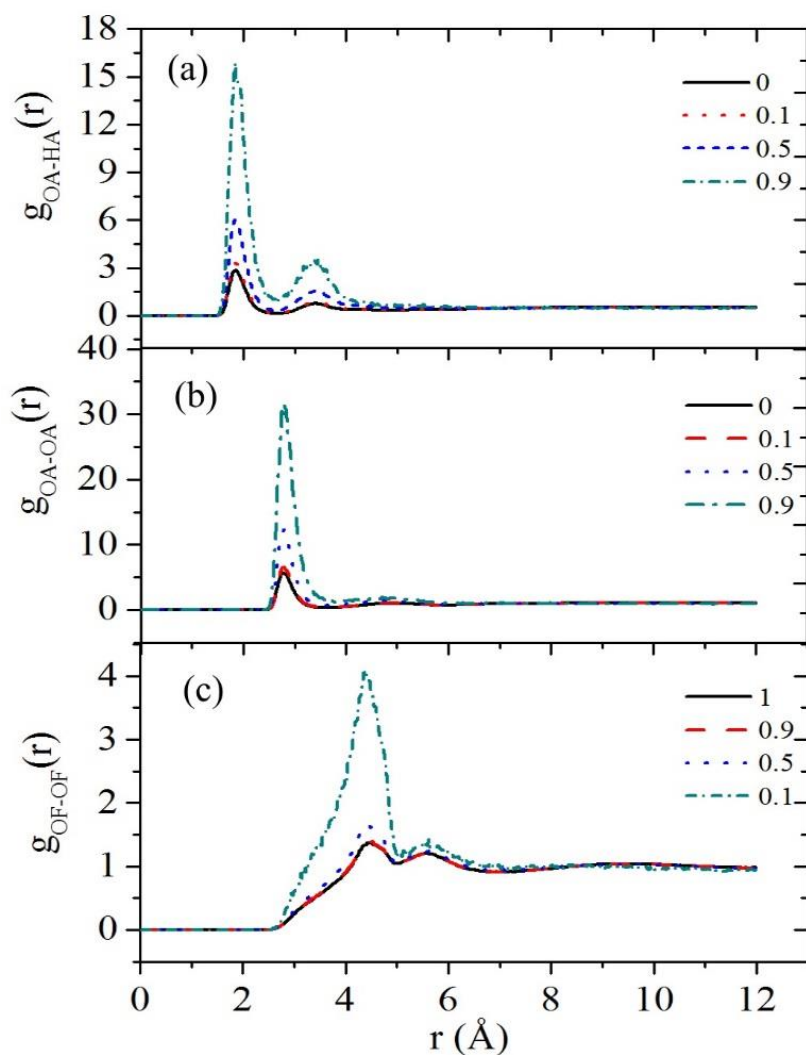


Figure 3.7 Intermolecular Radial distribution functions for different sites (a) oxygen (OA)-hydrogen (HA) [n-propanol/n-propanol] (b) oxygen (OA)-oxygen (OA) [n-propanol/n-propanol] (c) oxygen (OF)-oxygen (OF) [DFM/DFM]

The DFM intermolecular OF-OF RDFs show two strong peaks centered at 4.46 Å and 5.56 Å and a weak broad peak roughly centered at 9.71 Å. The peaks at 4.46 Å and 5.56 Å agree with the OF-OF intermolecular distances of the lowest energy dimer calculated at HF/6-31G (d) theory as shown in Figure 3.9. The peak at 9.71 Å represents the long-range interaction from the second solvation shell.

The RDFs for *n*-propanol acidic HA and OF (DFM) (Figure 3.8) show two peaks centered at 2.21 Å and 5.91 Å. The peak at 2.21 Å shows hydrogen bonding between these two species which is not surprising as hydrogen bonding through the furan oxygen has been reported elsewhere[42,53]. However, the peaks are broader with small intensities and occur at a slightly larger distance as compared to *n*-propanol HA-OA correlations, which indicate that the molecules are experiencing weak hydrogen bonding. The peak heights increase with increasing x_1 .

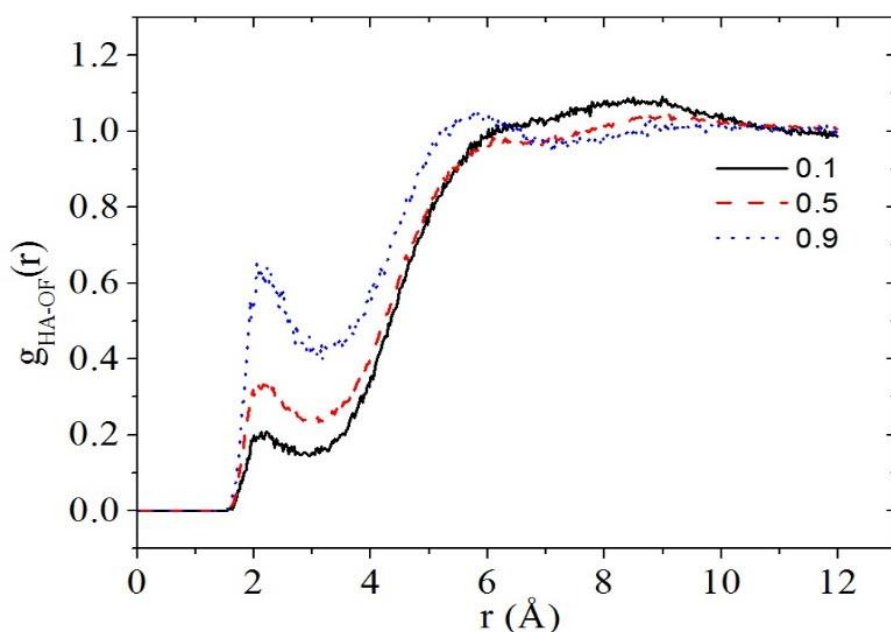


Figure 3.8 HA-OF Radial distribution functions for different DFM mole fractions.

To further investigate this, the gas phase dimeric structure of *n*-propanol/DFM was optimized using HF/6-31G (d) theory. The lowest energy structure (Shown in

Figure 3.10) is the hydrogen-bonded isomer. The hydrogen bond distance for the dimer is 2.20 Å, which is consistent with the peak position in the radial distribution function. We could not find any evidence on the RDF and the lowest energy structure about any interaction between the furan ring π -electron systems with the acidic hydrogen of *n*-propanol.

Also, shown in Figures 3.7 and 3.8 are the dependences of site-to-site radial distribution functions on the mole fraction of DFM. The positions of the RDF peaks and minima are hardly affected by the changes in the composition even when compared to pure systems. This shows

that the coordination shells of *n*-propanol or DFM are not significantly distorted in the mixture compared to pure systems. An apparent observation is the change in the RDF peak intensity when the mole fraction of DFM is increased (Figures 3.7 and 3.8). This is also true for the DFM site-to-site correlation (Figure 3.7 c). The large magnitude of HA-OA and OA-OA *n*-propanol peaks at low *n*-propanol mole fractions suggests that its molecules form clusters even in DFM rich environment[82,83].

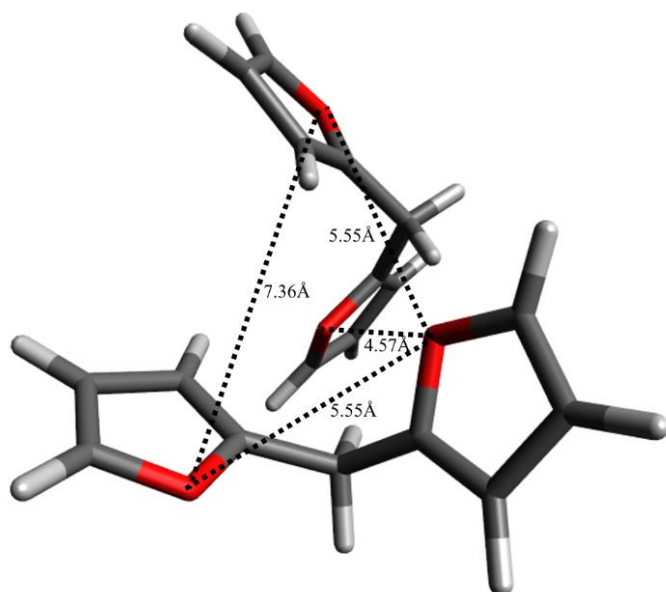


Figure 3.9 HF/6-31G (d) lowest energy optimized geometry of DFM dimer.

DFM OF-OF correlations also show this propensity to form clusters at low mole fractions but less so than *n*-propanol. Interestingly, DFM OF-OF correlations are less sensitive to changes in composition between $x_1 = 0.5$ and 0.9. The $g(r)$ values are close to one, which indicates random distribution of DFM molecules. In general, it can be deduced that, at high mole fractions of each respective mixture component homogeneity of that component is achieved. However, at high mole fraction *n*-propanol has higher tendency to form clusters than DFM does at high mole fraction.

Just like RDF, the spatial distribution functions (SDF) depict the probability of finding a particle at a particular point in space around a central reference molecule[84]. SDFs can be considered as a three dimensional modified RDF and can be used to clearly reflect the spatial distribution of the components in the mixture[44]. Figure 3.11 shows the SDF of DFM oxygen

(OF) atoms orientation about DFM. The SDFs were generated using TRAVIS software package[84] and visualized using VMD[85]. For low mole fractions of DFM, low OF populations are observed but increases as the DFM mole fraction increases. The OF appears to be mostly populated around the bridging carbon (C_H). When used in conjunction with SDF, the lowest energy optimized DFM dimer from Figure 3.9 shows that the closest OFs to C_H are the intermolecular OFs separated by 4.46 Å. The intermolecular OFs separated by 7.36 Å appear farthest and are more pronounced for higher DFM mole fractions. The SDFs present evidence of DFM molecule clusters which is consistent with RDFs from Figure 3.7 (c).

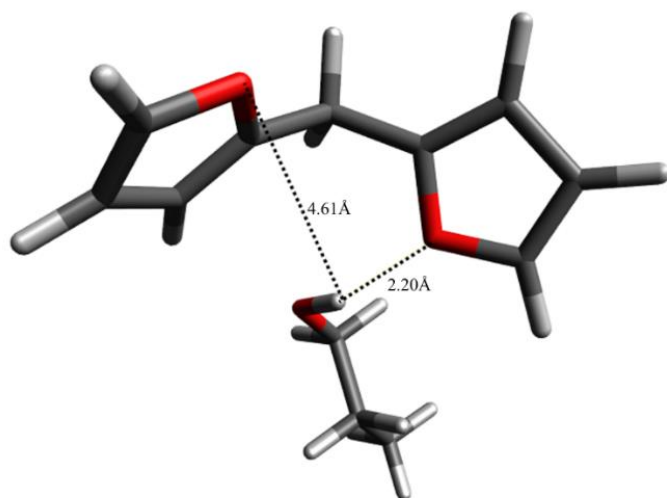


Figure 3.10 HF/6-31G (d) lowest energy optimized geometry of DFM-propanol dimer.

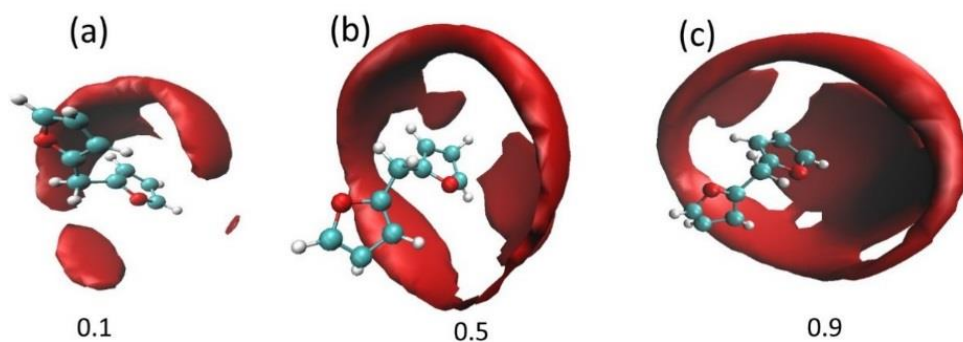


Figure 3.11 Variation of the spatial distribution functions (SDFs) with DFM mole fraction. Red surfaces denote regions populated by oxygen atoms of DFM molecules. The isovalues were set to 0.88 for all mole fractions.

b. Centre of mass radial distribution functions

To understand local solvation structures at different compositions center of mass radial distribution functions (COM-RDFs) were calculated. The COM-RDFs of *n*-propanol/*n*-propanol, DFM/*n*-propanol and DFM/DFM for different mole fractions are presented in Figure 3.12 (a-c), respectively. Also shown are the *n*-propanol/*n*-propanol and DFM/DFM COM-RDFs in pure systems.

In general, the COM-RDF trend mirrors those of ssRDF. The *n*-propanol/*n*-propanol COM-RDFs are narrower than for the DFM/DFM or DFM/*n*-propanol distributions, which indicate that *n*-propanol has more ordered local structure with respect to other *n*-propanol molecules. For *n*-propanol/*n*-propanol, the positions of the peak maxima and minima do not change significantly with composition (Figure 3.12 (a)). This shows that the local structures of *n*-propanol are hardly affected by the presence of DFM molecules. The main changes are with respect to the peak heights, which increase remarkably with a decrease in the mole fraction of *n*-propanol. As in site-site RDFs, this indicates the first coordination shells are not significantly distorted for mixed systems as compared to pure system.

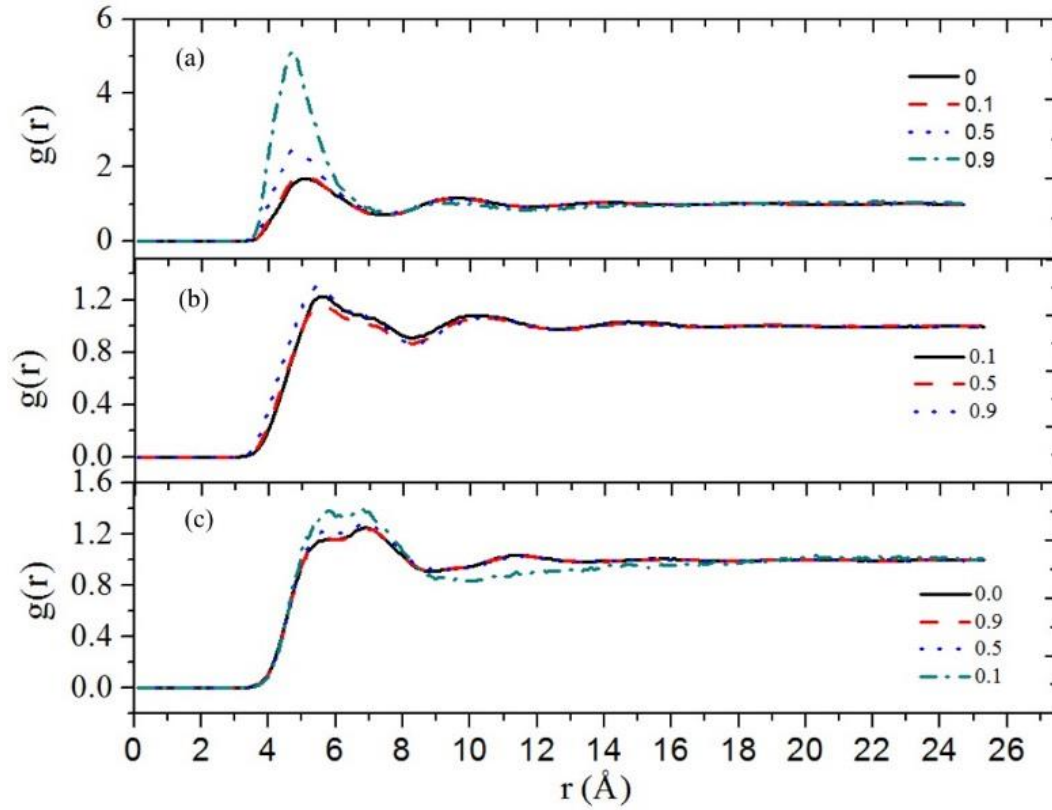


Figure 3.12 Center of mass to center of mass radial distribution functions for different DFM mole fractions; (a) *n*-propanol/*n*-propanol (b) DFM/*n*-propanol and (c) DFM/DFM

For DFM/DFM COM-RDFs (Figure 3.12 (c)) the peak heights are relatively small and less influenced by the variation of DFM mole fraction compared to *n*-propanol/*n*-propanol but the peaks and first minima positions are preserved. When the mole fraction of *n*-propanol is decreased, the bulk density also decreases but the local density does not reduce proportionately (see equation 3.3). This may be attributed to clustering of *n*-propanol that causes less mixing of the two components. This behavior has also been observed in other studies of binary mixtures of acetone/methanol and Water/Acetonitrile[16,86]. The clusters of *n*-propanol in DFM rich environment are mainly stabilized by Van der Waal's interactions and strong hydrogen bonds. This is expected due to the strong hydrogen bonds associations between *n*-propanol molecules in pure systems[40].

