Organics – Biodiesel Systems Phase Equilibrium Computation: Part 2

Loyiso Ntaka and Edison Muzenda

Abstract— In part 1, the infinite dilution activity coefficients of 30 organics in methyl linoleate and methyl palmitate were reported. This work tested the application of Modified UNIFAC (Dortmund) as a molecular thermodynamic method in organic – polymer systems phase equilibrium estimation. Infinite dilution activity coefficients of 30 volatile organic compounds (VOCs) in methyl oleate and ethyl stearate were predicted using the Modified UNIFAC (Dortmund) procedure. The infinite dilution activity coefficients obtained in this study compare very well with literature findings. For example the calculated infinite dilution activity coefficients for benzene and toluene agree to about ±5% with those obtained from headspace and dynamic gas–liquid chromatographic measurements. The two biodiesel polymers were found to absorb ethers and aromatics better compared to other VOC family groups.

Keywords— activity coefficient, estimation, measurements, molecular thermodynamic, polymers

I. INTRODUCTION

THIS work is a continuation of our interest in the solubility of volatile organic compounds in biodiesel. The Modified UNIFAC Dortmund is a successful and well known group contribution model for phase equilibria prediction [1]. This method is based on the UNIFAC correlation which follows the concept of group contribution as discussed [2]. The UNIFAC correlation is based on a semi empirical model for liquid mixtures called the Universal quasi-chemical activity coefficient (UNIQUAC) [3]. The principles and procedure for the UNIFAC procedure is well discussed in literature. The fundamental principles and differences of the Modified UNIFAC Dortmund compared to the original UNIFAC are reported [4].

II. METHODOLOGY

Reliable prediction of the activity coefficient at infinite dilution is important in understanding the real behaviour of components and their interactions. This study focused on the estimation of the phase equilibrium of 30 volatile organic compounds in two biodiesel polymers.

A. Assumptions made in the UNIFAC Dortmund model

L. Ntaka is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg 2028

E. Muzenda is with the Department of Chemical Engineering, University of Johannesburg, Doornfontein, Johannesburg, South Africa, 2028 (Tel: 0027115596817; 002711596430; Email: emuzenda@uj.ac.za

- The logarithm of the activity coefficient is taken as a sum of the combinatorial and residual contributions. Whereas the combinatorial part takes into account the size and shape of the molecule, the residual part considers the energy (enthalpic) interactions.
- Solutions are considered to be composed of groups rather than molecules since number of groups present are smaller compared to molecules, which make up the components of the mixture. Again, groups with interaction parameters derived from empirical study are chosen to be simple structural units such as; CH_3, CH_2, COO etc.
- The residual part resulting from group interactions is assumed to be the difference between the sum of the individual contributions of each solute group in the solution and the sum of the individual contribution in the pure component environment.
- The individual group contributions in a given environment are treated as a function of group concentrations and temperatures only.

The calculation procedure reported by [4] was adopted in this study.

III. RESULTS AND DISCUSSION

TABLE 1
SOLUBILITY COMPARISON: METHYL OLEATE AND WATER AT 303K

	Components	Methyl oleate	Water	Superiority Factor
1	Pentane	0.957	6700	7004
2	Hexane	1.002	277000	276509
3	Heptane	1.044	607000	581293
4	Trimethylamine	0.910	56	62
5	Toluene	0.643	8800	13683
6	Xylene	0.658	16500	25062
7	Cyclohexane	0.955	18500	19380
8	Butylacetate	1.086	75	69
9	Diethylether	0.609	77	126
10	Chloroform	0.448	611	1365
11	Acetone	1.441	7	5
12	Ethylmethylketone	1.246	109	88
13	Isobutylmethylketone	1.142	86	75

TABLE 2

SOLUBILITY COMPARISON: ETHYL STEARATE AND WATER AT 303K

	Components	Methyl stearate	Water	Superiority Factor
1	Pentane	0.824	6700	8130
2	Hexane	0.865	277000	320084
3	Heptane	0.904	607000	671112
4	Trimethylamine	0.811	56	69
5	Toluene	0.630	8800	13961
6	Xylene	0.667	16500	24740
7	Cyclohexane	0.848	18500	21818
8	Butylacetate	1.098	75	68
9	Diethylether	0.557	77	138
10	Chloroform	0.492	611	1243
11	Acetone	1.532	7	5
12	Ethylmethylketone	1.360	109	80
13	Isobutylmethylketone	1.246	86	69

Intermolecular forces (van der Waals forces) play an important role in the solubility of substances. The magnitude of the van der Waals forces is determined by polarizability of electrons of the atoms involved. Polarizability is the ability of electrons to respond to a changing electric field; it depends on how loosely or tightly the electrons are held. A rule of thumb for predicting solubility is that "like dissolves like".

