

# Alkenes – Ester Polymeric Solvents Thermodynamic Interactions - Part 2

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**Abstract**— This paper is a continuation of our work reported previously [1] on the interaction between ester solvents and alkene volatile organic compounds (VOCs). The interactions were presented in form of infinite dilution activity coefficients. A Microsoft Excel spreadsheet for the modified UNIFAC Dortmund group contribution method [2] was designed and used in computing the required phase equilibrium. The size of the solvent molecule (biodiesel) relative to the VOC molecule influenced the thermodynamic interactions. The degree of ester (biodiesel) bond saturation influenced the ease in which cyclic VOCs interacted with the solvent compared to their straight chain counterparts. The location of branches such as methyl branches in relation to the double-bonded carbons had an impact on the predicted infinite dilution activity coefficients.

**Keywords**— Activity coefficients, biodiesel, esters, group contribution, phase equilibrium, UNIFAC

## I. INTRODUCTION

THE release of volatile compounds (VOCs) and hazardous air pollutants (HAPs) into the atmosphere has to be avoided or limited to minimize their negative impacts on both the environment and humans. The technologies used for VOCs abatement can be of recovery and destructive type. Our interest lies in the treatment of volatile organic compounds through physical absorption using polymeric solvents as absorbents in place of water which quickly saturates. An absorption process can be attractive, efficient as well as profitable if a solvent which is easily generated and nonvolatile is available. There is an increasing trend and drive towards the use of ‘green’ absorbents (solvents). Fatty acid esters in particular fatty acid methyl esters (FAMES), show much promise in this regard. Biodiesel, consisting mainly of esters of various chain lengths has promise as a future polymeric solvent because apart from possessing all the properties of a good solvent, it is also environmentally friendly [3], [4].

This work focused the interactions of mainly methyl esters of various chain lengths with alkene VOCs in order to investigate their suitability as absorbents for VOCs treatment from gaseous contaminated air streams. VOCs requiring

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recovery are mostly present in very dilute concentrations in process effluent streams. Therefore the phase equilibrium in the very dilute region is essential in the design of absorption / stripping separation systems [5]. The required thermodynamic data can be obtained through measurements though these techniques are time consuming, laborious and can be very expensive. Appropriate and suitable thermodynamic models can be utilized to estimate required phase equilibrium. In this study, the Modified UNIFAC Dortmund excess Gibbs energy group contribution model, developed by Weidlich and Gmehling in 1987 [2] was used to predict the required phase equilibrium. A Microsoft Excel spreadsheet version of the model was developed to perform the required computations. The modified UNIFAC Dortmund group contribution method and the computational procedure have been previously described [2], [6], [7]. Previous studies relevant to this work have been presented and discussed [1], [3]-[7].

## II. RESULTS & DISCUSSION

Infinite dilution activity coefficients were predicted for 14 volatile organic compounds in 12 various methyl-, ethyl-, propyl- and butyl esters at 30°C. A mole fraction of  $1 \times 10^{-5}$  was used for all calculations. The notation of Gerpen et al [8] for VOCs and biodiesel was adopted and used as reported in our previous work [1].

### A. Comparison between Cyclic and Straight-chain Alkenes

The interactions of cyclic mono-alkenes with ester solvents are shown in Table I while those of straight-chained alkenes have been reported previously [1]. The comparative solubility studies are presented in Figs 1 and 2

TABLE I  
INTERACTIONS BETWEEN ESTER SOLVENTS AND CYCLIC MONO-ALKENES

Ester Solvent	Designation	Activity Coefficients - Ester/ Cyclic Alkene Solute Interactions					
		Cyclopentene	Cyclohexene	Cycloheptene	Cyclooctene	Cyclononene	Cyclodecene
M. Caproate	1-C6:0	1.270	1.368	1.458	1.542	1.621	1.696
M. Laurate	1-C12:0	0.849	0.913	0.968	1.018	1.062	1.102
M. Stearate	1-C18:0	0.689	0.747	0.798	0.844	0.886	0.924
M. Oleate	1-C18:1	0.701	0.769	0.833	0.893	0.949	1.003
M. Linoleate	1-C18:2	0.719	0.800	0.879	0.956	1.031	1.106
M. Linolenate	1-C18:3	0.742	0.840	0.937	1.036	1.135	1.237
E. Stearate	2-C18:0	0.671	0.727	0.778	0.824	0.866	0.904
E. Oleate	2-C18:1	0.681	0.748	0.810	0.868	0.924	0.976
P. Stearate	3-C18:0	0.653	0.709	0.760	0.805	0.847	0.885
P. Oleate	3-C18:1	0.662	0.728	0.789	0.846	0.900	0.951
B. Stearate	4-C18:0	0.637	0.692	0.742	0.788	0.829	0.867
B. Oleate	4-C18:1	0.645	0.709	0.769	0.825	0.878	0.929

