

Organics – Biodiesel Systems Phase Equilibrium Computation: Part 1

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Abstract— The group contribution concept can be applied in the estimation of thermodynamic properties of pure compounds and mixtures. The Modified UNIFAC (Dortmund) is a successful and well-known group contribution model for phase equilibria prediction. In this paper the application of this model to the phase equilibrium of biodiesel - volatile organic compounds systems was tested. Infinite dilution activity coefficients of 30 selected volatile organic compounds (VOCs) in methyl linoleate and methyl palmitate were estimated. The VOCs groups covered in the selection were alkanes, alkenes, alkynes, aromatics, ethers and ketones. The estimated phase equilibrium is favourable for the absorption of these organics into methyl linoleate. The solubility was found to decrease with increase in molecular weight of the VOCs in each group. Saturation was also found to have an effect on solubility. Experimental data are often not available, at least for preliminary design and feasibility studies of absorption processes, group contribution methods can be utilized to predict the required phase equilibria.

Keywords— activity coefficient, group contribution, phase equilibrium, solubility, volatile organic compounds.

I. INTRODUCTION

For preliminary design and feasibility studies, the use of group contribution methods is helpful as experimental data are often missing. Also the measurements of the necessary phase equilibrium and thermophysical data can be time consuming and expensive. The use of thermodynamic mixture information in particular the infinite dilution activity coefficients from compounds very different in size give an improved description of the real behaviour of these mixtures. A good example is the removal of volatile organic compounds from contaminated air streams by physical absorption using high boiling solvents. In group contribution methods, the liquid phase is considered to be a mixture of structural groups. This offers a great advantage in that, although there are thousands of chemical compounds of industrial and environmental interest, the number of functional groups required to describe the thermodynamic behaviour of these compounds and their mixtures is much smaller. In this work,

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the Modified UNIFAC (Dortmund) [1] is preferred instead of the Original UNIFAC [2]-[4].

Compared to the original UNIFAC, the modified model gave a relative improvement of 73% for the calculation of activity coefficients at infinite dilution. The original UNIFAC procedure has number of drawbacks such as the real phase behaviour in the diluted region of the compounds to be separated is not always in agreement with the experimental data. The Modified UNIFAC (Dortmund) is a g^E model, which allows the prediction of liquid – phase activity coefficients γ_i in nonelectrolyte systems as a function of temperature and composition. The activity coefficient is calculated as the sum of the combinatorial part (C) and residual part (R):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (1)$$

The combinatorial part represents the contribution of the excess entropy arising from the different sizes and shapes on molecules under study. The residual part represents the contribution from the excess enthalpy caused by the energetic interaction between molecules. In this model the temperature – independent combinatorial part is calculated using the van der Waals volume (R_k) and surface area (Q_k) values of the functional groups.

Compared to the original UNIFAC model, the modified UNIFAC (Dortmund) incorporates the following changes:

- The combinatorial term was empirically changed to allow for better description of asymmetric systems.
- Temperature-dependent group interaction parameters are used to allow a reliable description of the real behaviour in a wide temperature range.
- Van der Waals volume and surface area parameters were introduced for cyclic alkanes.
- Alcohols were reclassified as primary, secondary and tertiary with separate van der Waals volume and surface area parameters.
- Modified UNIFAC group interaction parameters were fitted to activity coefficients at infinite dilution, VLE and excess enthalpies.

Biodiesel is a good absorption medium for volatile organic compounds in particular aromatics and ethers as observed [4].

I. MODIFIED UNIFAC (DORTMUND)

In the original UNIFAC model, the relations for the combinatorial part are expressed in (1) – (3).