Methyl Oleate and Ethyl Stearate are compounds with long carbon chains, these compounds resembles alkanes more than esters. Therefore, only the CCOO group, a small part of the molecule is hydrophilic and the long carbon chain is hydrophobic. As a result, nonpolar VOCs are more soluble compared to polar VOCs. In Tables 1 and 2, the solubility of volatile organic compounds in water is compared to those in methyl oleate and ethyl stearate respectively. With the exception of acetone, biodiesel was found to be a better solvent compared to water with superiority factors varying from 60 to 582 000. Although water is readily available it quickly saturates when mixed with organics. The water molecule is highly polar and capable of forming strong hydrogen bonds. However, hydrogen bonding is limited to molecules with a hydrogen atom attached to an O, N or F atom. The hydrogen bond is weaker compared to the ordinary covalent bond, but is much stronger than the dipole – dipole interactions that occur in acetone, isobutyl methyl ketone and methyl ethyl ketone. Generally compounds with less than four carbon atoms are water soluble while those with five and higher are insoluble.

With the exception of the ketone family group, infinite dilution activity coefficients were found to increase with increasing molecular weight. This is so because as the molecular weight increases so does the molecular surface area as well as the van der Waals forces between molecules. Therefore, more energy is required to separate molecules from one another. On the other hand branching of chains makes a molecule more compact, reducing the surface area and the van der Waals forces. For example, cyclohexane is more soluble

than hexane in in both water and biodiesel. Alkenes and alkynes are more compact compared to alkanes of similar sizes and thus require less energy to overcome the van der Waals forces. Solubility was found to increase with the increase in the number of C-C bonds, thus in the order alkynes>alkenes>alkanes. This trend was also observed by [5].

TABLE 3
INFINITE DILUTION ACTIVITY COEFFICIENTS OF VARIOUS FAMILY GROUPS AT 303K

Family groups	Component	Methyl Oleate	Ethyl Stearate
Ketones	Acetone	1.441	1.532
	Ethylmethylketone	1.246	1.36
	Isobutylmethylketone	1.142	1.246
	2-Pentanone	1.186	1.294
	2-Hexanone	1.142	1.246
Aromatics	Benzene	0.589	0.598
	Toluene	0.643	0.63
	Xylene	0.658	0.667
	Ethyl Benzene	0.673	0.658
	Trimethyl Benzene	0.699	0.707
Ethers	Diethylether	0.609	0.557
	Dimethyl ether	0.561	0.523
	Methyl ethyl ether	0.589	0.538
	Diisopropyl ether	0.711	0.711
	Diisobutyl ether	0.704	0.642
Alkanes	Propane	0.868	0.743
	Butane	0.91	0.782
	Pentane	0.957	0.824
	Hexane	1.002	0.865
	Heptane	1.044	0.904
Alkenes	Propene	0.66	0.598
	1-butene	0.721	0.656
	1-Pentene	0.776	0.708
	1-Hexene	0.827	0.756
	1-Heptene	0.872	0.799
Alkynes	Propyne	0.846	0.815
	1-butyne	0.824	0.793
	1-Pentyne	0.825	0.795
	1-Hexyne	0.837	0.806
	1-Heptyne	0.855	0.823

TABLE 4
VARIATION OF INFINITE DILUTION ACTIVITY COEFFICIENTS AT 303K WITH LITERATURE (METHYL OLEATE)

Component	HGC[6]	GLC[7]	This work	DMD-UNI [6]	UNIFAC [6]	LBY-UNI [6]

| Benzene | 0.628 | 0.625 | 0.589 | 0.611 | 0.58 | 0.855 |
| Toluene | 0.651 | 0.645 | 0.643 | 0.643 | 0.649 | 0.838 |

Sources: [6] Bay et al, 2006 and [7] Bay et al 2004

TABLE 5
VARIATION OF INFINITE DILUTION ACTIVITY COEFFICIENTS AT 303K WITH LITERATURE (ETHYL STEARATE)

Component	HGC[6]	GLC[7]	This work	DMD-UNI[6]	UNIFAC [6]	LBY-UNI [6]
Benzene	0.628	0.625	0.598	0.611	0.58	0.855
Toluene	0.651	0.645	0.63	0.643	0.649	0.838

Sources: [6] Bay et al, 2006 and [7] Bay et al, 2004

As reported in Tables 4 and 5, computational results obtained in this work agree well with literature findings [5] and [6] obtained through headspace and dynamic gas liquid chromatographic measurements.