At longer distances, second and third coordination shells are more pronounced for *n*-propanol/*n*-propanol for $x_1 = 0.1$ and 0.5 mixtures whereas for DFM/DFM only a second shell is pronounced for $x_1 = 0.9$ and 0.5. This shows long-range order for *n*-propanol at high

mole fraction than for DFM. At low mole fractions, long-range order diminishes for both mixture components with *n*-propanol showing two pronounced peaks while DFM shows only one peak. Thus, *n*-propanol is more structured at all mole fractions than DFM. From Figure 3.12 (b) it is clear that DFM and *n*-propanol interactions are similar at all mole fractions displaying long-range order but less so in comparison to *n*-propanol/*n*-propanol correlations.

c. *Coordination shell analysis*

To study the effect of composition on the solvation structure around each molecule, we have calculated the coordination numbers, which describe how many closest neighbors an atom, or molecule has. By integrating center of mass RDFs up to the first minimum, coordination number can be defined as

$$N_{ij} = 4\pi\rho_j \int_0^{R_{min}} g_{ij}(r)r^2 dr \quad (3.4)$$

where N_{ij} represents the number of species j surrounding species i in a shell extending from zero to R_{min} (the first minimum in the RDF) and ρ_j is the number density of species j . The coordination numbers of DFM and *n*-propanol molecules around *n*-propanol and DFM are presented in Table 3.3.

It is observed from Table 3.3 that when the mole fraction of the surrounding species in the mixture is increased its coordination number also increases. For pure systems, *n*-propanol is highly surrounded by the *n*-propanol molecules than DFM molecules are surrounding DFM. As the mole fraction of DFM is increased the number of *n*-propanol molecules around *n*-propanol (N_{22}) decreases which suggests that DFM takes up some of the local volume that was originally occupied by *n*-propanol molecules. The decrease in the number of DFM molecules around DFM molecules (N_{11}) as the mole fraction of *n*-propanol increases is also noticed.

To quantify this observation, we have calculated the ratio R_{ij} according to equation 3.5

$$R_{i \rightarrow j} = \frac{N_{ij}(x_i)}{N_{ii}(x_i=1) - N_{ii}(x_i)} \quad (3.5)$$

This may be interpreted as the number of j molecules replacing i molecules from a cluster of N_{ii} molecules relative to the number of i molecules replaced.

Table 3.3 Coordination numbers calculated from molecule-molecule center of mass radial distribution functions of DFM/n-propanol mixtures and pure systems.

x_{DFM}	N_{11} (DFM around DFM)	N_{12} (n -propanol around DFM)	N_{21} (DFM around n - propanol)	N_{22} (n -propanol around n - propanol)
0	0			13.11
0.1	2.33	14.56	1.53	11.21
0.2	4.30	11.66	2.92	9.98
0.3	6.22	8.88	3.80	8.44
0.4	7.32	7.80	5.20	7.11
0.5	8.87	6.01	5.90	6.21
0.6	9.52	4.57	6.85	4.95
0.7	9.82	3.26	7.61	3.84
0.8	10.97	2.13	8.50	2.57
0.9	11.94	1.05	9.26	1.48
1	12.3			0

Ideally, under ideal mixing conditions this ratio should remain constant at all compositions. As shown from Figure 3.13 at low DFM mole fractions for $x_1 \leq 0.4$ there are approximately 1.4 n -propanol molecules replacing each DFM molecule. The ratio fluctuates about $R_{1 \rightarrow 2} = 1.4$ as DFM mole fraction is increased but eventually increases sharply to $R_{1 \rightarrow 2} = 2.9$ for $x_1 = 0.9$. This deviation reflects the change in nature of interaction. The deviation for $R_{2 \rightarrow 1}$ fluctuates around 0.8 which is less in comparison to $R_{1 \rightarrow 2}$. This may be associated with the available space that an external molecule in the vicinity can enter after a loss of local molecule. The

space left by *n*-propanol molecule cannot accommodate a complete DFM molecule, but the space left by DFM molecule can accommodate more than one *n*-propanol molecules. For DFM's first solvation shell, a large distance between DFM molecules as evidenced from OF-OF RDFs and *ab initio* calculations, open the possibility of interstitial accommodation of *n*-propanol molecules, which may be through dipole-dipole or hydrogen bonding interactions. It may not be the case for DFM molecules surrounding *n*-propanol molecules since the distance between *n*-propanol molecules are relatively small and DFM being only hydrogen bond acceptor, would require *n*-propanol molecules that are not participating in hydrogen bonding within the cluster to draw the DFM molecules to the first solvation shell through hydrogen bonding interaction. This is less likely and would account for the observed values of $R_{2 \rightarrow 1}$.

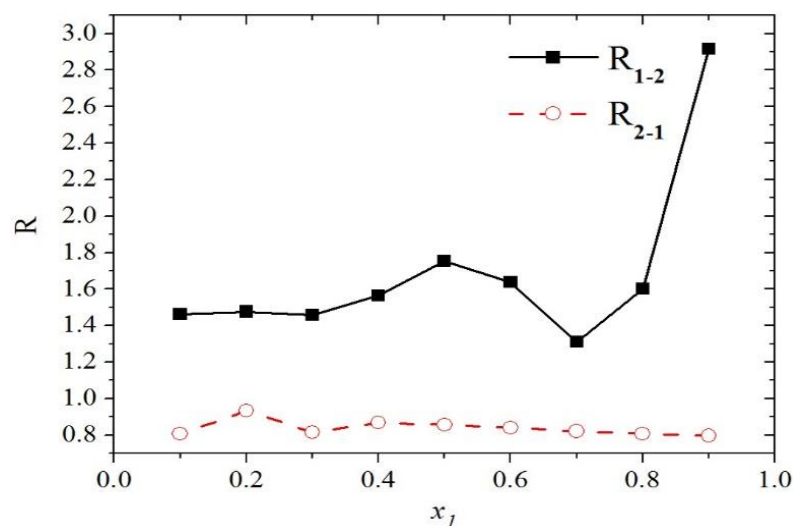


Figure 3.13 Ratio of *n*-propanol molecules replacing each DFM molecule around DFM (black line with closed square symbols) and ratio of DFM molecules replacing each *n*-propanol molecule around *n*-propanol (red dashed line with open circle symbols)

From Figure 3.13 the trends show that the first coordination shell of DFM is able to accommodate a large number of *n*-propanol molecules at all composition than the first coordination shell of *n*-propanol occupying DFM molecules. The difference in the number of molecules (shift from linearity) replaced as the mole fraction is altered also reflects the non-ideal mixing in the present systems[80]. It is more apparent in the replacement of DFM molecules by *n*-propanol around DFM. This could be attributed to enhanced hydrogen bonding interaction and the size of the molecules. The less bulky the molecule the better they can enter the local solvation shell.

Site to site coordination numbers for $x_1 = 0.1, 0.5$ and 0.9 mixtures were further calculated and examined. The coordination numbers in the first shell for OA-OA as well as HA-OF and OF-OF are summarized in Table 3.4. The data is compared with pure systems.

*Table 3.4 Coordination numbers for site-site radial distribution functions of Difurylmethane/*n*-propanol mixtures and pure systems.*

x_{DFM}	OA-OA <i>n</i> -propanol/ <i>n</i> -propanol	HA-OF <i>n</i> -propanol/DFM	OF-OF DFM/DFM
0	1.91		
0.1	1.85	0.11	1.60
0.5	1.47	0.08	3.12
0.9	0.62	0.02	4.07
1			4.29

For OA-OA in pure system, the coordination number is consistent with reported values[46]. When the mole fraction of DFM is increased the coordination numbers of OA-OA and HA-OF reduces which is a sign of hydrogen bond disruption. It is more apparent in the range $x_1 = 0.1 - 0.5$ than in $x_1 = 0.5 - 0.9$ mixtures. This means there is enhanced hydrogen bonding between *n*-propanol and *n*-propanol/DFM molecules at high *n*-propanol mole fractions. The coordination number calculated for HA-OF is extremely low which is not surprising as most of acidic hydrogen participates in hydrogen bonding between *n*-propanol molecules. The OF-OF coordination numbers also increase with increase in DFM mole fraction which signifies better association of DFM molecules at high DFM mole fractions.

To further probe local composition of binary mixtures, excess local mole fractions, δx , of component *i* were calculated as follows

$$\delta x = x_i^{local} - x_i^{bulk} \quad (3.6)$$

$$x_i^{local} = \frac{N_{ii} + N_{ij}}{N_{ii} + N_{ij} + N_{jj} + N_{ji}} \quad (3.7)$$

where x_i^{bulk} is the ideal bulk mole fraction of component i , x_i^{local} is the local mole fraction of component i calculated based on RDF first minimum. The coordination numbers are those from Table 3.3.

For a binary mixture excess local mole fraction can be thought of as preferential solvation[87], the more positive δx the better solvated is component i . From Figure 3.14 at low DFM mole fraction there is an increase in excess local mole fraction and a maximum is observed for $x_1 = 0.3$. However, at high mole fractions there is a decrease in excess mole fraction with a minimum observed for $x_1 = 0.9$. Interestingly, it is at these compositions that the minimum and maximum in the calculated excess molar volumes are observed. This implies that the local composition influences the bulk behavior of the mixture. In general, formation of clusters will lead to positive values of δx and negative values of δx with respect to the other component.

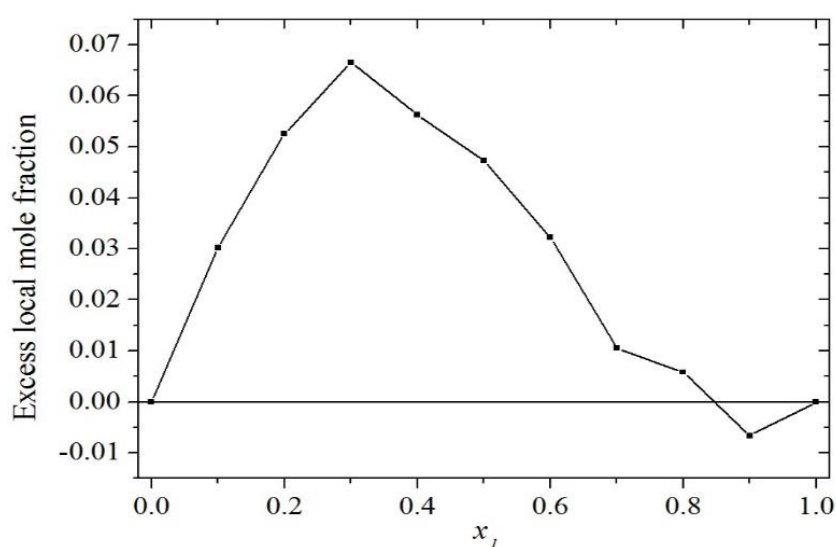


Figure 3.14 Excess local mole fraction of *n*-propanol as a function of DFM mole fraction

d. Conformational analysis

Studies on molecular structures of *n*-propanol has shown that *n*-propanol molecule at room temperature has five non-equivalent conformers (see Table 3.5): Tt (*Trans-trans*), Tg+ (*Trans-gauche+*), Gt (*Gauche-trans*), Gg+ (*Gauche-gauche+*), Gg- (*Gauche-gauche-*) determined from C-C-C-O and C-C-O-H dihedral angles [88,89]. The dihedral angle distributions can give information about the most dominant conformer under specified conditions.

Table 3.5 The main structural differences of the five conformers of *n*-propanol

Dihedral	Tt	Tg ⁺	Gt	Gg ⁺	Gg ⁻
C-C-C-O (degrees)	180 ⁰	180 ⁰	60 ⁰	60 ⁰	60 ⁰
C-C-O-H (degrees)	180 ⁰	60 ⁰	180 ⁰	60 ⁰	-60 ⁰

The structure of the conformers determines whether hydrogen bonding is favored or not. From Figure 3.15, it must be noted that some conformers have an orientation that has the oxygen or acidic hydrogen more or less encumbered by the alkyl chain. To study effect of DFM composition on the *n*-propanol conformer population, the dihedral angle distribution for pure *n*-propanol C-C-C-O, C-C-O-H and H-C-O-H dihedral angles were calculated and compared with those of mixtures ($x_1 = 0.1, 0.5$ and 0.9).

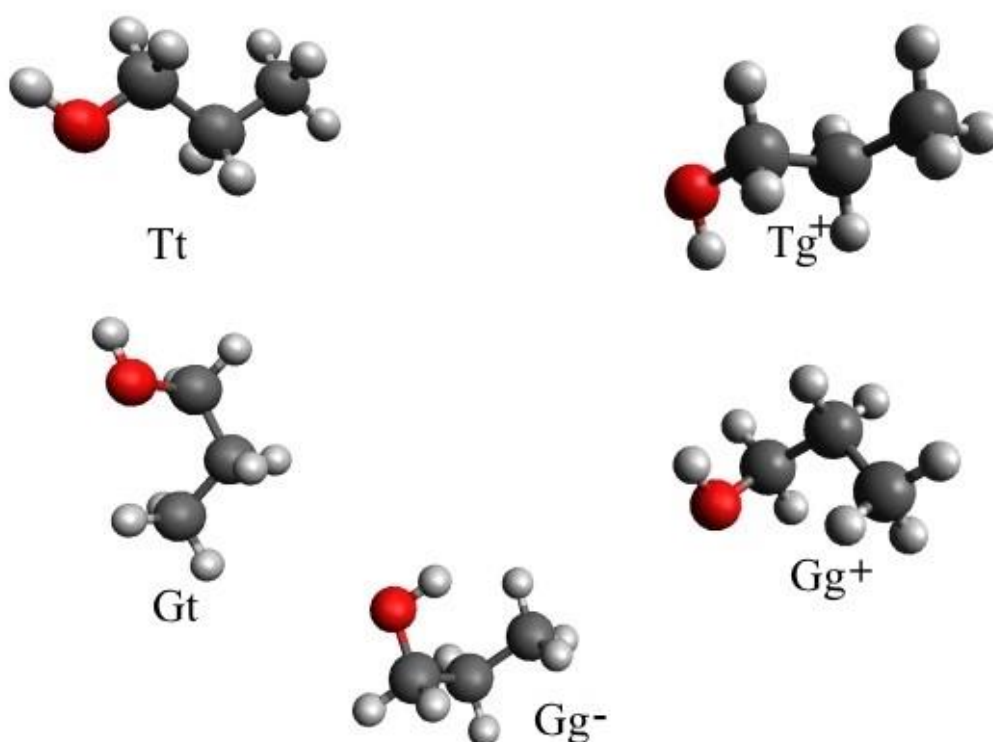


Figure 3.15 Geometry structures of the five conformers: Tt, Tg⁺, Gt, Gg⁺ and Gg⁻ of *n*-propanol.