$$\ln \gamma_i^C = 1 - \phi_i + \ln \phi_i - 5q_i \left(1 - \frac{\phi_i}{\theta_i} + \ln \frac{\phi_i}{\theta_i} \right) \quad (1)$$

$$\phi_i = \frac{r_i}{\sum_j r_j x_j} \quad (2)$$

$$\theta_i = \frac{q_i}{\sum_j q_j x_j} \quad (3)$$

In the modified UNIFAC (Dortmund), the following expressions were introduced

$$\ln \gamma_i^C = 1 - \phi'_i + \ln \phi'_i - 5q_i \left(1 - \frac{\phi'_i}{\theta_i} + \ln \frac{\phi'_i}{\theta_i} \right) \quad (4)$$

$$\phi'_i = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j} \quad (5)$$

The expressions for ϕ_i and θ_i , remain unchanged as in the original UNIFAC. The introduction of the temperature – dependent parameters in the residual part is shown in (6)

$$\psi_{nm} = \exp\left(-\left(a_{nm} + b_{nm}T + c_{nm}T^2\right)/T\right) \quad (6)$$

II. RESULTS AND DISCUSSION

The solubility of selected volatile organic compounds expressed in form of infinite dilution activity coefficients in methyl linoleate and methyl palmitate is presented in Table 1. The presented phase equilibrium show that the two biodiesels can be used for the scrubbing of VOCs from contaminated air streams. When compared to the most common industrial solvent water, the two biodiesels are far much better absorbents with superiority factors ranging from 5 to 25 000, Tables II and III. The infinite dilution activity coefficients increase with increase in carbon number in each family group. Solubility was also found to increase with the increase in degree of saturation observed from the phase equilibrium data of alkanes, alkenes and alkynes. As a modified natural product, biodiesel is liable to changes on its fatty acid methyl ester (FAME) composition. In all cases, methyl esters with a hydrocarbon chain of 18 carbon atoms with 1, 2 and 3 unsaturated bonds dominate. The presence of these unsaturated bonds account for the better solubility in biodiesel of alkenes and alkynes compared to alkanes, as “like dissolves like”. The low vapour pressure of biodiesel is desirable as it prevents secondary emissions or its loss during absorption.

TABLE I
INFINITE DILUTION ACTIVITY COEFFICIENTS OF
SELECTED VOC FAMILY GROUPS AT 303K

Functional group	Component	Methyl Lineate	Methyl Palmitate	
Alkanes	Propane	0.967	0.901	
	Butane	1.03	0.950	
	Pentane	1.098	1.003	
	Hexane	1.167	1.057	
	Heptane	1.235	1.108	
	Alkenes	Propene		0.671
		Butene		0.737
Pentene		0.808	0.798	
Hexene		0.864	0.854	
Heptene		0.915	0.906	
Alkynes		Propyne		0.692
		Butyne		0.697
	Pentyne	0.824	0.703	
	Hexyne	0.84	0.743	
	Heptyne	0.855	0.781	
	Aromatics	Benzene	0.584	0.616
		Toluene	0.623	0.647
Xylene		0.667	0.681	
Ethyl benzene		0.688	0.687	
1,3,5 Trimethyl benzene		0.716	0.719	
Ethers	Dimethyl ether	0.57	0.559	
	Ethyl methyl ether	0.608	0.585	
	Diethyl ether	0.632	0.602	
	Diisopropyl ether	0.714	0.726	
	Diisobutyl ether	0.745	0.684	
Ketones	Acetone	1.34	1.405	
	Ethyl methyl ketone	1.181	1.167	
	2-Pentanone	1.13	1.119	
	Isobutyl methyl ketone	1.094	1.190	
	2-Hexanone	1.094	1.190	

Solubility is governed by molecular attractions. For solubility to take place the absorbent molecules must overcome the intermolecular stickiness in the solute and find their way between and around the solute molecules and vice versa. This is best achieved when the attractions between the molecules of both components are similar. Solubility is influenced by the deviations in the electron shell density of molecules which give rise to a minute magnetic imbalance. The molecule as whole becomes a small magnet or dipole.

The electron density deviations are governed by physical architecture of the molecule resulting in varying degree of polarity. Substances with similar polarities like aromatics and biodiesel will be soluble in each other. However increasing deviations in polarity between the VOCs and absorbent make solubility increasing difficult. Beside intermolecular forces, the nature of composite forces also influences solubility. Substances will also dissolve in each other if their composite forces such as hydrogen bonds, induction, orientation effects and dispersion forces are made up in the same way.