Fig. 2 Variation of infinite dilution activity coefficients with mole fraction of alkenes in methyl oleate
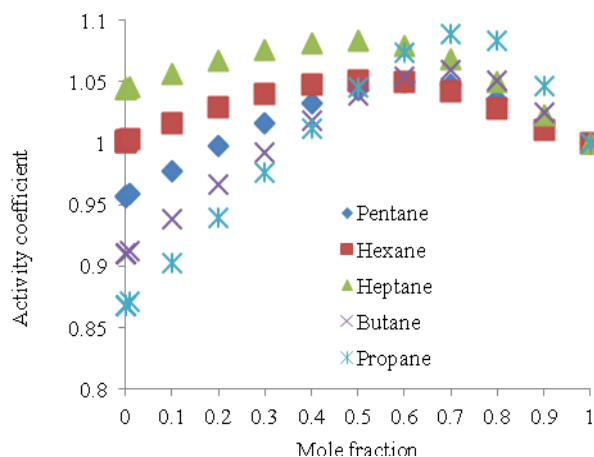
Fig. 1 Variation of infinite dilution activity coefficients with mole fraction of alkanes in methyl oleate
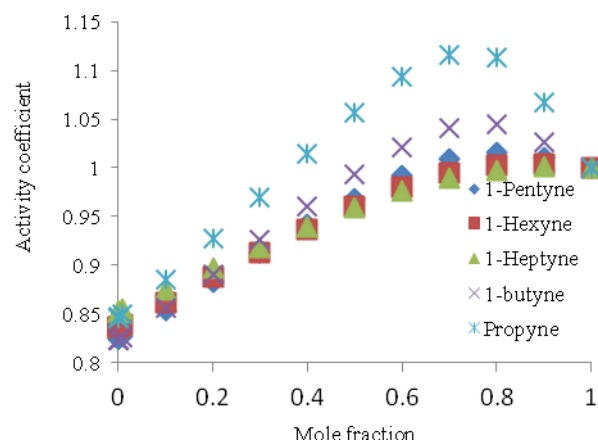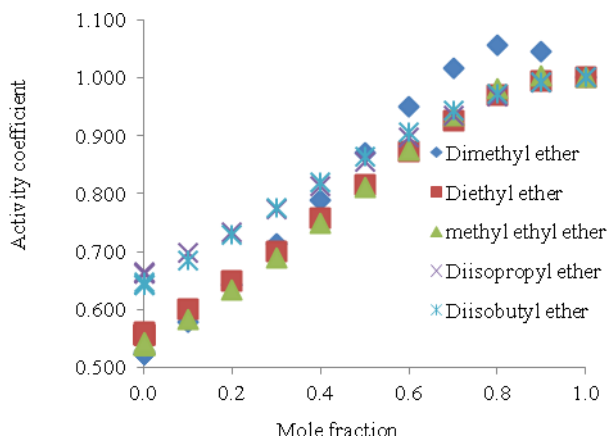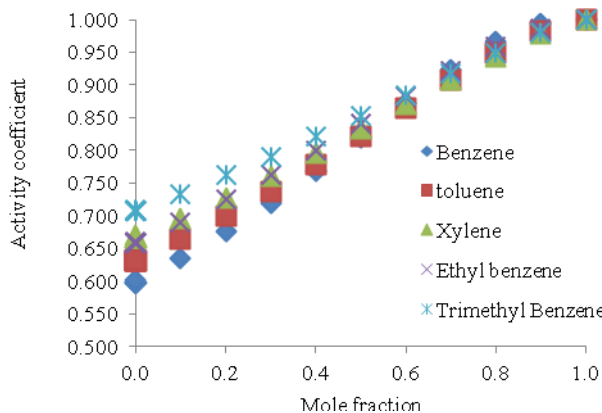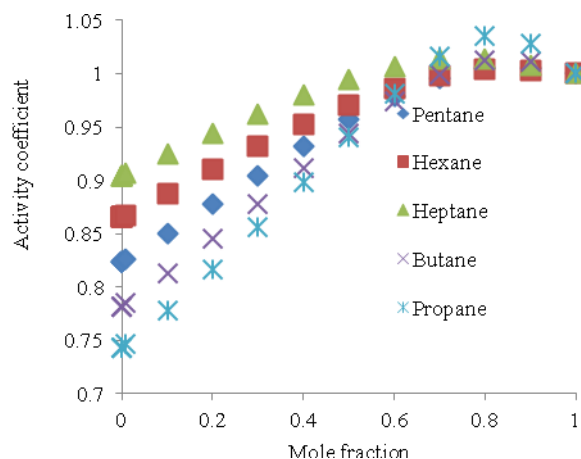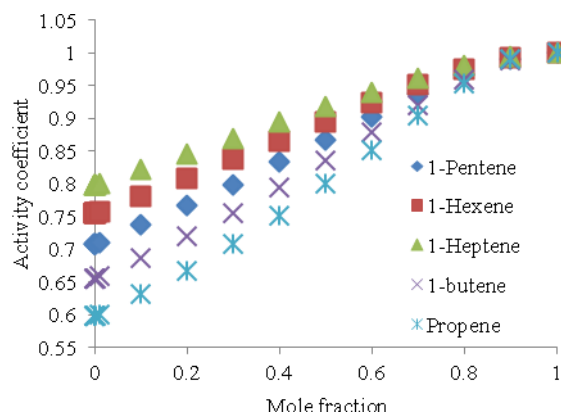