From Figure 3.16 (a) for pure *n*-propanol the most dominant conformer is trans conformer which is consistent with Jorgensen's calculations[46]. The same trend is observed for $x_1 = 0.1$ and 0.5 mixtures. For $x_1 = 0.9$ the trend takes a shift with the most dominant conformer being the gauche conformer. This shows that the most stable conformer at high *n*-propanol mole fractions is the trans conformer while the gauche conformer is the more stable for lower mole fractions. The C-C-O-H and H-C-O-H dihedral angle distributions also support this observation as shown in Figure 3.16 (b-c). The oxygen atoms in Gg- and Gg+ isomers are less encumbered by the alkyl chain than the acidic hydrogen atoms making the molecule more of hydrogen bond acceptor than a donor. When comparing Tt and Gg+, it can be realized that Tt can be both a better Hydrogen bond donor and acceptor than Gg+. This supports the observation that there is enhanced hydrogen bonding at higher *n*-propanol mole fractions. For all the calculated dihedral distributions from Figures 3.16 and 3.17, a shift in dihedral angle is observed only for distributions involving the acidic hydrogen atom. The C-C-O-H and H-C-O-H dihedral distributions show a slight shift for $x_1 = 0.5$. At high DFM mole fraction ($x_1 = 0.9$), a significant angle shift is more apparent. This indicates that the presence of DFM molecules disrupt the intermolecular *n*-propanol hydrogen bonding by itself participating in hydrogen bonding.

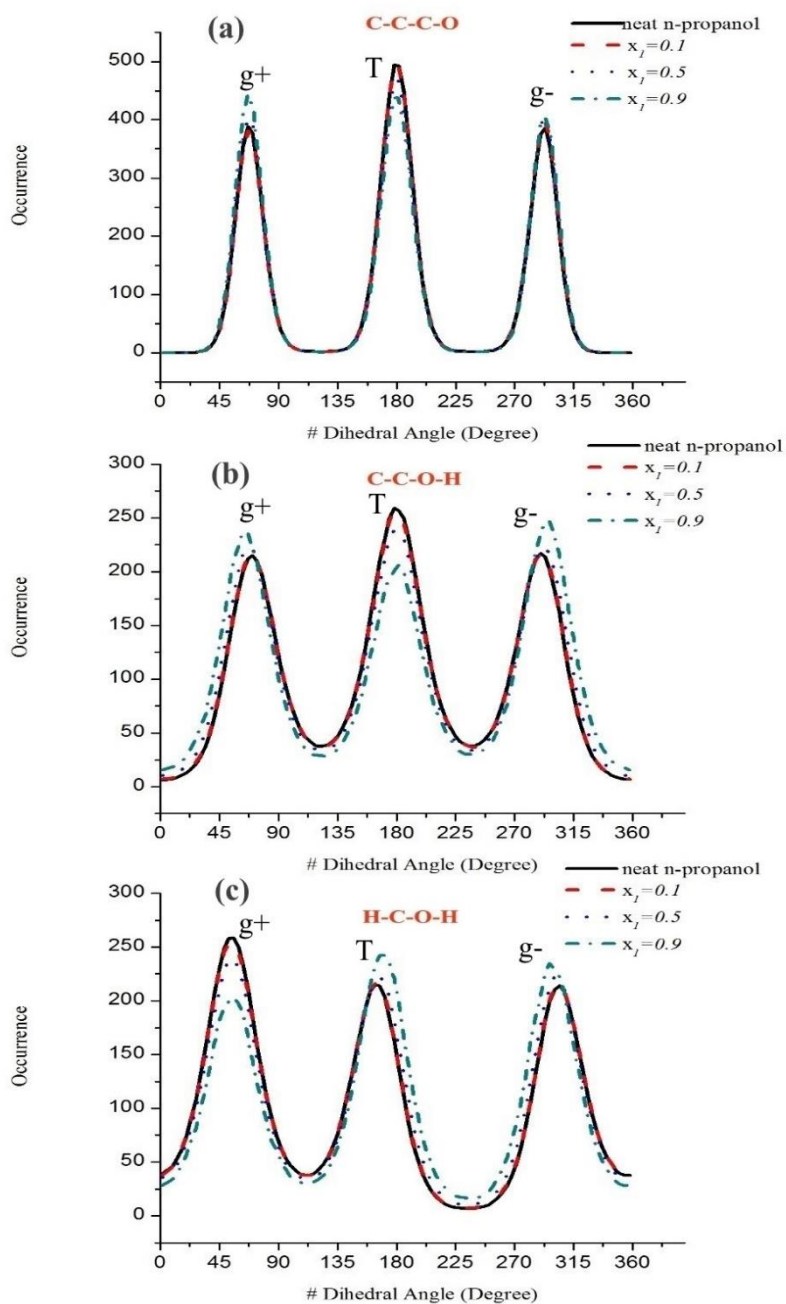


Figure 3.16 Dihedral angle distributions for C-C-C-O, C-C-O-H and H-C-O-H dihedral angles for n-propanol (where T represents Trans conformer and g^+ and g^- represent gauche conformers of 60° and -60° respectively)

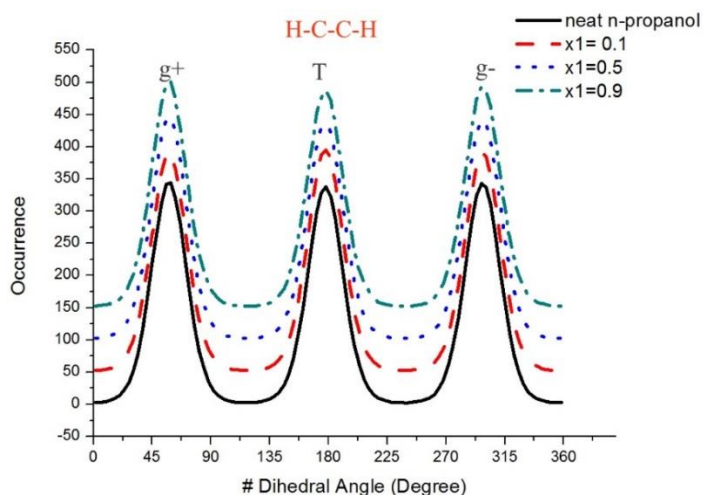


Figure 3.17 Dihedral angle distributions for H-C-C-H dihedral angle for *n*-propanol. Peaks offset by 50 units for clarity.

3.3 Conclusions

In this Chapter, we have studied the thermodynamic properties and structure of DFM and *n*-propanol binary mixtures. The densities and molar volumes for all systems are in good agreement with experimental data with a difference of less than 2%. The enthalpy of vaporization and isothermal compressibility for *n*-propanol is also in agreement with literature values. For the calculated isothermal compressibility of DFM, it must be pointed out however that the data is not direct experimental measurements. The experimental excess molar volumes are well captured by the theoretically derived model with a minimum and maximum at $x_1 = 0.2$ and 0.9 respectively.

For structural aspects, radial distribution functions are applied. The results show that when the mole fraction of DFM is decreased the peaks and minima positions are preserved indicating insignificant changes in the local structures. However, *n*-propanol tends to form tight clusters in comparison to DFM. From the RDF and lowest energy structure there is evidence of weak hydrogen bonding interaction between *n*-propanol and DFM via acidic hydrogen and one of the oxygen. The coordination numbers for all systems have been obtained by integrating the respective RDFs. The results show that *n*-propanol is able to accommodate the local volume of DFM rather easily than DFM occupies the local volume of *n*-propanol. Coordination numbers of selected sites show that at $x_1 = 0.1$ and 0.5 hydrogen bond breakdown is less than $x_1 =$

0.5 and 0.9. The excess local mole fractions also reveal the tendency of DFM to cluster at low concentrations. The dihedral angle distributions reveal the most stable conformers for various mole fractions of DFM. The shift in the dihedral angle for those involving the *n*-propanol acidic hydrogen proves that DFM and *n*-propanol are able to interact through hydrogen bonding.

Chapter IV

4 CASE STUDY 2: Comparative molecular dynamics simulation study of 2,2'-difurylmethane with *n*-propanol and *n*-butanol liquid mixtures

Introduction

In this Chapter, DFM/*n*-propanol mixtures are revisited to serve as reference systems for comparison with DFM/*n*-butanol mixtures. The latter also exhibits negative and positive deviations of the excess molar volumes over the whole composition range of DFM mole fractions. However, unlike DFM/*n*-propanol mixture, the DFM/*n*-butanol mixtures show mostly positive deviations with negative deviations mainly occurring at low DFM mole fractions (see Figure 4.1).

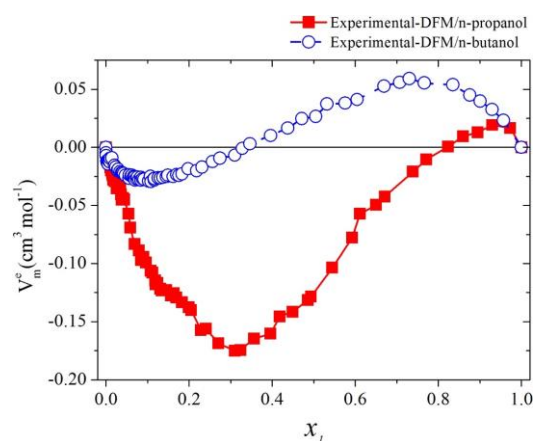


Figure 4.1 Comparison of experimental excess molar volumes for DFM/*n*-propanol and DFM/*n*-butanol mixtures[9].

4.1 Simulation details

Molecular Dynamics simulations of pure and mixtures of DFM/*n*-butanol using OPLS-AA force fields have been performed for mole fraction compositions of DFM ranging from 0.0 to 1.0 using the DL_POLY Classic code[72]. The Lennard-Jones parameters used for DFM/*n*-propanol mixtures were also applied for DFM/*n*-butanol. *Ab initio* molecular geometries of *n*-butanol and DFM/*n*-butanol dimers were optimized at the Hartree-Fock theory using the 6-31G (d) basis set. All *ab initio* calculations were performed using GAMESS-US program[68,75]. The initial configurations of all mixtures comprising of 1000 molecules (DFM + *n*-butanol) with distance tolerance of 2.0 Å in a cubic box of size (60 * 60 * 60) Å³ were generated using Packmol[76].

Isothermal-isobaric ensemble dynamics were performed at 1 atm and 298.15 K by applying Nose-Hoover thermostat and barostat with relaxation times of 0.1 ps and 0.5 ps, respectively. Verlet leapfrog algorithms were used with a timestep of 1 fs for the integration of Newton's equations of motion in all the calculations. Each system was equilibrated for 350 ps, which was sufficient to establish equilibrium values for the energies and volumes. The statistics were sampled over 400 ps of production runs. A cut-off distance of 1.2 nm was applied for both the van der Waals interactions and electrostatic interactions, which were evaluated using the smooth particle-mesh-ewald technique[77].

4.2 Results and Discussions

In the previous Chapter, the importance of system monitoring to assess its stability was emphasized. Figure 4.2 shows the (pressure, temperature, configurational energy and volume) profiles for DFM/*n*-butanol mixture ($x_1 = 0.5$). From Figure 4.2 (a – b) it is clear that after equilibration period (350 ps) the fluctuations occur about the desired pressure and temperature. Also evident are the equilibrated configurational energy (Figure 4.2 c) and volume (Figure 4.2 d). These profiles indicate that, as in the case of DFM/*n*-propanol mixtures, DFM/*n*-butanol binary mixtures were also stable which vindicated an investigation on thermodynamic and structural properties.

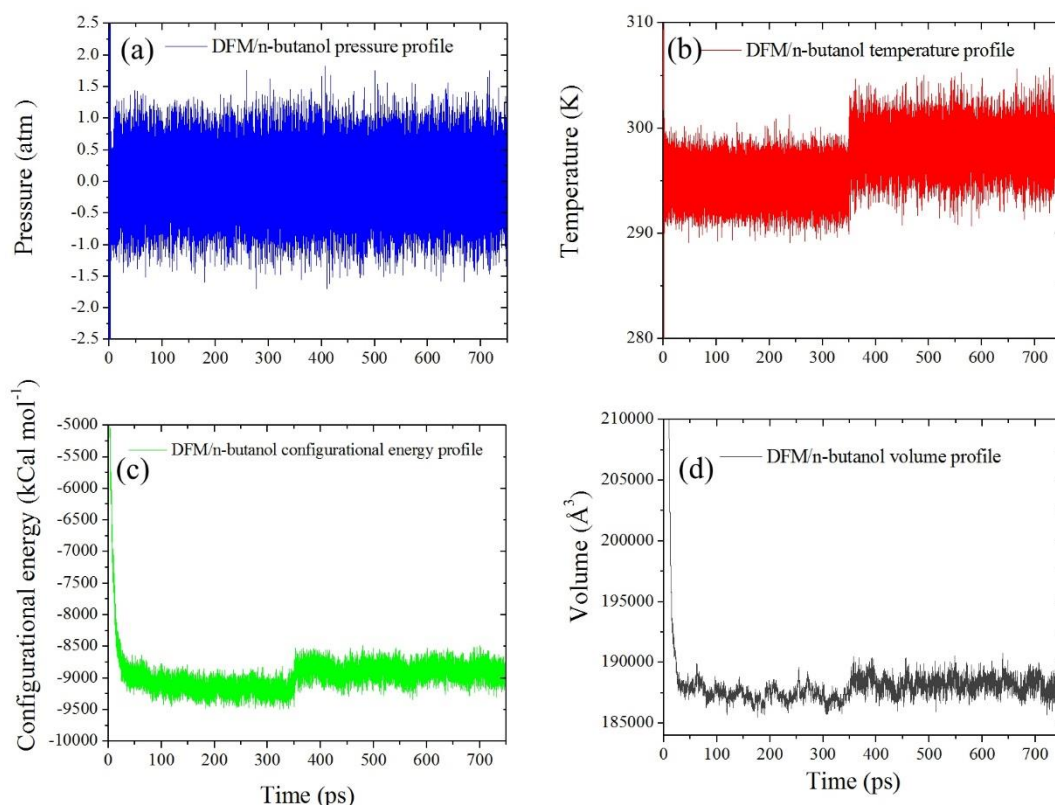


Figure 4.2 (a) Pressure, (b) temperature, (c) configurational energy and (d) volume profiles for DFM/*n*-butanol ($x_1 = 0.5$) as a function of time.

4.2.1 Thermodynamic properties

We pointed out earlier that thermodynamic properties like density are related to the internal structure and molecular interactions of liquid mixtures. Thus, the density for all mixtures were calculated for the entire composition range (from $x_1(\text{DFM}) = 0 - 1$ at 0.1 intervals) and compared with experimental results. For *n*-butanol

Figure 4.3 shows the densities (top panel) and excess volumes (lower panel) for DFM/*n*-butanol mixtures. The general trend for the simulated densities for all the mixtures is in accord with the experimental values. As expected, the density and the deviation from experimental results increase with increasing x_1 .

The relation of density to structure becomes more vivid when deducing excess molar volumes.

Figure 4.3 (b) presents the simulated and experimental excess molar volumes.