Cyclic alkenes were less soluble than their straight chain alkenes counter parts in 1-C6:0 Methyl Caproate and the opposite is true for 1-C12:0 and 1-C18:0. This can be attributed to the relative size of the solvent (biodiesel) molecules in relation to the solute molecules. The smaller 1-C6:0 molecules can possibly deflect the straight-chain alkene electron cloud easier than a bulky cyclic alkene solute electron cloud, thus the net dispersion force effect is more evident on the straight chain molecules. As the biodiesel molecule increases in size, its dispersion forces also increase and can easily influence the cyclic molecular clouds.

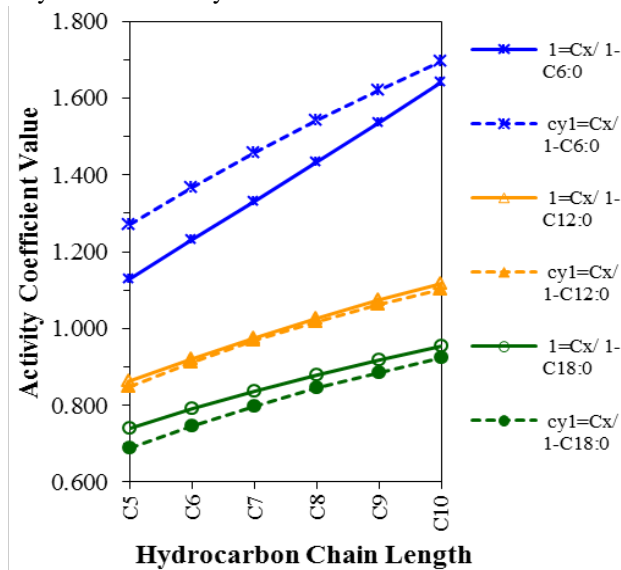


Fig.1 Activity coefficients of straight-chain and cyclic alkenes in selected saturated hydrocarbon-tailed esters

Fig. 2 presents interactions of cyclic mono-alkenes compared to straight-chain alkenes with saturated and unsaturated C18 esters. For smaller VOCs molecules, infinite dilution activity coefficients for straight-chain alkenes were higher than those of the cyclic mono-alkenes. However a point was reached where the cyclic mono-alkene/ ester interactions yielded higher activity coefficients than their straight-chain counterparts.

This point (referred to in this work as the *cross-over point*) was reached at a solute carbon number of C8, C9 and C10 for methyl linolenate (1-C18:3), methyl linolenate (1-C18:2) and methyl stearate (1-C18:1) respectively. This cross-over phenomenon also occurred with alkane-ester interactions [7], with 1-C18:2 and 1-C18:3, 1-C18:1 and 1-C18:0 achieving the cross-over at a carbon number of about C6, C7 and at C8 respectively. No cross-over points in activity coefficients occurred between straight-chain and cyclic alkenes in saturated ester/ alkene interactions, Fig. 1.

A clear trend where the solute/ solvent interactions with the weakest net dispersion force (i.e. alkanes in 1-C18:3) achieved cross-over at the lowest carbon number.

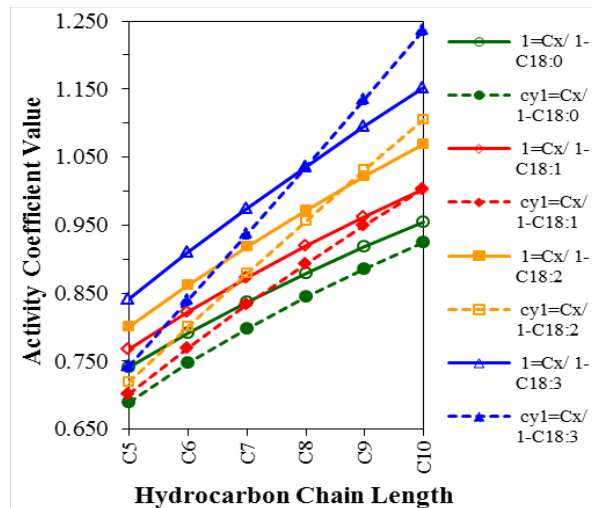


Fig.2 Activity coefficients of straight-chain and cyclic alkenes in various C18 hydrocarbon-tailed esters

Thereafter, there is a clear progression in net dispersion force between solute/ solvent interactions until the strongest interaction is attained (Alkenes in 1-C18:0). Naturally the strongest interaction yields the lowest activity coefficient.