Fig. 3 Variation of infinite dilution activity coefficients with mole fraction of alkynes in methyl oleate
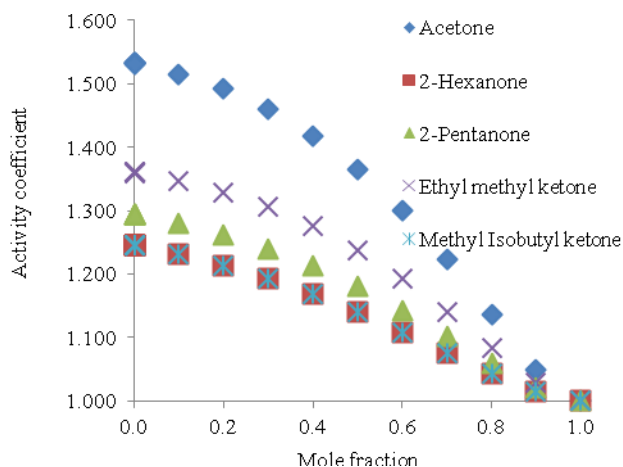
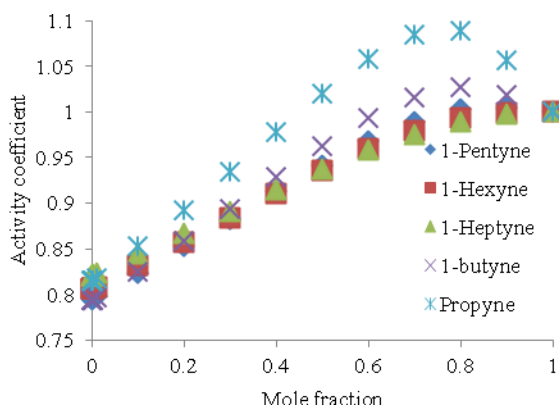Fig. 4 Variation of infinite dilution activity coefficients with mole fraction of ketones in methyl oleate

Fig. 7 Variation of infinite dilution activity coefficients with mole fraction of alkanes in ethyl stearate

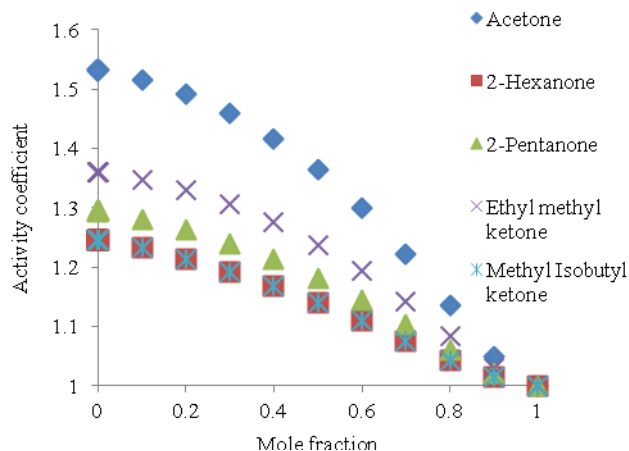Fig. 5 Variation of infinite dilution activity coefficients with mole fraction of ethers in methyl oleate