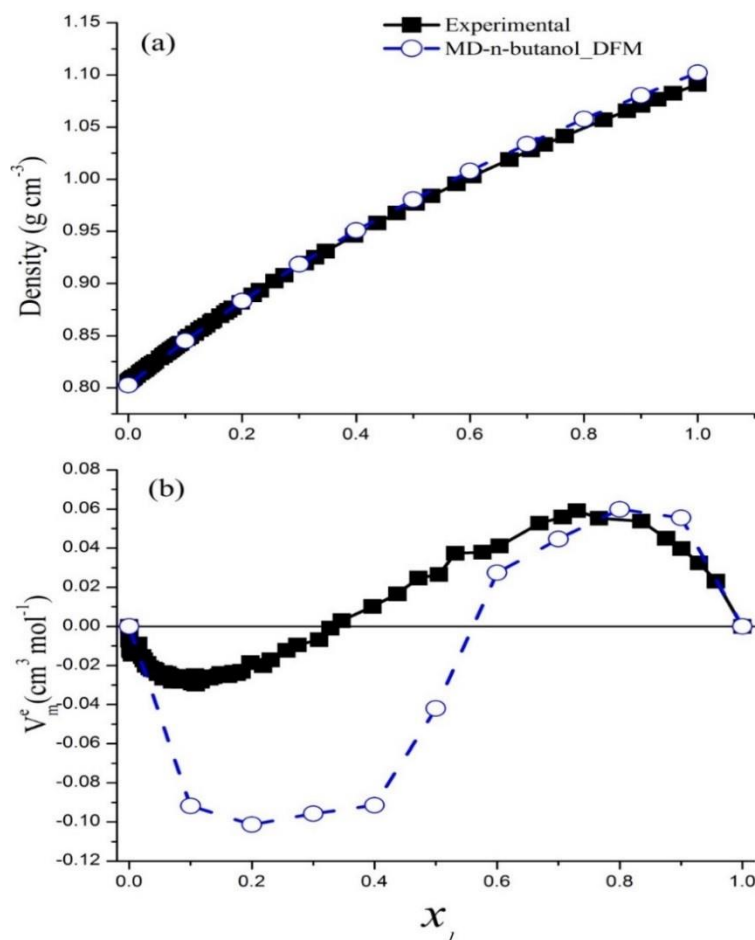


Figure 4.3 Calculated values (open blue circles) and experimental values[9] (closed black squares) for (a) the densities and (b) excess molar volumes of DFM/*n*-butanol mixtures as a function of DFM mole fraction.

This thermodynamic property depends on the density of the mixture as well as the densities of the pure components (see equation 1.1). This means that if the simulated density of pure components or the mixture does not exactly reproduce the experimental results, one may expect slightly different excess volumes, which explains the deviation of simulated excess molar volumes from experimental values. However, as in the case of DFM/*n*-propanol mixtures, the general trend is also well captured for DFM/*n*-butanol. It is clear that both simulated and experimental excess volumes assume both negative and positive values. The deviation between molecular dynamics and experiment in DFM/*n*-butanol results seem to be worse than that in

DFM/*n*-propanol. This may be due to a large number of possible isomers that could be formed by *n*-butanol, which brings some complexity to the DFM/*n*-butanol mixtures. However, the trends in experimental values are well captured by the calculated excess molar volumes. The point where the deviations tend to positive and the extent of negative deviation in DFM/*n*-butanol experiment are less than that of DFM/*n*-propanol, as in the simulation (Figure 4.4).

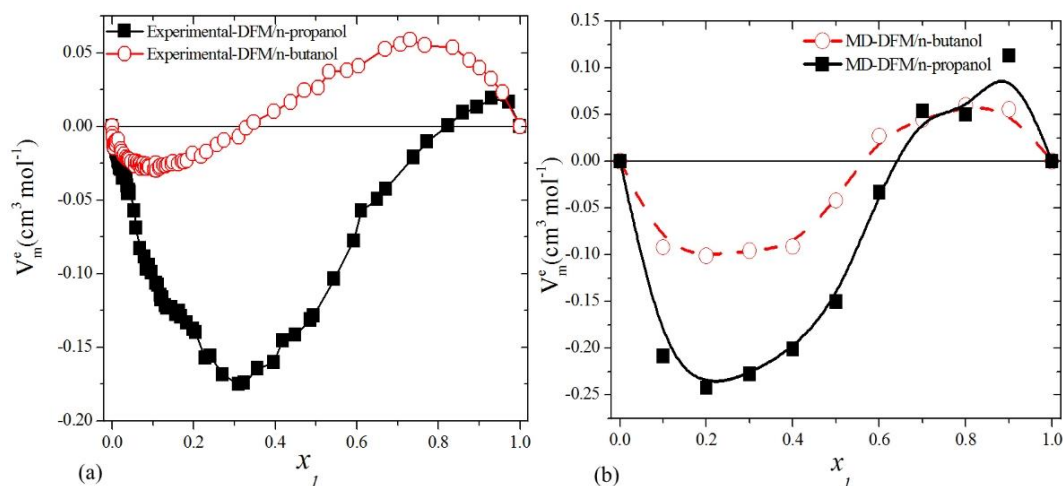


Figure 4.4 Comparison between experimental and simulated excess molar volumes for DFM/*n*-propanol and DFM/*n*-butanol mixtures

4.2.2 Structural properties

The fact that alcohols associate through strong hydrogen bonding and the evidence (from Chapter III) that DFM/*n*-propanol can interact through weak hydrogen bonding allows us to investigate the current systems' oxygen-oxygen self and cross correlations. The extra $-\text{CH}_2$ group in *n*-butanol also presents the opportunity to study the effect of the terminal methyl carbon-carbon correlations. In this section, we present the radial distribution functions, coordination numbers and the dihedral angle distributions of DFM/*n*-butanol mixtures.

a. Atom-atom radial distributions

The selected site-to-site radial distribution functions (ssRDFs) of DFM/*n*-butanol mixtures for various mole fractions of DFM are shown in Figure 4.5. For both molecules the selected sites

are the oxygen atoms and the terminal methyl carbon of *n*-butanol, these sites are investigated for comparison with DFM/*n*-propanol systems.

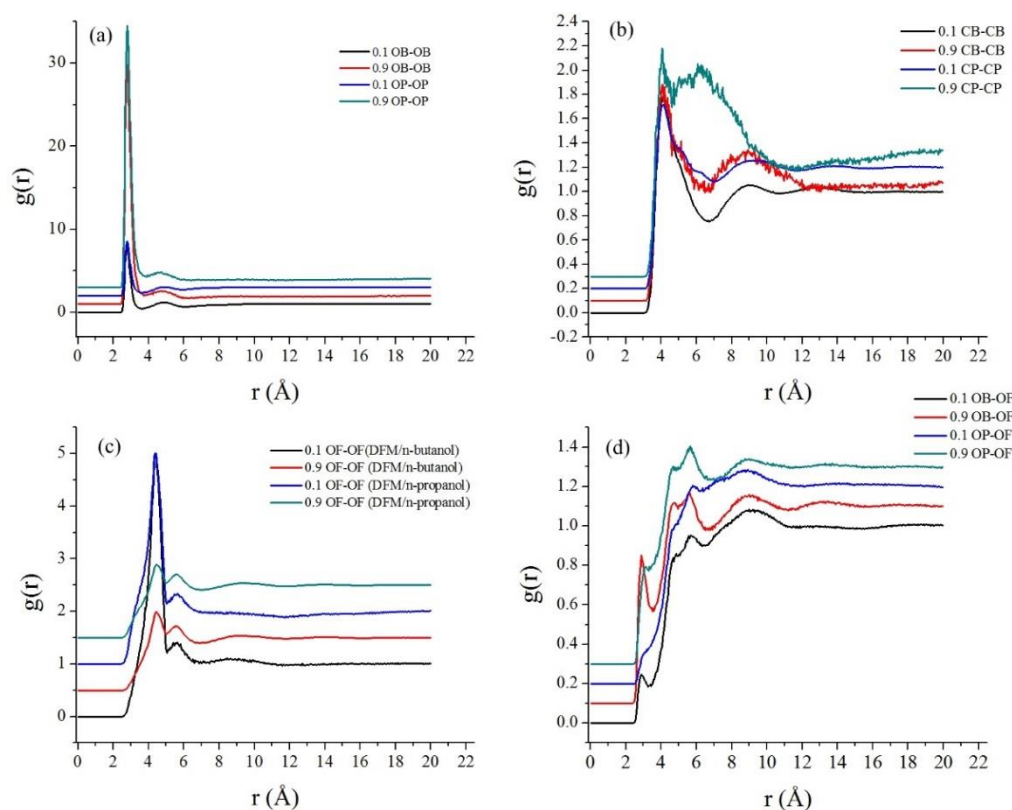


Figure 4.5 Selected site to site radial distribution functions for *n*-butanol/*n*-butanol, *n*-propanol/*n*-propanol and DFM/DFM as well as DFM/alcohol calculated for DFM mole fractions of $x_1 = 0.1$ and 0.9

The oxygen atoms from *n*-butanol and DFM are denoted OB and OF respectively, while the terminal methyl carbon is denoted CB. For *n*-propanol, the oxygen and carbon atoms are denoted OP and CP respectively. As stated earlier, the difference between *n*-propanol and *n*-butanol is with respect to the extra $-\text{CH}_2$ in *n*-butanol. Therefore, it is not surprising to see OB–OB RDFs (Figure 4.5 a) behaving similarly to OP–OP RDFs. For OB–OB, the first and second peak maxima appear at 2.79–2.83 Å and 4.86–4.90 Å, which is consistent with the OP–OP RDFs. The OB–OB peak heights also show greater sensitivity as x_1 varies. As x_1 increases, the peak height increases dramatically due to clustering in DFM rich regions.

For CB–CB RDFs the two prominent peaks are centered at 4.05–4.12 Å and 8.93–9.08 Å (Figure 4.5 b). The peak shoulders appearing on the right-hand side of the first coordination

shell of CP–CP RDFs are absent for CB–CB. The first peak positions are consistent with those of CP–CP. The first coordination shell peak height for CB–CB is extremely insensitive to changes in x_1 . This shows the methyl groups in DFM/*n*-butanol are more randomly distributed for various mole fractions of DFM[16]. Also noticed is that the second peak position is preserved for higher x_1 , which is not the case for CP–CP.

The OF–OF RDFs show peaks centered at 4.36–4.43 Å, 5.53 – 5.69 Å and 9.04 –9.12 Å (Figure 4.5 c). These peaks are similar to the OF–OF peaks from DFM/*n*-propanol mixtures. As x_1 increases, the peak heights reduce showing more random distributions. The peak heights for OF–OF RDFs in DFM/*n*-butanol are higher than in DFM/*n*-propanol at all x_1 indicating more systematic distribution of DFM-DFM clusters in DFM/*n*-butanol mixtures.

For OB–OF interactions, we refer to Figure 4.4 (d) and 4.5. The RDFs show four coordination shells centered at 2.87–2.95 Å, 4.70–4.86 Å, 5.60–5.68 Å and 9.00–9.19 Å. These peak positions are fairly close to those of OP–OF peak positions. The first peak for OB–OF which is due to hydrogen bonding interaction between DFM oxygen and *n*-butanol acidic hydrogen are narrower and appear at relatively shorter distance than for OP–OF signifying a stronger interaction than in DFM/*n*-propanol. This is corroborated by the *ab initio* calculations, (3.109 Å for OB–OF and 3.118 Å for OP–OF). The OB–OF peak height magnitude exceeds that of OP–OF but shows the same tendency to increase as x_1 is increased. The increase as x_1 is increased and the preserved positions of the peaks mean the local structure is maintained for various x_1 .

A detailed analysis for the ssRDFs from Figure 4.5 a-d illustrate that even though the interactions are similar, the differences are in hydrogen bonding between DFM and alcohol, alcohol methyl-methyl and DFM-DFM cluster structures in the two environments of these mixtures.

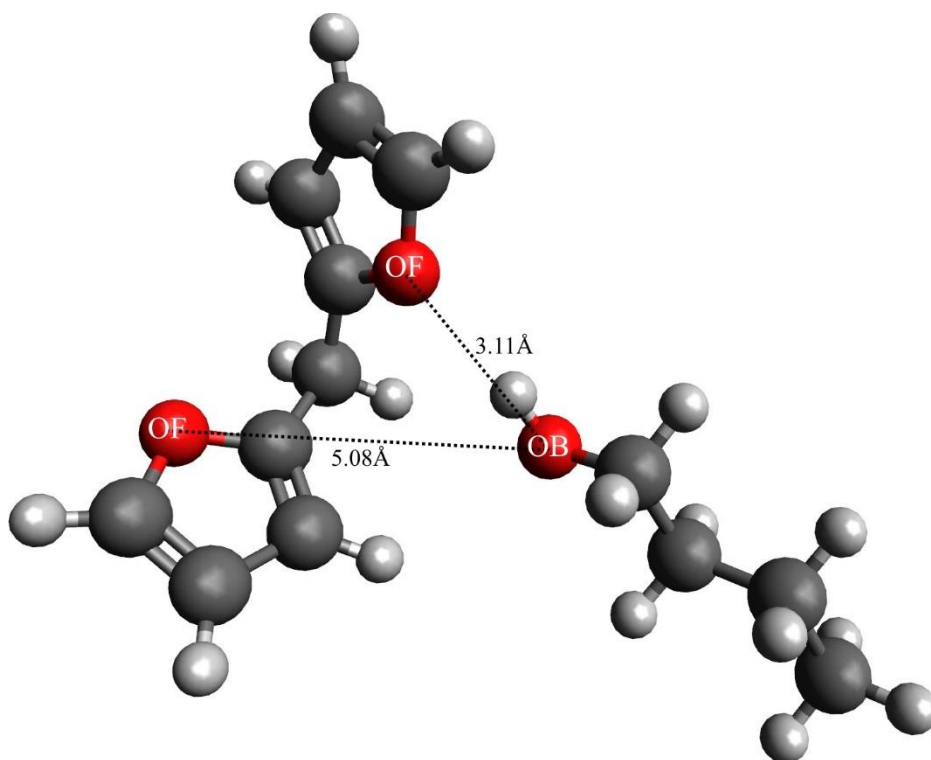


Figure 4.6 HF/6-31G (d) lowest energy optimized geometry of DFM/*n*-butanol dimer.

b. *Molecule-molecule center of mass radial distributions*

Figure 4.7 shows the center of geometry RDFs for *n*-propanol and *n*-butanol in DFM environment as well as DFM in *n*-propanol and *n*-butanol environments. In particular, Figure 4.7 (a) presents the self-correlations between the two alcohols. For *n*-propanol, two distinct coordination shells can be identified in the RDFs. The peaks are centered at 4.7-5.0 Å and 9.8 Å. These positions are well preserved as x_1 is varied. The center of geometry RDFs for *n*-butanol also reveal these distinct peaks, which occur at slightly longer distance than for *n*-propanol due to the different molecular sizes and orientations. The first peak is located at 5.25-5.35 Å, while the second 10.2 Å. As the mole fraction of DFM is varied, the peak positions are preserved which is consistent with those of *n*-propanol. In comparison, the peak height magnitudes for both molecules differ at various compositions. The peaks for *n*-propanol are narrower and appear closer to the reference point indicating that *n*-propanol molecules are closer to one another than *n*-butanol molecules. This can be attributed to the tight clusters formed by *n*-propanol molecules due to their smaller molecular sizes.