From this work, it is evident that the shape of the solvent (biodiesel) molecule affects the cross-over point. As the amount of kinks in the solvent molecule increases, the strength of the van der Waals dispersion force decreases. As a consequence the ability of the solvent molecule to deflect the solute electron cloud (and thereby induce a temporary dipole) decreases, especially as the cyclic molecule becomes more bulky in size and its dispersion force also increases in magnitude.

#### B. Effect of Branch Location on Activity Coefficients

Computations were performed to study the effect of methyl branch location on straight-chain alkenes on their interactions with biodiesel, Table II and Fig. 3.

TABLE II  
INFLUENCE OF METHYL BRANCH LOCATION ON ESTER/ STRAIGHT-CHAIN ALKENE INTERACTIONS

Ester Solvent	Designation	Activity Coefficients - Ester/ Straight Chain Solute Interactions			
		2,3-DM-2-Hex	1,2-DM-1-Hex	2,3-DM-1-Hex	3,4-DM-1-Hex
M. Caproate	1-C6:0	1.722	1.585	1.506	1.434
M. Laurate	1-C12:0	1.128	1.088	1.055	1.027
M. Stearate	1-C18:0	0.927	0.913	0.895	0.879

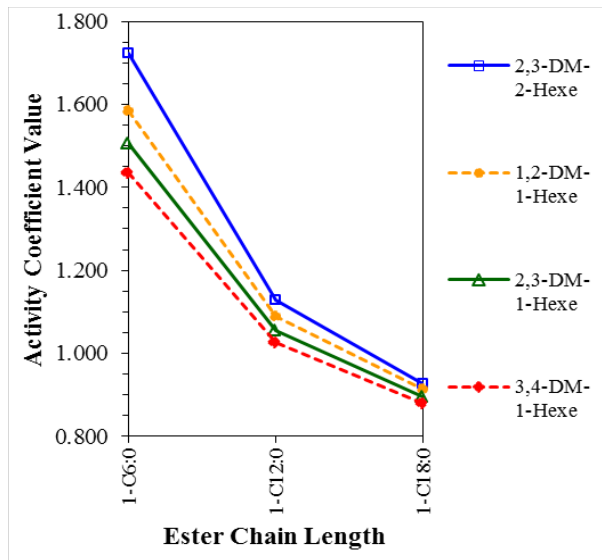


Fig.3 Activity coefficients of branched straight-chain alkenes in selected ester solvents

It is evident from Fig.3 that the location of the methyl branches in relation to the double bond has a profound impact on the activity coefficient of 1-hexene. The order of the resulting activity coefficients was 3-dimethyl-2-hexene (2,3-DM-2-Hexe) > 1,2-dimethyl-1-hexene (1,2-DM-1-Hexe) > 2,3-dimethyl-1-hexene in ester solvents. In 2,3-dimethyl-2-hexene (2,3-DM-2-Hexe) and 1,2-dimethyl-1-hexene (1,2-DM-1-Hexe) methyl branches were attached to both double-bonded carbons while in 2,3-dimethyl-1-hexene only one of the methyl groups was on a double-bonded carbon. 3,4-dimethyl-2-hexene with no methyl groups attached to the double-bonded carbons gave the most favourable phase equilibrium. This variation can possibly be described by the effect the methyl group location has on the van der Waals dispersion forces of the solute molecule.

As previously discussed, the appearance of a double-bond in the VOC causes a kink in its molecule. This kink results in part of the solute molecule being positioned further away from the solvent molecule which leads to a diminished van der Waals dispersion force being exerted by that portion on the solvent molecule. This results in increased solubility (lower activity coefficients) due to increased attractive forces between solute and solvent. However the appearance of a methyl group on the double-bonded carbon reduces the effect of the kink resulting in an increase in solute (VOC) dispersion force. This leads to a decrease in net dispersion force between solute and solvent decreasing the solubility (increased activity coefficients) of these VOCs in biodiesel. The results for a similar study on cyclic alkenes are shown in Table III and Fig.4.

A similar behaviour was found with the VOCs activity coefficients in the following order 1,2-dimethylcyclohexene (1,2-DM-CyHexe) (with a methyl branch attached to each of its double-bonded carbons) > 1,5-dimethylcyclohexene (1,5-DM-CyHexe) (with a methyl branch attached to only one of its double-bonded carbon atoms) > 3,3-dimethylcyclohexene and

4,5-dimethylcyclohexene (with no methyl groups attached to the double-bonded carbons). The interactions of 3,3-dimethylcyclohexene and 4,5-dimethylcyclohexene were similar to those of cyclooctene (Cy=C8), Table III.