TABLE II
SOLUBILITY COMPARISON: METHYL LINOLEATE
AND WATER

VOC	γ^∞ at 303.15 K		Superiority factor
	Methyl linolate	H ₂ O[5]	
Pentane	1.098	6700	6102.004
Hexane	1.167	277	237.361
Heptane	1.235	607	491.498
Triethyl amine	0.911	56	61.471
Toluene	0.623	8800	14125.201
Xylene	0.667	16500	24737.631
Cyclohexane	1.039	18500	17805.582
Butyl acetate	1.056	75	71.023
Diethyl ether	0.632	77	121.835
Chloroform	0.422	611	1447.867
Acetone	1.34	7	5.224
Ethyl methyl ketone	1.181	109	92.295
Isobutyl methyl ketone	1.094	86	78.611

TABLE III
SOLUBILITY COMPARISON: METHYL PALMITATE
AND WATER

VOC	γ^∞ at 303.15 K		Superior factor
	This work	H ₂ O[1]	
Pentane	1.003	6700	6679.96
Hexane	1.057	277	262.06
Heptane	1.108	607	547.83
Triethyl amine	0.865	56	64.74
Toluene	0.647	8800	13601.24
Xylene	0.681	16500	24229.07
Cyclohexane	0.95	18500	19473.68
Butyl acetate	1.122	75	66.84
Diethyl ether	0.602	77	127.91
Chloroform	0.489	611	1249.49
Acetone	1.405	7	4.98
Ethyl methyl ketone	1.167	109	93.40
Isobutyl methyl ketone	1.19	86	76.85

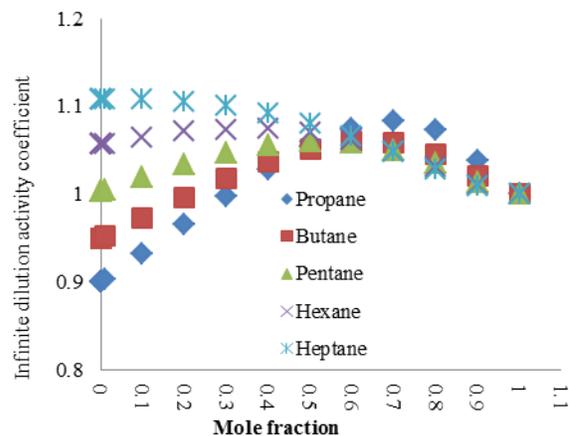


Fig. 1 Variation of infinite dilution activity coefficients with mole fraction of alkanes in methyl palmitate

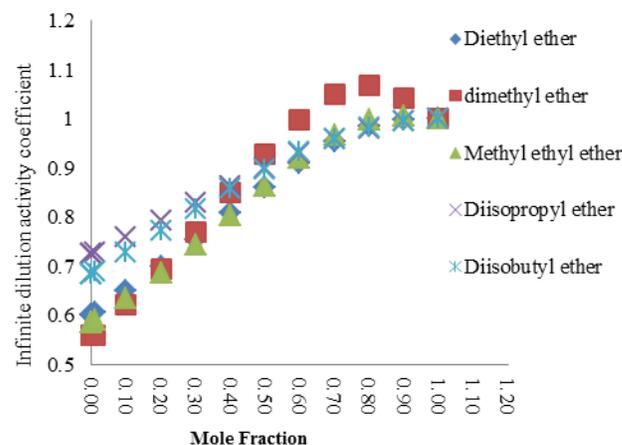


Fig. 2 Variation of infinite dilution activity coefficients with mole fraction of alkenes in methyl palmitate

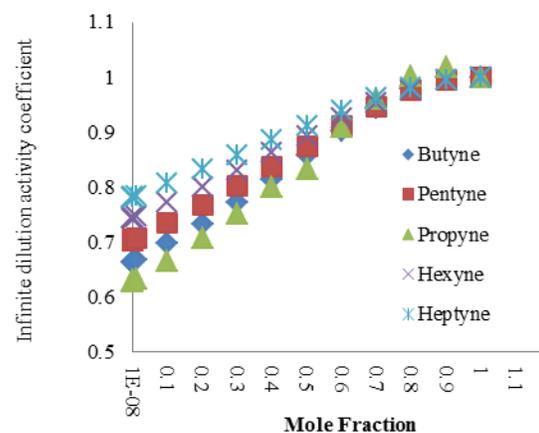


Fig. 3 Variation of infinite dilution activity coefficients with mole fraction of alkynes in methyl palmitate