With the exception of $x_1 = 0.1$ for DFM/*n*-propanol, two coordination shells appear. For DFM-DFM RDFs in both *n*-propanol and *n*-butanol mixtures (see Figure 4.7 (b)). For both systems, two peaks characterize the first coordination shell. DFM has its center of mass located in both the furan rings. Therefore, the peak at 5.65-5.75 Å is due to the correlation with the first ring. Consequently, the second peak located at 6.75-6.85 Å is due to the correlations with the center of mass centered on the other furan ring. For visual conceptualization, Figure 4.8 is used to illustrate this point. From a reference molecule's center of mass (point *x*) to the center of mass (point *y*) of the target molecule, the distance as calculated from the geometry-optimized dimer is 5.9 Å, which is in close agreement with where the first peak is located. From the reference molecule's center of mass (point *x*) to the other center of geometry (point *z*), the calculated distance is 7.4 Å, which is also fairly close to the values from the RDFs. For both systems, the peak positions are well preserved, in fact the differences between the peak positions for both systems are insignificant.

Figure 4.7 (c) shows the RDFs for DFM and the two alcohols correlations. The RDFs show three distinct coordination shells, the first of which is characterized by a shoulder on the right-hand side. This is not surprising, as we have previously pointed out that DFM has two center of mass points, which means the observed shoulder occurs merely due to the correlations with the second furan ring. Even though the peak positions are relatively well preserved, the second coordination shell of DFM and *n*-butanol for $x_1 = 0.9$ appear to have shifted towards the right-hand side whereas the peak for $x_1 = 0.1$ is more to the left-hand side in comparison to DFM and *n*-propanol correlations. The shift to the right means the molecules are farther apart which causes volume expansions. The peaks for DFM and *n*-propanol are located at 5.55 Å, 10.45 Å, and 14.85 Å whereas those of DFM and *n*-butanol correlations are located at 5.5-5.6 Å, 10-10.9 Å, and 14.95-15.05 Å.

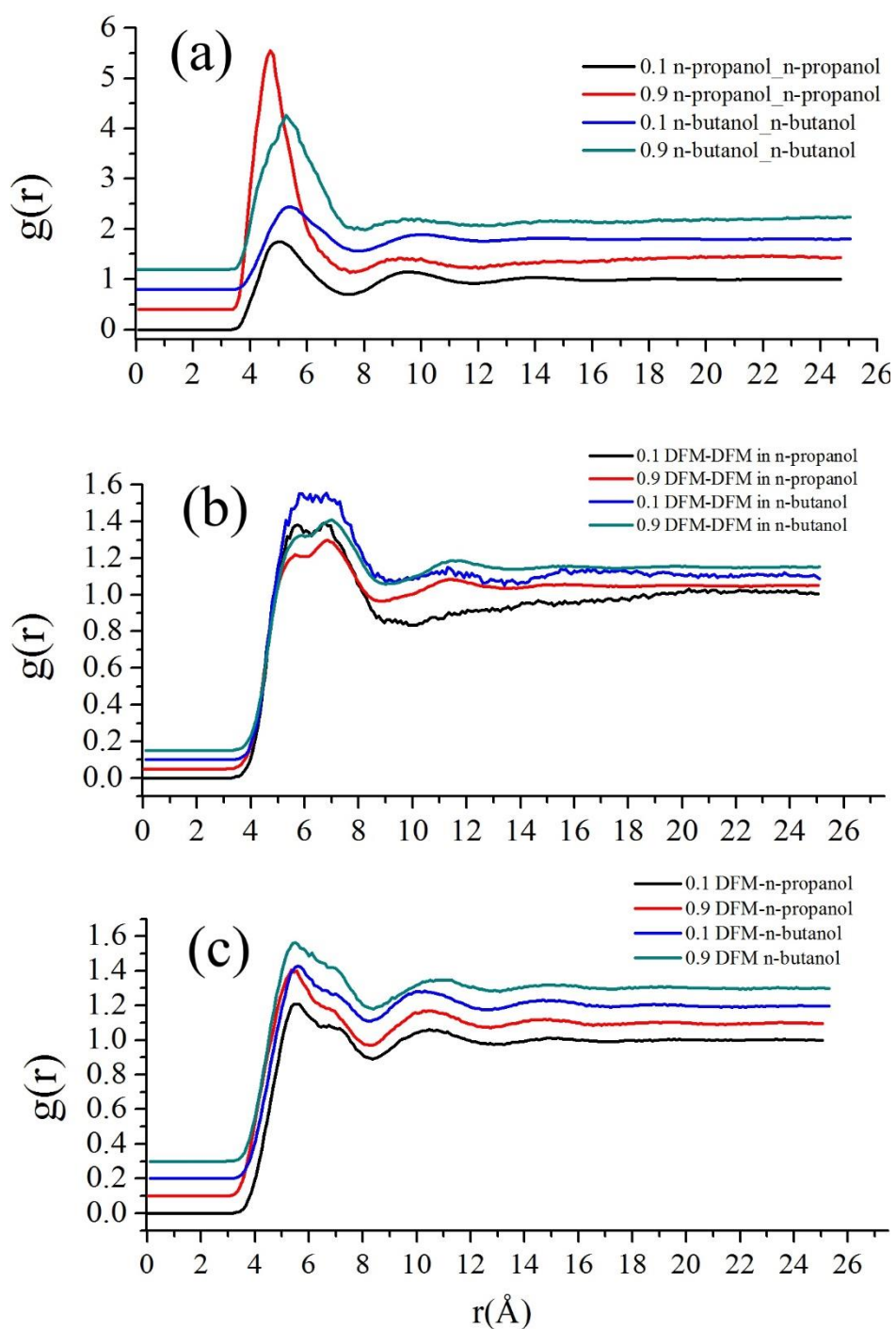


Figure 4.7 Center of mass radial distribution functions calculated for $x_1 = 0.1$ and 0.9 for (a) n-propanol/n-propanol and n-butanol/n-butanol (b) DFM-DFM in n-propanol and n-butanol environments and (c) DFM/n-propanol and DFM/n-butanol

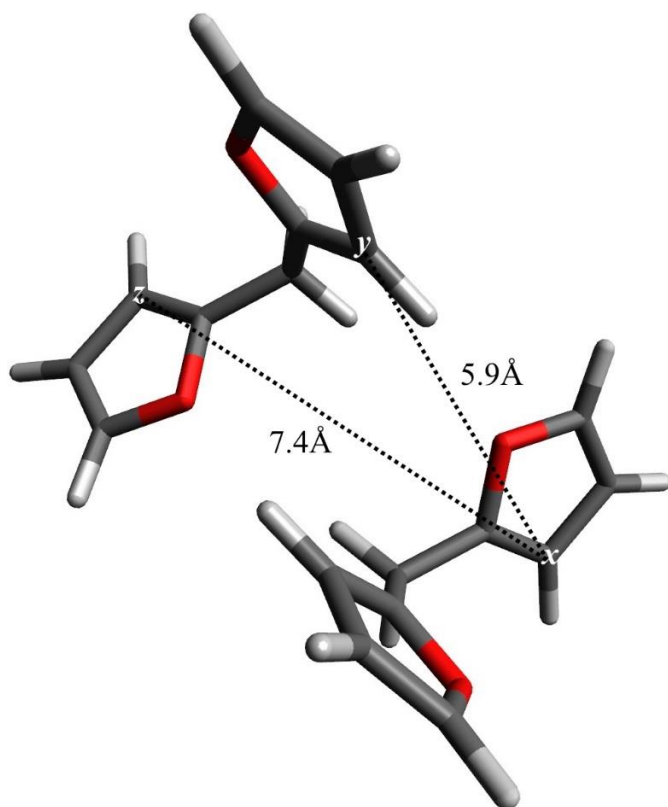


Figure 4.8 HF/6-31G (d) lowest energy optimized geometry of DFM dimer showing the center of mass to center of mass interactions.

The coordination numbers (N_{ii}) of the molecules in pure and mixtures for the first coordination shell have been calculated by integrating the center of geometry RDFs up to the first minimum. Table 4.1 presents the coordination numbers of DFM and *n*-butanol molecules. The calculated coordination numbers for DFM and *n*-butanol show a similar trend shown by the DFM/*n*-propanol mixtures.

With an increase in x_1 there is a decrease in N_{22} , this is also noticed for N_{11} as x_2 is increased. Interestingly, in comparison to DFM/*n*-propanol coordination numbers, N_{22} , N_{12} and N_{21} values for DFM/*n*-butanol are all less than the values for DFM/*n*-propanol. This implies that, the mixtures of DFM/*n*-butanol are less homogenously mixed than DFM/*n*-propanol mixtures. An exception is with respect to N_{11} , for DFM/*n*-butanol mixtures (of composition range $x_1 = 0.7 - 0.9$), the values of which are higher than for DFM/*n*-propanol of the same composition. It has been shown from *ab initio* calculations and RDFs that the intermolecular distances between DFM molecules are relatively large, hence the large N_{11} explains why DFM/*n*-butanol volume expansions are observed for earlier x_1 than DFM/*n*-propanol.

As in the previous Chapter we have calculated the R_{ij} values according to equation 3.6, Figure 4.9 illustrates the differences between $R_{1\rightarrow 2}$ and $R_{2\rightarrow 1}$ for the mixtures of DFM/*n*-propanol and DFM/*n*-butanol. For the $R_{1\rightarrow 2}$ of DFM/*n*-propanol, which shows the number of *n*-propanol molecules occupying the free volume left by an exit of DFM molecule from the coordination shell, the ratio fluctuates around 1.46-1.75 and suddenly increases to 2.92 for $x_1 = 0.9$. The $R_{1\rightarrow 2}$ for DFM/*n*-butanol increases gradually from 1.22 – 1.79 and eventually increases sharply to 3.96 for $x_1 = 0.9$. The $R_{1\rightarrow 2}$ for DFM/*n*-butanol shows better linearity than $R_{1\rightarrow 2}$ for DFM/*n*-propanol. The linearity signifies ideality, the more linear the R values the more ideal the system is. The better linearity of $R_{1\rightarrow 2}$ for DFM/*n*-butanol than for DFM/*n*-propanol is not surprising given that for the calculated excess molar volumes, a shift from $V_m^e = 0$ is more for DFM/*n*-propanol. The $R_{1\rightarrow 2}$ in the composition range $x_1 = 0.7 - 0.9$ for DFM/*n*-butanol exceeds those of DFM/*n*-propanol.

*Table 4.1 Coordination numbers calculated from molecule-molecule center of mass radial distribution functions of DFM/*n*-butanol mixtures and pure systems. For comparison with DFM/*n*-propanol mixtures, see Table 3.3.*

x_{DFM}	N_{11} (DFM around DFM)	N_{12} (<i>n</i> -butanol around DFM)	N_{21} (DFM around <i>n</i> -butanol)	N_{22} (<i>n</i> -butanol around <i>n</i> -butanol)
0	0			12.30
0.1	2.21	12.35	1.37	10.76
0.2	3.71	10.44	2.61	9.37
0.3	5.22	8.77	3.76	8.08
0.4	7.32	7.00	4.67	7.07
0.5	7.97	5.63	5.63	5.96
0.6	9.15	4.33	6.49	4.98
0.7	10.16	3.17	7.40	3.74
0.8	11.14	2.07	8.29	2.86
0.9	12.03	1.06	9.52	1.36
1	12.30			0

For the $R_{2\rightarrow 1}$ of DFM/*n*-propanol, which signifies the number of DFM molecules occupying the available free volumes left by an *n*-propanol molecule. The $R_{2\rightarrow 1}$ fluctuates around 0.79 –

0.87. This shows that a complete DFM molecule is unable to occupy the full space left by *n*-propanol molecule. From the geometry optimized DFM/*n*-propanol dimer (

Figure 3.10) and the RDFs for center of mass between DFM and *n*-propanol (Figure 4.7) we have shown that the interactions occur between the first furan ring at a shorter distance and with the second furan ring at longer distance. This means the complete first furan ring is most likely to occupy the available space while only part of the second furan ring occupies the available space. The $R_{2 \rightarrow 1}$ values for DFM/*n*-butanol exceed those of DFM/*n*-propanol as they fluctuate around 0.83-0.90 and shows better linearity than $R_{2 \rightarrow 1}$ for DFM/*n*-propanol.

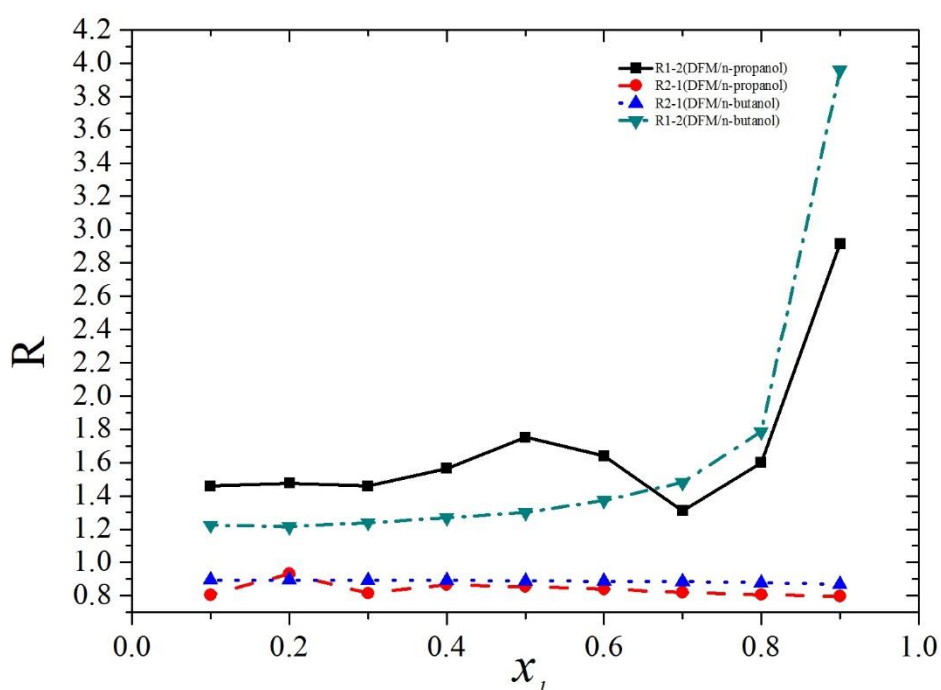


Figure 4.9 The ratio of *n*-butanol (in green) and *n*-propanol (in black) molecules replacing each DFM molecule around DFM and the ratio of DFM molecules replacing each *n*-propanol (in red) and *n*-butanol (in blue) molecule around *n*-propanol (black line with closed square symbols)

To further probe local composition of DFM/*n*-propanol and DFM/*n*-butanol binary mixtures, we have calculated the excess local mole fractions δx . For a binary mixture, δx can be thought of as preferential solvation[87], the more positive δx the better solvated is component *i* and the more negative the less solvated is component *i*. Figure 4.10 shows the δx for DFM/*n*-propanol and DFM/*n*-butanol calculated at the entire mole fraction range of DFM. For both systems, the

more positive values are observed for $x_1 = 0.3 - 0.4$ and the more negative values are at higher DFM mole fractions ($x_1 = 0.8 - 0.9$). These values are consistent with the computed excess molar volumes minima and maxima. In Comparison, δx for DFM/*n*-propanol are more positive at lower mole fractions of DFM than for DFM/ *n*-butanol. These differences in δx values signify better solvation in DFM/*n*-propanol mixtures than in DFM/*n*-butanol at these conditions. This is consistent with the strong negative deviations in excess molar volumes observed in DFM/*n*-propanol mixtures at lower x_1 .