TABLE III  
INFLUENCE OF METHYL BRANCH LOCATION ON ESTER/ CYCLIC ALKENE INTERACTIONS

Ester Solvent	Designation	Activity Coefficients - Ester/ Cyclic Solute Interactions				
		1,2-DM-CyHexe	1,5-DM-CyHexe	cy1=C8	4,5-DM-CyHexe	3,3-DM-CyHexe
M. Caproate	1-C6:0	2.042	1.717	1.542	1.552	1.465
M. Laurate	1-C12:0	1.215	1.081	1.018	1.008	0.999
M. Stearate	1-C18:0	0.961	0.874	0.844	0.823	0.835

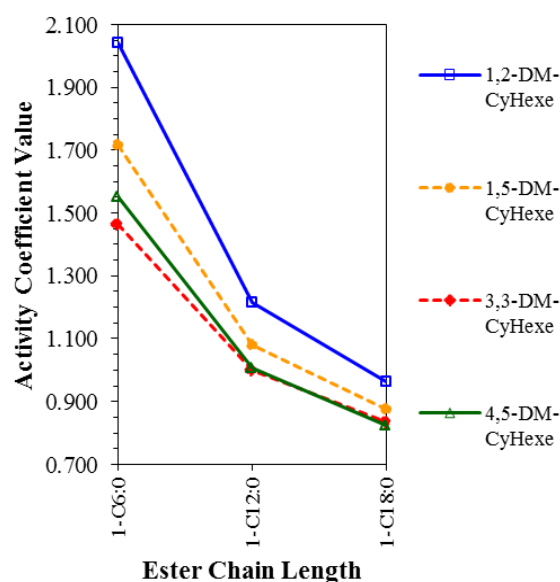


Fig.4 Activity coefficients of branched cyclic alkenes in selected ester solvents

### III. CONCLUSION

The results of this work and those previously published by the same authors [7] have shown that compared to alkanes, alkenes are more soluble in biodiesel making them easier to absorb from waste gas streams. The relative size of the solvent (biodiesel) molecules in relation to the solute molecules influenced the thermodynamic interactions. The shape of the solvent (biodiesel) molecule was found to have an effect on the cross-over point. The phase equilibrium of 1-hexene in biodiesel was influenced by the location of methyl group branches in relation to the double bond.

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#### REFERENCES

- [1] J. J. Scheepers and E. Muzenda, "Alkenes – Ester Polymeric Solvents Thermodynamic Interactions – Part 1" *International Conference on Ecology, Agriculture and Chemical Engineering*, Bangkok, Thailand, December 18-19 2012. *Unpublished*
- [2] U. Weidlich and J. Gmehling, "A Modified UNIFAC Model. 1. Prediction of VLE, hE, and  $\gamma^\infty$ ," *Ind. Eng. Chem. Res.*, vol. 26, no. 7, pp. 1372–1381, Jul. 1987.
- [3] K. Bay, H. Wanko, and J. Ulrich, "Absorption of Volatile Organic Compounds in Biodiesel: Determination of Infinite Dilution Activity Coefficients by Headspace Gas Chromatography," *Chem. Eng. Res. Des.*, vol. 84, no. A1, pp. 22–27, Jan. 2006.
- [4] K. Bay, H. Wanko, and J. Ulrich, "Biodiesel - Hoch Siedendes Absorbens für die Gasreinigung," *Chemie Ingenieur Technik*, vol. 76, no. 3, pp. 328–333, Mar. 2004.
- [5] P. Alessi, M. Fermeglia, and I. Kikic, "Significance of Dilute Regions," *Fluid Phase Equilibria*, vol. 70, no.2-3, pp. 239 – 250, Dec. 1991.
- [6] J. J. Scheepers, E. Muzenda and M. Belaid, "Influence of Temperature and Molecular Structure on Organics-Biodiesel Interactions using Group Contribution Methods", The 2012 International Conference of Manufacturing Engineering and Engineering Management, *World Congress on Engineering 2012*, IAENG, London, UK, 4-6 July 2012
- [7] J.J. Scheepers, E. Muzenda, and M. Belaid, "Influence of Structure on Fatty Acid Ester-Alkane Interactions," in *Internat. Conf Proc. PSRC Internat. Conf. Educ. Humanities. Chemical. Environ. Sciences*, Bangkok, Sept. 2012, pp. 93–102.
- [8] J. van Gerpen, B. Shanks, R. Pruszko, D. Clements, and G. Knothe, "Biodiesel Production Technology: August 2002–January 2004," National Renewable Energy Laboratory (NREL), Colorado, Subcontractor Report July 2004