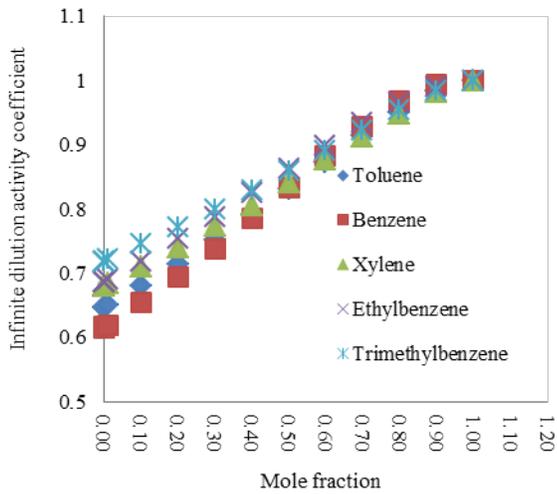


Fig. 4 Variation of infinite dilution activity coefficients with mole fraction of aromatics in methyl palmitate

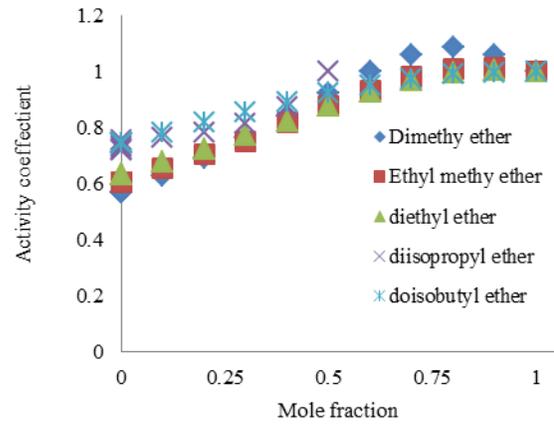


Fig. 7 Variation of infinite dilution activity coefficients with mole fraction of ketones in methyl linoleate

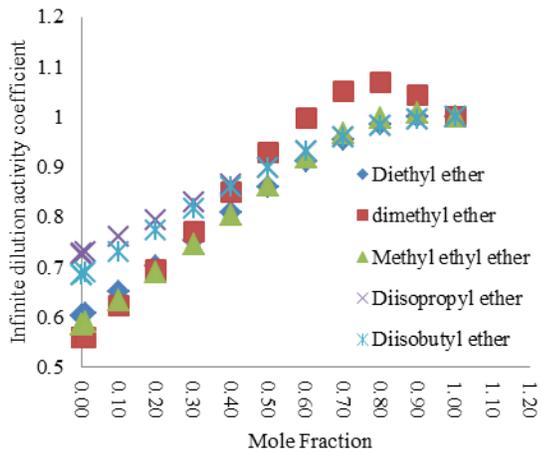


Fig. 5 Variation of infinite dilution activity coefficients with mole fraction of ketones in methyl palmitate

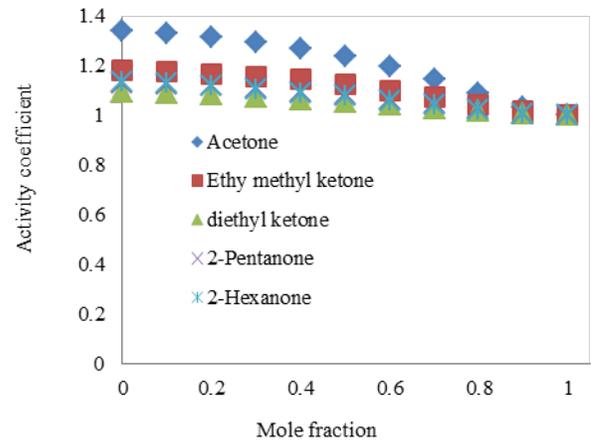


Fig. 8 Variation of infinite dilution activity coefficients with mole fraction of ketones in methyl linoleate