Fig. 8 Variation of infinite dilution activity coefficients with mole fraction of alkenes in ethyl stearate

Fig. 6 Variation of infinite dilution activity coefficients with mole fraction of aromatics in methyl oleate

Fig. 9 Variation of infinite dilution activity coefficients with mole fraction of alkynes in ethyl stearate

Fig. 10 Variation of infinite dilution activity coefficients with mole fraction of ketones in ethyl stearate
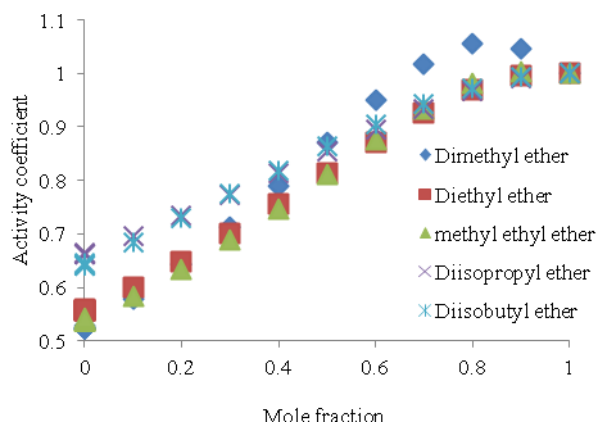

Fig. 11 Variation of infinite dilution activity coefficients with mole fraction of ethers in ethyl stearate
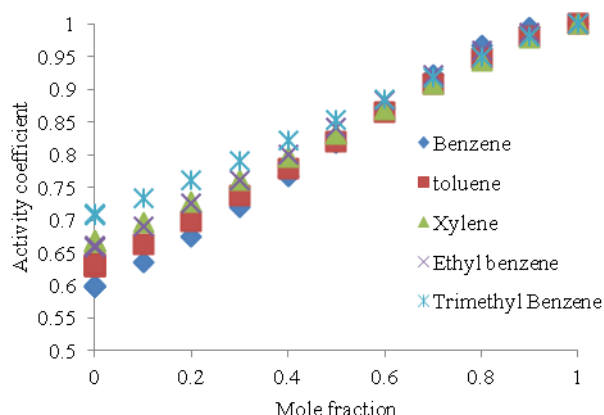

Fig. 12 Variation of infinite dilution activity coefficients with mole fraction of aromatics in ethyl stearate

Figs 1 to 12 show typical activity coefficient versus mole fraction plots. The activity coefficients approach a value of 1, an ideal case with increase in mole fraction. This is mainly because, in an ideal mixture, the interaction between each pair of chemical species are the same, thus the enthalpy of mixing is zero.

V. CONCLUSION

Structural arrangements for example in the case of aliphatic, cyclic and aromatic compounds was found to affect solubility. The Dortmund UNIFAC model is very reliable in vapour – liquid equilibrium as confirmed with the agreement with measurements. Therefore for feasibility and preliminary design studies, it is recommended to use computational techniques. Computational techniques are simple, less time consuming and inexpensive.

ACKNOWLEDGEMENTS

REFERENCES

[1] A. Jakob, H. Grensemann, J. Lohmann, and J. Gmehling, "Further development of Modified UNIFAC (Dortmund): Revision and Extension5," *Ind. Eng. Chem. Res.*, vol. 45, pp. 7924-7933, 2006.

[2] A. Fredenslund, J. Gmehling, P. Rasmussen, Vapour – Liquid Equilibria Using UNIFAC, Elsevier, Amsterdam, 1977.

[3] D. S. Abrams, and J. M. Prausnitz, "Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly and completely miscible systems," *AIChE J.*, vol. 21, pp. 116-128, 1975.

[4] N. P. Nkosi, P. V. Mokoena, E. Muzenda, and M. Belaid, "Organics – biodiesel systems phase equilibrium computation: part 1," *Unpblished*, 2012

[5] K. Bay, H. Wanko, and J. Ulrich, "Absorption of volatile organic compounds in biodiesel: Determination of infinite dilution activity coefficients by headspace chromatography," *Trans IChemE, Part A, Chem. Eng. Res. Des*., vol. 84, no. Al, pp. 22-27, 2006.

[6] K. Bay, H. Wanko, and J. Ulrich, "Biodiesel—Hochsidendes Absorbens fu¨r die Gasreinigung," *Chemie Ingenieur Technik*, 76 (3) 328–333, 2004.

[7] T. W. G. Solomons, "Organic Chemistry," University of South Florida, vol.5, pp. 80 – 88, 1992.