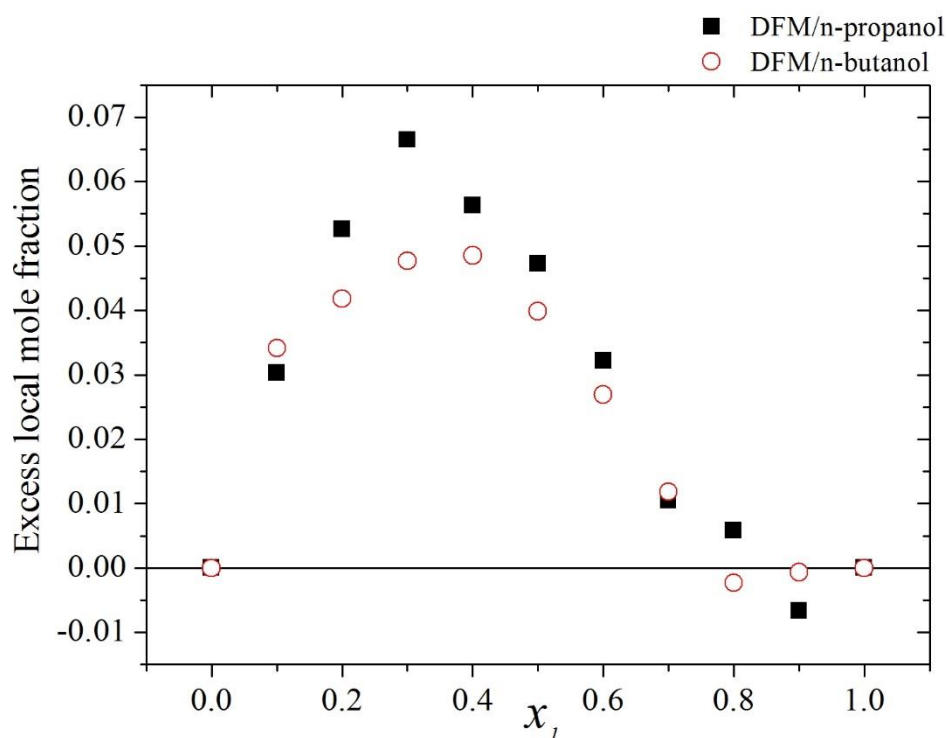


Figure 4.10 Excess local mole fractions of *n*-propanol (closed black squares) and *n*-butanol (red open circle) as a function of DFM mole fraction

For both mixtures, the δx exhibit the less positive values for $x_1 = 0.7 - 0.9$, with DFM/*n*-butanol and DFM/*n*-propanol showing the most negative values for $x_1 = 0.8$ and $x_1 = 0.9$ respectively. Interestingly, it is at these compositions that the most positive excess molar volumes are observed.

c. *Dihedral angle distributions*

Since we are dealing with flexible molecules, the possible conformations for the molecules can be studied by calculating dihedral angle distributions at different compositions. The dihedral angle distributions (C-C-C-O and C-C-O-H) for *n*-butanol and *n*-propanol, which give information about the most dominant conformer for various mole fractions of DFM, are shown in Figure 4.11. For $x_1 = 0.1$, the probability distributions (C-C-C-O and C-C-O-H) for *n*-propanol and *n*-butanol are quite similar with the trans conformer being the most dominant. *n*-butanol shows higher probability for trans conformation in both (C-C-C-O and C-C-O-H) than for *n*-propanol. However, for C-C-C-O dihedral angles *n*-propanol shows higher probability distributions for gauche (+) and gauche (-) conformers than *n*-butanol.

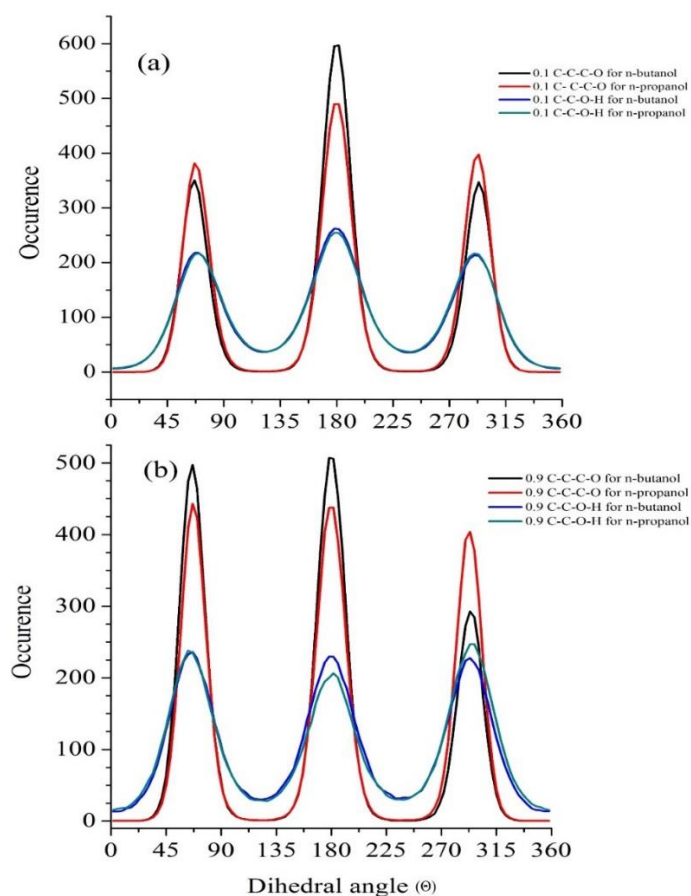


Figure 4.11 Comparisons between dihedral angle distributions (C-C-C-O and C-C-O-H) for *n*-propanol and *n*-butanol.

At composition $x_1 = 0.9$, in both systems, only C-C-C-O dihedral angle distributions display similar trends. However, *n*-butanol shows higher probability distributions for gauche (+) and trans conformations than *n*-propanol, which only shows higher distributions for the gauche (-). For C-C-O-H dihedral angles, *n*-butanol appear to have similar probability distributions. For *n*-propanol, the gauche conformations dominate over the trans conformer. This shows that in the low mole fractions of DFM, both *n*-propanol and *n*-butanol distribute in the same manner for the considered dihedral angles. However, for higher mole fractions of DFM the observed differences in the C-C-O-H dihedral angles mean that the molecular interactions for propanol and *n*-butanol are quite different.

To give a complete picture of *n*-butanol we have also calculated the C-C-C-C dihedral angle distributions (Figure 4.12). By picking only the most probable dihedral angle distributions, the possible structures of *n*-propanol (Figure 4.13) and *n*-butanol (Figure 4.14) conformers were deduced for $x_1 = 0.9$. This mole fraction was selected due to the vast differences in the observed dihedral angle distribution trends. The naming conventions used for *n*-butanol and *n*-propanol conformers are presented in Table 4.2.

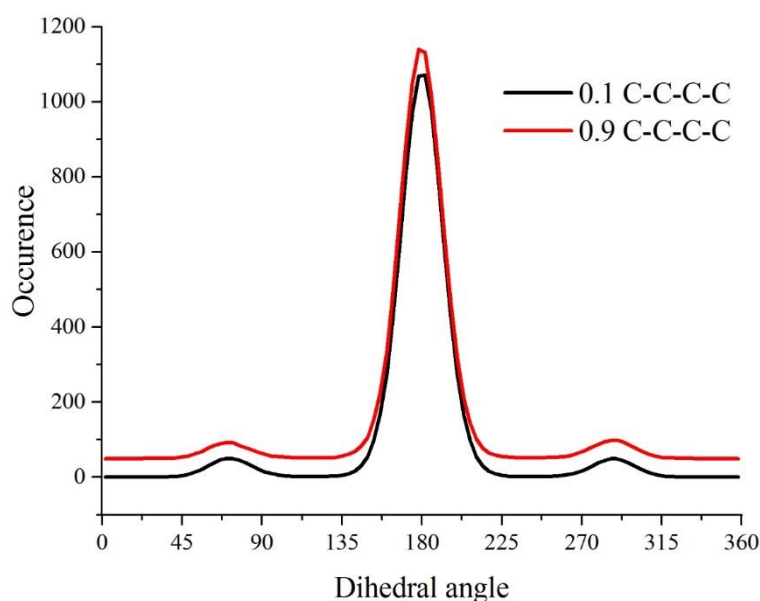


Figure 4.12 C-C-C-C dihedral angle distributions for *n*-butanol for $x_1 = 0.1$ and 0.9

An example to clarify the naming conventions: TTt for *n*-butanol means (trans) C-C-C-C, (trans) C-C-C-O, (trans) C-C-O-H and Tt for *n*-propanol means (trans) C-C-C-O, (trans) C-C-

O-H. From Figure 4.14 all the conformers of *n*-butanol are linearly structured. This means they are likely to occupy large volumes. The *n*-propanol Gg⁺ and Gg⁻ are more squeezed up, forming semi-cyclic orientations than the *n*-butanol conformers, which means the *n*-propanol molecules can occupy less space as compared to *n*-butanol. This can be linked to the calculated excess molar volumes.

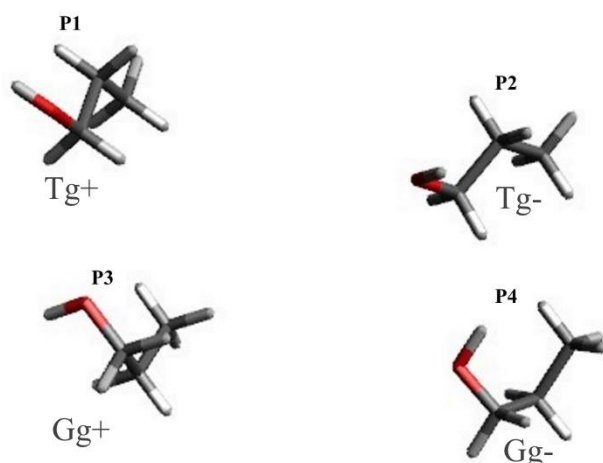


Figure 4.13 Images showing the most probable conformers of *n*-propanol for $x_1 = 0.9$

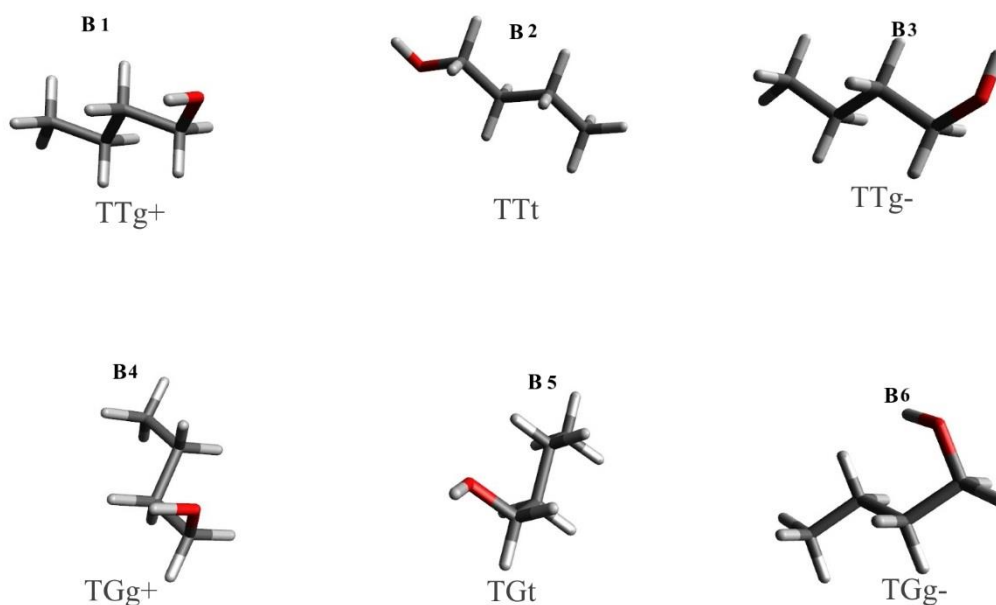


Figure 4.14 Images depicting the most probable conformers of *n*-butanol for $x_1 = 0.9$

Table 4.2 Naming conventions for the conformers in Figures 4.13 and 4.14

<i>n</i> -propanol		<i>n</i> -butanol	
Figure 4.12	Name of Conformer	Figure 4.13	Name of Conformer
P1	Tg+	B1	TTg+
P2	Tg-	B2	TTt
P3	Gg+	B3	TTg-
P4	Gg-	B4	TGg+
		B5	TGt
		B6	TGg-

4.3 Conclusions

The thermodynamic and structural aspects of DFM/*n*-butanol mixtures have been investigated using molecular dynamics and compared with results from Chapter III. The calculated excess molar volumes for DFM/*n*-butanol are in agreement with experimental values but less so than DFM/*n*-propanol mixtures. For the calculated RDFs the methyl-methyl interactions for *n*-propanol at high mole fractions of DFM are different from *n*-butanol, which signifies formations of unique molecular orientations. Enhanced hydrogen-bonding interactions is confirmed for DFM/*n*-butanol for than in DFM/*n*-propanol. DFM behaves similarly in both *n*-propanol and *n*-butanol. *n*-propanol molecules form tight clusters than *n*-butanol in DFM. This is corroborated by the excess local mole fractions. The dihedral angle distributions shows unique molecular orientations for high mole fractions of DFM. *n*-propanol seems to prefer a semi-cyclic orientation whereas *n*-butanol molecules assume mostly linear arrangement.

Chapter V

5 Summary and conclusions

The purpose of this dissertation was to investigate the thermodynamic properties as well as the structural aspects of binary liquid mixtures involving 2,2'-difurylmethane (DFM) with *n*-propanol and *n*-butanol using molecular dynamics and *ab initio* methods. The following results were obtained:

In Chapter III, the binary liquid mixtures of 2,2'-difurylmethane (DFM) and *n*-propanol were investigated using molecular dynamics. The thermodynamic properties such as densities and excess molar volumes were calculated and compared with experimental values. There was good agreement between the calculated and experimental thermodynamic data. The studied structures reveal the presence of weak hydrogen bonding interactions through *n*-propanol acidic hydrogen and one of DFM oxygen atoms. This was supported by a shift in dihedral angles involving *n*-propanol acidic hydrogen. The results also showed that *n*-propanol molecules are able to accommodate the local volume of DFM rather easily than DFM occupies the local volume of *n*-propanol molecules.

In Chapter IV, a comparative study was performed for liquid binary mixtures of 2,2'-difurylmethane (DFM) with *n*-propanol and *n*-butanol. The calculated excess molar volumes for DFM/*n*-butanol were in agreement with experimental values but less so than DFM/*n*-propanol mixtures. For the calculated RDFs the methyl-methyl interactions for *n*-propanol at high mole fractions of DFM were different from those of *n*-butanol, which signified formations of unique molecular orientations. Enhanced hydrogen-bonding interactions between one of DFM oxygen atoms and acidic hydrogen of the alcohol were realized for DFM/*n*-butanol than in DFM/*n*-propanol mixtures. DFM appeared to behave similarly in both *n*-propanol and *n*-butanol mixtures. *n*-propanol molecules formed tight clusters than *n*-butanol in DFM mixtures. This was corroborated by the excess local mole fractions. The dihedral angle distributions revealed unique molecular conformations for high mole fractions of DFM. *n*-propanol seemed

to prefer a semi-cyclic orientation whereas *n*-butanol molecules assumed mostly linear arrangement.

5.1 Possible future experiments

Although the results presented in Chapter III and IV show agreement between calculated and experimental excess molar volumes, there is still need to reduce the calculated thermodynamic data discrepancies. This can be done by a number of ways, which include; significantly increasing the simulation time and system sizes to a constant number of atoms for all mixture compositions. Albeit increasing the number of particles is computationally expensive, it has the benefit of producing well-resolved structural properties. In addition, since DFM molecule has not been extensively studied theoretically, its force fields may have to be reparametrized and validated. These changes may improve agreement between calculated and experimental values and enable the study to include other thermodynamic properties such as diffusion coefficient.