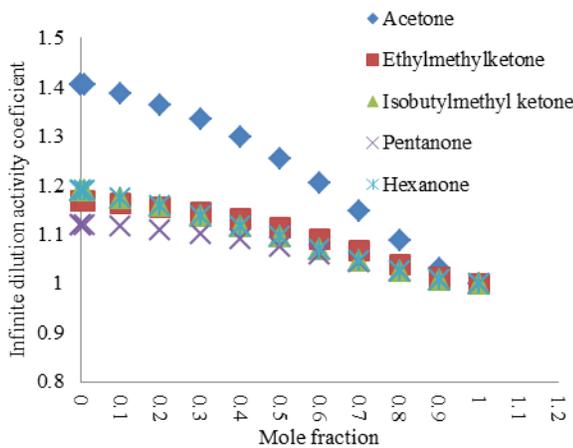


Fig. 6 Variation of infinite dilution activity coefficients with mole fraction of ketones in methyl linoleate

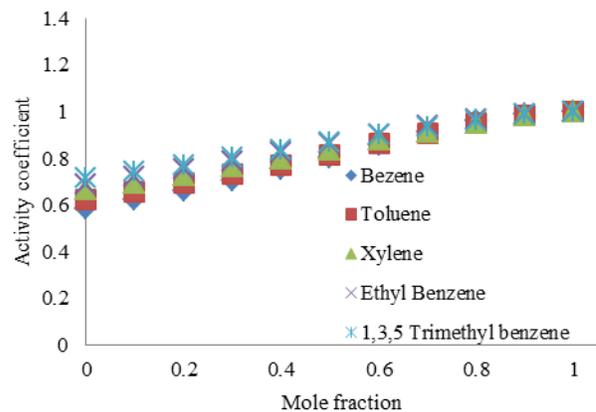


Fig. 9 Variation of infinite dilution activity coefficients with mole fraction of aromatics in methyl linoleate

Figs 1- 9 show the variation of activity coefficients with mole fraction. In all cases the deviation from ideal behaviour decreases with increase in mole fraction with activity coefficients approaching unity, ideal situation. However the

infinite dilution is of interest in this study as environmental concern focuses in this region.

IV. CONCLUSION

Infinite dilution activity coefficients of thirty VOCs of environmental concern were estimated for the purpose of designing a gas treatment process with biodiesel. The low VOCs infinite dilution activity coefficients obtained in this study indicate good solubility in biodiesel. The results agree well with published data for methyl oleate [6]. Group contribution methods like the UNIFAC (Dortmund) can reliably predict the phase equilibrium data and are timesaving. The required properties for example particular interaction parameters are available in most data bases.

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REFERENCES

- [1] U. Weidlich, and J. Gmehling, "A modified UNIFAC model. 1. Prediction of VLE, h^E and γ^∞ ," *Ind. Eng. Chem. Res.*, vol. 26, pp. 1372-1381, 1987.
- [2] A. Fredenslund, R. L. Jones, and J. M. Prausnitz, "Group contribution estimation of activity coefficients in non ideal liquid mixtures," *AIChE J.*, vol. 21, no. 6, pp. 1086 -1099, November 1975.
- [3] A. Fredenslund, J. Gmehling, P. Rasmussen, *Vapour – Liquid Equilibria Using UNIFAC*, Elsevier, Amsterdam, 1977.
- [4] A. Fredenslund, J. Gmehling, M. L. Michelsen., P. Rasmussen, and J. M. Prausnitz, "Computerized Design of Multicomponent Distillation Column Using the UNIFAC Group Contribution Method for the Calculation of Activity Coefficients," *Ind. Eng. Chem. Process. Des. Dev.*, vol. 16, no. 4, pp. 450-462, 1977.
- [5] E. Muzenda, "Solubility of organics in water and silicon oil: A comparative study," in *Proc. World Academy of Science, Engineering and Technology*, Paris, 2011, vol. 79, pp. 1 – 4.
- [6] 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. A1, pp. 22-27, 2006.