Furthermore, we have seen that DFM alters the conformations of *n*-propanol more than it does for *n*-butanol, and behaves similarly in both *n*-propanol and *n*-butanol mixtures. We also know that the excess molar volumes are affected by changes in temperature[10]. This implies that the local structures are affected by temperature. Therefore, computational methods applied in this work can be extended to study the effect of temperature on the clusters and conformations of linear alcohols($C_1 - C_6$).

References

- [1] B. Zohuri, Combined Cycle Driven Efficiency for Next Generation Nuclear Power Plants, Springer International Publishing Switzerland, 2015. doi:10.1007/978-3-319-15560-9_2.
- [2] K. Srinivasan, J.C. Manayil, C.A. Antonyraj, Heterogeneous Catalysis for Perfumery Chemicals, in: S.S. Joshi, V. V Ranade (Eds.), Industrial Catalytic Processes for Fine and Specialty Chemicals, Elsevier Inc., 2016: pp. 463–508. doi:10.1016/B978-0-12-801457-8.00011-2.
- [3] U. Domańska, P. Morawski, M. Piekarska, Solubility of perfumery and fragrance raw materials based on cyclohexane in 1-octanol under ambient and high pressures up to 900 MPa, J. Chem. Thermodyn. 40 (2008) 710–717. doi:10.1016/j.jct.2007.10.004.
- [4] M.K. Figueiredo, A. V Alvarenga, R.P.B. Costa-félix, Ultrasonic attenuation and sound velocity assessment for mixtures of gasoline and organic compounds, Fuel. 191 (2017) 170–175. doi:10.1016/j.fuel.2016.11.076.
- [5] T.M. Foong, K.J. Morganti, M.J. Brear, Y. Yang, F.L. Dryer, G. da Silva, The octane numbers of ethanol blended with gasoline and its surrogates, Fuel. 115 (2014) 727–739. doi:10.1016/j.fuel.2013.07.105.
- [6] A. Turanov, A.K. Khitrin, Proton exchange in gasoline-ethanol fuel blends, Fuel. 189 (2017) 440–442. doi:10.1016/j.fuel.2016.11.002.
- [7] Y. Huang, G. Hong, R. Huang, Effect of injection timing on mixture formation and combustion in an ethanol direct injection plus gasoline port injection (EDI þ GPI) engine, Energy. 111 (2016) 92–103. doi:10.1016/j.energy.2016.05.109.
- [8] O. Mokate, W.A.A. Ddamba, Volumetric Properties of Difurylmethane in Methanol from 288.15 to 308.15 K, J. Solution Chem. 34 (2005) 1327–1339. doi:10.1007/s10953-005-8023-z.
- [9] O. Mokate, W.A.A. Ddamba, Volumetric properties of (difurylmethane + alkan-1-ol)

- binary mixtures at 298.15 K, J. Solution Chem. 35 (2006) 1493–1503. doi:10.1007/s10953-006-9080-7.
- [10] O. Mokate, W.A.A. Ddamba, Effect of Temperature on the Volumetric Properties of [Difurylmethane + (C 2 – C 6) Alkan-1-ol] Binary Systems : Analyses of New and Literature Density Data in the Temperature Range 288 . 15 – 308 . 15 K, J. Solution Chem. 37 (2008) 331–350. doi:10.1007/s10953-007-9243-1.
- [11] T.A. Nevolina, T.A. Stroganova, M. V Shevlyakov, A. V Butin, Synthesis of amines of the di- and trifurylmethane series, Chem. Heterocycl. Compd. 43 (2007) 408–415.
- [12] K. Ji, Y. Shen, X. Shu, H. Xiao, Synthesis of Difurylmethane Derivatives via the Gold-Catalyzed, Adv. Sythesis Catal. 350 (2008) 1275–1280. doi:10.1002/adsc.200800130.
- [13] A. Vrhovsek, O. Gereben, A. Jamnik, L. Pusztai, Hydrogen Bonding and Molecular Aggregates in Liquid Methanol , Ethanol , and 1-Propanol, J. Phys. Chem. B. 115 (2011) 13473–13488. doi:10.1021/jp206665w.
- [14] B.T. Mmereki, I. Oathotse, W.A.A. Ddamba, Ultrasonic speeds and isentropic compressibilities of {difurylmethane+(C1–C6) n-alkanol} binary mixtures at T=298.15K, J. Chem. Thermodyn. 42 (2010) 1346–1351. doi:10.1016/j.jct.2010.05.016.
- [15] S.S. Sastry, S.M. Ibrahim, L.T. Kumar, S. Babu, H.S. Tiong, Excess Thermodynamic and Acoustic Properties for Equimolar Mixture of Ethyl Benzoate and 1-Alkanols with Benzene At 303.15 K, Int. J. Eng. Res. Technol. 4 (2015) 315–324.
- [16] A. Perera, L. Zoranić, F. Sokolić, R. Mazighi, A comparative Molecular Dynamics study of water-methanol and acetone-methanol mixtures, J. Mol. Liq. 159 (2011) 52–59. doi:10.1016/j.molliq.2010.05.006.
- [17] A. Pal, R. Gaba, Densities, excess molar volumes, speeds of sound and isothermal compressibilities for {2-(2-hexyloxyethoxy)ethanol plus n-alkanol} systems at temperatures between (288.15 and 308.15) K, J. Chem. Thermodyn. 40 (2008) 750–758. doi:10.1016/j.jct.2008.01.015.
- [18] D.M. Cristancho, D.R. Delgado, F. Martínez, A. Mohammad, Volumetric properties of

- glycerol + water mixtures at several temperatures and correlation with the Jouyban-Acree model, *Rev. Colomb. Cienc. Quím. Farm.* 40 (2011) 92–115.
- [19] W.A.A. Ddamba, T.T. Mokoena, P. Mokgweetsi, M.S. Nadiye-Tabbiruka, Modeling of excess molar volumes of [difurylmethane + (acetonitrile or propionitrile or benzonitrile)] binary Mixtures using the Prigogine – Flory – Patterson theory, *Am. J. Phys. Chem.* 4 (2015) 1–5. doi:10.11648/j.ajpc.20150401.11.
- [20] M. V Rathnam, S. Mankumare, K.J.M.S.S. Kumar, Densities , Viscosities and Speeds of Sound of Binary Mixtures of Ethyl Benzoate + Hydrocarbons at (303 . 15 , 308 . 15 and 313 . 15 K), *J. Solution Chem.* 41 (2012) 475–490. doi:10.1007/s10953-012-9802-y.
- [21] S.L. Dahire, Y.C. Morey, P.S. Agrawal, Excess molar volumes, intermolecular free lengths, adiabatic compressibilities and acoustic impedance of binary mixtures of anisole, toluene and ethylbenzene with dioxane at different temperatures, *Int. Lett. Chem. Phys. Astron.* 42 (2015) 72–83. doi:10.18052/www.scipress.com/ILCPA.42.72.
- [22] D.H. Ghafeli, M. Almasi, The measurement of excess molar volumes (V_m^e) in two-component mixture containing ethyl formate and 1-pentanol in the temperature range from 293 . 15K to 323 . 15 K, *Am. J. Oil Chem. Technol.* 4 (2016) 11–15.
- [23] S. Keshri, A. Sarkar, B.L. Tembe, Molecular Dynamics Simulation of Na⁺-Cl⁻ Ion-Pair in Water-Methanol Mixtures under Supercritical and Ambient Conditions, *J. Phys. Chem. B.* 119 (2015) 15471–15484. doi:10.1021/acs.jpcc.5b05401.
- [24] A.G. Peshwe, B.R. Arbad, S.P. Pachaling, Volumetric and viscometric studies on n , n-dimethylacetamide and methanol binary mixtures at different temperatures, *Int. J. Chem. Sci.* 7 (2009) 1505–1517.
- [25] D. Rahul, T.S. Krishna, M. Gowrisankar, D. Ramachandran, Molecular interactions and theoretical estimation of ultrasonic speeds using scaled particle theory in binary mixtures of 3-chloroaniline and 1-alkanols (C 6 – C 10) at different temperatures, *J. Mol. Liq.* 212 (2015) 618–628. doi:10.1016/j.molliq.2015.09.046.
- [26] M. Janardhanaiah, S. Gangadhar, V. Govinda, K. Sreenivasulu, P. Venkateswarlu,

- Effect of alkanol chain length on excess thermodynamic properties of, *J. Mol. Liq.* 211 (2015) 169–177. doi:10.1016/j.molliq.2015.07.008.
- [27] H.H. Ghazoyan, A. Markarian, Densities , excess molar and partial molar volumes for diethylsulfoxide with methanol or ethanol binary binary systems at temperature range 298.15–323.15 K, in: *Proc. Yerevan State Univ. Chem. Biol.*, 2014: pp. 17–25.
- [28] R.C. Verma, A.P. Singh, V.K. Yadav, The study of Excess Molar volume and deviation in viscosity of binary mixtures of Ethyl Propionate in Pentanol-1 and Hexanol-1 at 308K Ultrasonically, *Am. Int. J. Res. Formal, Appl. Nat. Sci.* 7 (2014) 41–42.
- [29] S.S. Patil, S.R. Mirgane, B.R. Arbad, Excess molar volumes and deviation in viscosities of binary liquid mixtures of acrylic esters with hexane-1-ol at 303 . 15 and 313 . 15 K, *J. Saudi Chem. Soc.* 18 (2014) 945–952. doi:10.1016/j.jscs.2011.11.018.
- [30] I.R. Grguri, A.Z. Tasic, B.D. Djordjevic, M.L. Kijevcanin, S.P. Serbanovic, Excess molar volume of the acetonitrile + alcohol systems at 298 . 15 K . Part I: Density measurements for acetonitrile + methanol , + ethanol systems, *J.Serb.Chem.Soc.* 67 (2002) 581–586.
- [31] I.R. Grguri, M.L. Kijevcanin, B.D. Djordjevic, A.Z. Tasic, S.P. Serbanovic, Excess molar volume of acetonitrile + alcohol systems at 298.15 K. Part II: Correlation by cubic equation of state, *J. Serbian Chem. Soc.* 68 (2003) 47–56.
- [32] A. Pal, R. Gaba, Volumetric properties of (alkoxypropanol + n -alkanol) systems at 298 . 15 K, *J. Mol. Liq.* 135 (2007) 146–152. doi:10.1016/j.molliq.2006.11.008.
- [33] S.L. Oswal, H.S. Desai, Studies of viscosity and excess molar volume of binary mixtures: 4. 1-Alkanol+ tri-n-butylamine mixtures at 303.15 and 313.15 K, *Fluid Phase Equilib.* 204 (2003) 281–294. doi:10.1016/S0378-3812(98)00318-5.
- [34] A. Mikusinska-planner, X-ray Diffraction Study of the Structure of 1-Propanol at - 25°C, *Acta Cryst.* 33 (1977) 433–437.
- [35] G.W. Neilson, A.K. Adya, S. Ansell, Neutron and X-ray diffraction studies on complex liquids, *Annu. Rep. Prog. Chem., Sect.* 98 (2002) 273–322. doi:10.1039/b111168j.

- [36] I. Bako, T. Megyes, T. Grosz, G. Palinkas, J. Dore, Structural investigation of water – acetonitrile mixtures : Small-angle and wide-angle neutron diffraction study compared to molecular dynamics simulation, *J. Mol. Liq.* 125 (2006) 174–180. doi:10.1016/j.molliq.2005.11.022.
- [37] A. Sahoo, S. Sarkar, P.S.R. Krishna, V. Bhagat, R.N. Joarder, Molecular conformation and structural correlations of liquid D-1-propanol through neutron diffraction, *Pramana – J. Phys.* 71 (2008) 133–141.
- [38] T. Takamuku, T. Yamaguchi, M. Asato, M. Matsumoto, N. Nishi, Structure of Clusters in Methanol-Water Binary Solutions Studied by Mass Spectrometry and X-ray Diffraction, *Zeitschrift Für Naturforsch. A. J. Phys. Sci.* 55 (2000) 513–525. doi:org/10.1515/zna-2000-0507.
- [39] R.K. Lam, J.W. Smith, R.J. Saykally, Communication : Hydrogen bonding interactions in water-alcohol mixtures from X-ray absorption spectroscopy, *J. Chem. Phys.* 144 (2016) 1–4. doi:10.1063/1.4951010.
- [40] I. Akiyama, M. Ogawa, K. Takase, T. Takamuku, T. Yamaguchi, N. Ohtori, Liquid Structure of 1-Propanol by Molecular Dynamics Simulations and X-Ray Scattering, *J. Solution Chem.* 33 (2004) 797–809.
- [41] M.A.M. Cordeiro, J.M.M. Cordeiro, Structure and weak hydrogen bonds in liquid acetaldehyde, *J. Braz. Chem. Soc.* 15 (2004) 351–357. doi:10.1590/S0103-50532004000300003.
- [42] N.A. McDonald, W.L. Jorgensen, Development of an All-Atom Force Field for Heterocycles. Properties of Liquid Pyrrole, Furan, Diazoles, and Oxazoles, *J. Phys. Chem. B.* 102 (1998) 8049–8059. doi:10.1016/S0166-1280(97)00237-6.
- [43] K. Kahn, T.C. Bruice, Parameterization of OPLS-AA force field for the conformational analysis of macrocyclic polyketides, *J. Comput. Chem.* 23 (2002) 977–996. doi:10.1002/jcc.10051.
- [44] G. Zhu, Y. Wang, L. Zhang, Y. Luo, M. Sha, X. Xu, Thermodynamic properties and microstructures of the mixture of N-butylpyridinium tetrafluoroborate with acetonitrile

- studied by molecular dynamics simulation, *J. Mol. Liq.* 203 (2015) 153–158. doi:10.1016/j.molliq.2015.01.003.
- [45] J.A. Padro, L. Saiz, E. Guardia, Hydrogen bonding in liquid alcohols: A computer simulation study, *J. Mol. Struct.* 416 (1997) 243–248. doi:10.1016/S0022-2860(97)00038-0.
- [46] W.L. Jorgensen, Optimized intermolecular potential functions for liquid alcohols, *J. Phys. Chem.* 90 (1986) 1276–1284. doi:10.1021/j100398a015.
- [47] W.L. Jorgensen, D.S. Maxwell, J. Tirado-Rives, Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids, *J. Am. Chem. Soc.* 118 (1996) 11225–11236.
- [48] W.L. Jorgensen, J.D. Madura, C.J. Swenson, Optimized intermolecular potential functions for liquid hydrocarbons, *J Am Chem Soc.* 106 (1984) 6638. doi:10.1021/ja00334a030.
- [49] W.L. Jorgensen, Optimized Intermolecular Potential Functions for Liquid Alcohols, *J. Phys. Chem.* 90 (1986) 1276–1284. doi:10.1021/j100398a015.
- [50] P.S. Serbanovic, M.L. Mijajlovic, I.R. Radovic, B.D. Djordjevic, M.L. Kijevcanin, E.M. Djordjevic, A.Z. Tasic, Vapour – liquid equilibria of the OPLS (Optimized Potentials for Liquid Simulations) model for binary systems of alkanes and alkanes + alcohols, *J. Serbian Chem. Soc.* 70 (2005) 527–539.
- [51] L. Saiz, J.A. Padro, Structure and Dynamics of Liquid Ethanol, *J. Phys. Chem. B.* 101 (1997) 78–86. doi:10.1021/jp961786.
- [52] Y. Lei, H. Li, H. Pan, S. Han, Structures and Hydrogen Bonding Analysis of N , N -Dimethylformamide and N , N -Dimethylformamide–Water Mixtures by Molecular Dynamics Simulations, *J. Phys. Chem. A.* 107 (2003) 1574–1583. doi:10.1021/jp026638+.
- [53] D. Kaur, S. Khanna, Intermolecular hydrogen bonding interactions of furan, isoxazole and oxazole with water, *Comput. Theor. Chem.* 963 (2011) 71–75.

doi:10.1016/j.comptc.2010.09.011.

- [54] M.K. Dahlgren, P. Schyman, J. Tirado-rives, W.L. Jorgensen, Characterization of Biaryl Torsional Energetics and its Treatment in OPLS All-Atom Force Fields, *J. Chem. Inf. Model.* 53 (2013) 1191–1199. doi:10.1021/ci4001597.
- [55] A.R. Leach, *Molecular Modelling principles and applications*, Second edi, Pearson education Limited, 2001.
- [56] D.C. Young, *Computational Chemistry: A Practical Guide for Applying Techniques to Real-World Problems*, John Wiley & Sons, Inc, 2001.
- [57] K.I. Ramachandran, G. Deepa, K. Namboori, *Computational Chemistry and Molecular Modeling Principles and Applications*, Springer-Verlag Berlin Heidelberg, Berlin, 2008. doi:10.1007/978-3-540-77304-7.
- [58] F. Jensen, *Introduction to Computational Chemistry*, Second edi, John Wiley & Sons Ltd, 2007.
- [59] M.P. Allen, D.J. Tildesley, *Computer simulation of liquids*, Oxford University Press, 1987.
- [60] R. Böhmer, C. Gainaru, R. Richert, Structure and dynamics of monohydroxy alcohols — Milestones towards their microscopic understanding , 100 years after Debye, *Phys. Rep.* 545 (2014) 125–195. doi:10.1016/j.physrep.2014.07.005.
- [61] S.W.I. Siu, K. Pluhackova, R.A. Bo, Optimization of the OPLS-AA Force Field for Long Hydrocarbons, *J. Chem. Theory Comput.* 8 (2012) 1459 – 1470. doi:10.1021/ct200908r.
- [62] M.J. Robertson, J. Tirado-Rives, W.L. Jorgensen, Improved Peptide and Protein Torsional Energetics with the OPLS-AA Force Field, *J. Chem. Theory Comput.* 11 (2015) 3499–3509. doi:10.1021/acs.jctc.5b00356.
- [63] M. Freindorf, Y. Shao, T.R. Furlani, J. Kong, Lennard-Jones parameters for the combined QM/MM method using the B3LYP/6-31G*/AMBER potential., *J. Comput.*

- Chem. 26 (2005) 1270–1278. doi:10.1002/jcc.20264.
- [64] E. Lewars, COMPUTATIONAL CHEMISTRY Introduction to the Theory and Applications of Molecular and Quantum Mechanics, 1st ed., Springer US, 2003. doi:10.1007/b101871.
- [65] M.J. Frisch, Geometry Optimization with QM / MM , ONIOM , and Other Combined Methods . I . Microiterations, 9627775 (2003).
- [66] C. Peng, P.Y. Ayala, B.H. Schlegel, M.J. Frisch, Using Redundant Internal Coordinates to Optimize Equilibrium Geometries and Transition States, J. Comput. Chem. 17 (1996) 49–56.
- [67] T. Vreven, M.J. Frisch, K.N. Kudin, H.B. Schlegel, K. Morokuma, M.J. Frisch, K.N. Kudin, H.B. Schlegel, K. Morokuma, Geometry optimization with QM / MM methods II : Explicit quadratic coupling Geometry optimization with QM / MM methods II : Explicit quadratic coupling, Mol. Phys. 104 (2007) 701–714. doi:http://dx.doi.org/10.1080/00268970500417846.
- [68] M.S. Gordon, M.W. Schmidt, Advances in electronic structure theory: GAMESS a decade later, in: Theory Appl. Comput. Chem., 2005: pp. 1167–1189. doi:10.1016/B978-044451719-7/50084-6.
- [69] G.B. Macpherson, M.K. Borg, J.M. Reese, Generation of initial molecular dynamics configurations in arbitrary geometries and in parallel, Mol. Simul. 33 (2007) 1199–1212. doi:http://dx.doi.org/10.1080/08927020701730724.
- [70] L. Martinez, R. Andrade, E.G. Birgin, J.M. Martinez, Packmol: A Package for Building Initial Configurations for Molecular Dynamics Simulations, J. Comput. Chem. (2008) 1–14. doi:10.1002/jcc.
- [71] J.M. Martinez, L. Martinez, Packing Optimization for Automated Generation of Complex System ' s Initial Configurations for Molecular Dynamics and Docking, J. Comput. Chem. 24 (2003) 819–825.
- [72] W. Smith, I.T. Todorov, A short description of DL_POLY, Mol. Simul. 32 (2006) 935–

943. doi:10.1080/08927020600939830.

- [73] C.W. Yong, DL_FIELD - A force field and model development tool for DL_POLY, CSE Front. STFC Comput. Sci. Eng. Daresbury Lab. (2010) 38–40.
- [74] I.B. Christopher, C. Piotr, D.W. Cornell, A.K. Peter, A well-behaved electrostatic potential based method using charge restraints for deriving atomic charges: the RESP model, J. Phys. Chem. 97 (1993) 10269–10280.
- [75] M.. Schmidt, K.. Baldrige, J.. Boatz, S.. Elbert, M.. Gordon, J.. Jensen, S. Koseki, N. Matsunaga, K.. Nguyen, S.. Su, T.. Windus, M. Dupuis, J.. Montgomery, General atomic and molecular electronic structure System, J.Comput.Chem. 14 (1993) 1347–1363.
- [76] L. Martinez, R. Andrade, E.G. Birgin, J.M. Martinez, Packmol: A package for building initial configurations, J. Comput. Chem. 30 (2009) 2157–2164.
- [77] U. Essmann, L. Perera, M.L. Berkowitz, A smooth particle mesh Ewald method, J Chem Phys. 103 (1995) 8577–8593. doi:http://dx.doi.org/10.1063/1.470117.
- [78] J. Peleteiro, D. González-Salgado, C.A. Cerdeiriña, L. Romaní, Isobaric heat capacities, densities, isentropic compressibilities and second-order excess derivatives for (1-propanol+n-decane), J. Chem. Thermodyn. 34 (2002) 485–497. doi:10.1006/jcht.2001.0924.
- [79] S.-P. Ju, S.-H. Yang, M.-L. Liao, Study of molecular behavior in a water nanocluster: size and temperature effect., J. Phys. Chem. B. 110 (2006) 9286–90. doi:10.1021/jp056567p.
- [80] J. McGregor, R. Li, J.A. Zeitler, C. D’Agostino, J.H.P. Collins, M.D. Mantle, H. Manyar, J.D. Holbrey, M. Falkowska, T.G.A. Youngs, C. Hardacre, E.H. Stitt, L.F. Gladden, Structure and dynamics of aqueous 2-propanol: a THz-TDS, NMR and neutron diffraction study, Phys. Chem. Chem. Phys. 17 (2015) 30481–30491. doi:10.1039/C5CP01132A.
- [81] G.G. Almeida, A. Borges, J.M.M. Cordeiro, On the hydrogen bonding between N-methylformamide and acetone and tetrahydrofuran, Chem. Phys. 434 (2014) 25–29.

doi:10.1016/j.chemphys.2014.02.013.

- [82] A. Luzar, D. Chandler, Structure and hydrogen bond dynamics of water–dimethyl sulfoxide mixtures by computer simulations, *J. Chem. Phys.* 98 (1993) 8160–8173. doi:10.1063/1.464521.
- [83] C. Oldiges, K. Wittler, T. Tonsing, A. Alijah, MD calculated structural properties of clusters in liquid acetonitrile/water mixtures with various contents of acetonitrile, *J. Phys. Chem. A*. 106 (2002) 7147–7154. doi:10.1021/jp025506d.
- [84] M. Brehm, B. Kirchner, “TRAVIS - A Free Analyzer and Visualizer for Monte Carlo and Molecular Dynamics Trajectories,” *J. Chem. Inf. Model.* 51 (2011) 2007–2023.
- [85] W. Humphrey, A. Dalke, K. Schulten, VMD - Visual Molecular Dynamics, *J. Molec. Graph.* 14 (1996) 33–38.
- [86] R.D. Mountain, Microstructure and Hydrogen Bonding in Water - Acetonitrile Mixtures, *J. Phys. Chem. B*. 114 (2010) 16460–16464. doi:10.1021/jp105272q.
- [87] P.E. Smith, E. Matteoli, J.P.O. Connell, *Fluctuation Theory of Solutions: Applications in Chemistry, Chemical Engineering, and Biophysics*, 1st Editio, CRC Press, 2013.
- [88] S. Jarmelo, N. Maiti, V. Anderson, P.R. Carey, R. Fausto, C r - H Bond-Stretching Frequency in Alcohols as a Probe of Hydrogen-Bonding Strength : A Combined Vibrational Spectroscopic and Theoretical Study of n - [1-D] Propanol, (2005) 2069–2077.
- [89] Z.H. Luo, Electron momentum spectroscopy study of a conformationally versatile molecule :, *J. Phys. B At. Opt. Phys.* 42 (2009) 1–9. doi:10.1088/0953-4075/42/16/165205.

Appendices:

Appendix A. Published paper(s)

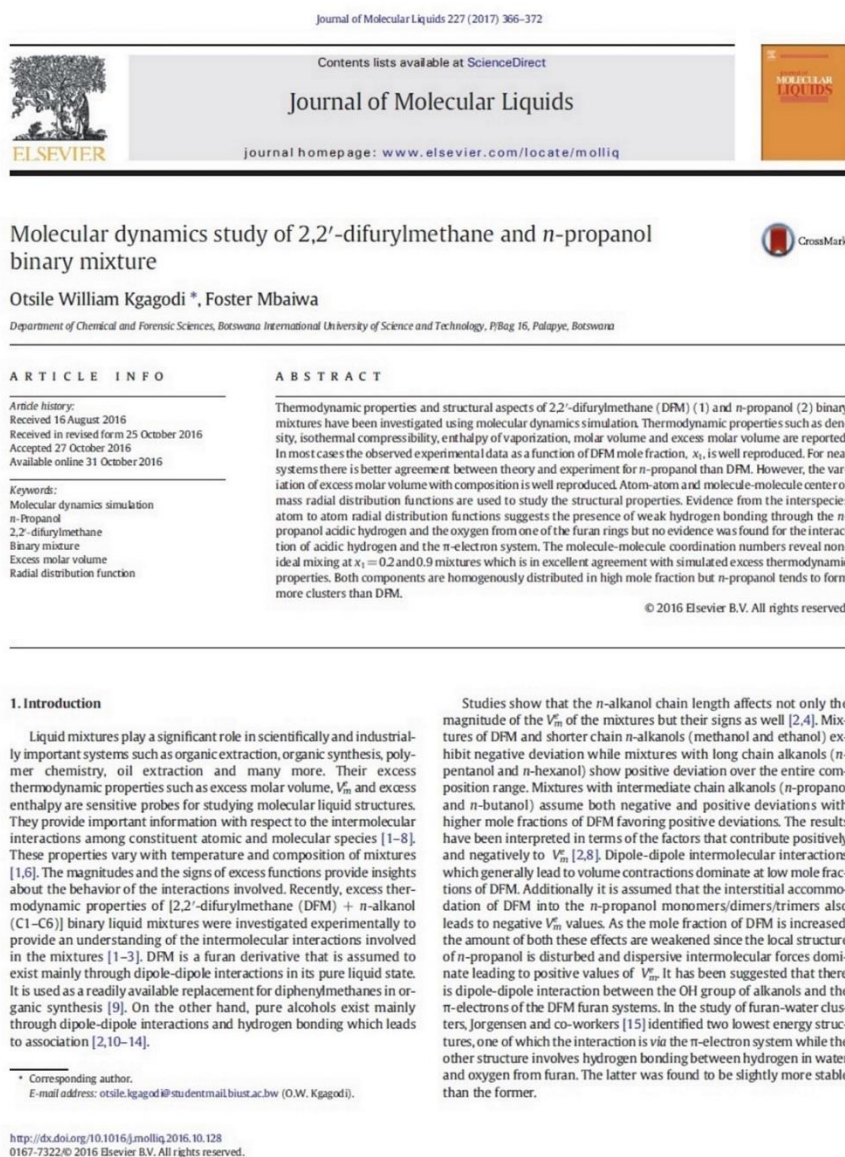


Figure A.0.1 Excerpt from a published paper used with permission from © 2016 Elsevier B.V. All rights reserved.

Appendix B. Single molecule coordinate files (.XYZ)

DFM molecule

```
19
DFM
O_F      0.98500      -0.67200      0.10700
C_1      0.82100      0.26500     -0.94900
C_2     -0.24000      1.09900     -0.66000
H_2     -0.58700      1.91700     -1.28100
C_2     -0.78200      0.68000      0.62000
H_2     -1.62600      1.11800      1.14100
C_1     -0.02500     -0.38400      1.06000
H_1     -0.03900     -1.02400      1.93100
C_H      1.82700      0.16400     -2.06600
C_1      1.32600      0.74100     -3.35600
H_C      2.05200     -0.90000     -2.24000
H_C      2.77500      0.65000     -1.78000
C_2      1.03300      0.21800     -4.60000
O_F      1.09900      2.14600     -3.37900
C_1      0.64900      2.46200     -4.68600
C_2      0.60000      1.31400     -5.44700
H_1      0.42900      3.50500     -4.86300
H_2      1.10800     -0.82700     -4.88300
H_2      0.29700      1.25100     -6.48600
```

n-propanol molecule

```
12
Propan-1-ol
C      -1.9638695678  -0.1457998488   0.0000077850
C      -0.5798041781   0.5108133995   0.0000061865
H      -2.1078257324  -0.7781370157   0.8852357229
H      -2.1078299931  -0.7781374674  -0.8852189742
H      -2.7571907830   0.6097134239   0.0000097834
C       0.5549409125  -0.5059059317  -0.0000025584
H      -0.4637494263   1.1568617928  -0.8796012850
H      -0.4637456930   1.1568615867   0.8796127125
O       1.7871624988   0.2091028038   0.0000024495
H       2.5078547398  -0.4387521481  -0.0000111490
H       0.4713669426  -1.1555439107   0.8882905020
H       0.4713602801  -1.1555466843  -0.8882911758
```

n-butanol molecule

15

C_3	0.5784656877	0.8827711026	-0.1472008429
C_B	-0.4038173948	2.0551639771	-0.0285287893
H_B	1.5252853636	1.2126165442	-0.5925169615
H_B	0.1642118556	0.0777052438	-0.7594083280
H_B	0.8029824415	0.4615465900	0.8411237989
C_B	-1.7590684278	1.7143973298	0.6170409058
H_B	-0.5839915201	2.4871574958	-1.0245633284
H_B	0.0655677582	2.8536206033	0.5631314324
C_A	-2.7207356451	0.8983199712	-0.2422200517
H_B	-2.2753949706	2.6514535926	0.8698862663
H_B	-1.6028116456	1.1791644067	1.5641679156
O_A	-2.2289541897	-0.4344103108	-0.3808771718
H_B	-2.8339575012	1.3806032791	-1.2284820572
H_B	-3.7151150948	0.8934835207	0.2352898685
H_A	-2.8421067170	-0.9183033461	-0.9548326569