

Role of Molecular Structure in Ester/ Alkane Phase Equilibria

Jacques J. Scheepers, Edison Muzenda, and Mohamed Belaid

Abstract—The activity coefficients of alkane structures in various types of fatty acid ester solvents was measured in order to determine the effect of bond interactions. It is important to understand the mechanics of these interactions for the design of absorbers and strippers. Activity coefficients were determined by use of a Microsoft Excel spreadsheet designed for this purpose. It was found that the length of the ester chain, as well as ester chain saturation had an impact on activity coefficients. Saturated ester chains and longer ester chains yielded lower activity coefficients. Multiple branched cycloalkanes yielded lower activity coefficients than straight chain hydrocarbons and un-branched cycloalkanes. It was also established that the location of the carboxyl group in the ester chain had no influence on activity coefficients.

Keywords—Absorption, activity coefficients, biodiesel, esters, volatile organic compounds.

I. INTRODUCTION

VOLATILE organic compounds (VOCs) and hazardous air pollutants (HAPs) have a globally negative impact on the well-being of the environment. Many of these compounds are highly flammable, are classified as irritants, and some are even suspected carcinogens or teratogens. VOCs and HAPs are also major contributors to global air pollution, hence the drive by national and international authorities to limit the release of these toxins into the environment through the imposition of increasingly stringent environmental legislation on industrial manufacturers and consumers of VOCs and HAPs.

A. Technology Selection

In order to comply with legal requirements, chemical industries often employ VOCs abatement technologies to recover and purify process emissions (waste gas streams). The technologies used for VOC recovery are mostly separation processes of the phase contacting type such as physical and chemical absorption [1]. If a suitable solvent is available (i.e.

one that is easily regenerated), then an absorption process could be considered as an attractive end-of-pipe VOC treatment technology for recovering the required VOCs from the solvent for further processing.

B. Solvent Selection

The selection of a suitable solvent can impact profoundly on the profitability of an absorption process. There is an increasing trend towards the use of ‘green’ absorbents, of which fatty acid esters, in particular fatty acid methyl esters (FAMEs), show much promise. Biodiesel, comprising predominantly of esters of various chain lengths has particular promise as a future absorbent because, apart from it possessing most of the properties of a good solvent biodiesel is also environmentally friendly. Bay, Wanko and Ulrich [2], [3] have demonstrated that biodiesel which is composed of FAMEs is well-suited as a solvent for VOC absorption.

Biodiesel is predominantly manufactured using a base-catalyzed trans-esterification process, in which the natural triglycerides of the feedstock, usually a suitable vegetable oil, are substituted with a suitable alcohol. Methanol is mainly used as the alcohol feedstock since it is more readily available and is also more cost-effective [4] – reaction of triglycerides with methanol yields FAMEs as products. However ethanol, propanol and butanol can also be used yielding varying chain lengths of ethyl esters, methyl esters and butyl esters respectively. This work examines the interactions of methyl, ethyl, propyl and butyl esters of various chain lengths with alkane VOCs in order to determine the most suitable absorbent solvent for abating these VOCs.

C. Thermodynamic Model Selection

Optimization and efficiency are paramount in separation system design. Since operation of separation systems such as absorbers can often account for between 60 – 80% of total plant operating costs [4], it is essential that these systems are designed to operate as optimally and efficiently as possible. This implies maximum VOC removal efficiency with minimal energy and process material input. VOCs requiring recovery are mostly present in very dilute concentrations in process streams. It is for this reason that knowledge of how a given VOC/ process stream mixture behaves in the dilute region is essential in the design of separation systems [5].

Activity coefficients, which in thermodynamic computations account for the deviations from ideal behavior (i.e. from Raoult’s Law) of a system, are often used in the

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development of phase-equilibrium ratios (K-values). The required thermodynamic data can be ascertained via experimental techniques, but this is time consuming and measurement of the required parameters is often complex. Appropriate thermodynamic models are therefore utilized to obtain estimated values of the required thermodynamic data. For the purposes of this work the Modified UNIFAC (Dortmund) excess Gibbs energy group contribution model, developed by Weidlich and Gmehling in 1987 [6], was used to predict infinite dilution activity coefficients for the various VOC-ester mixtures studied. A Microsoft Excel spreadsheet version of the model was generated in order to perform the required computations.

II. THERMODYNAMIC FUNDAMENTALS

A. Phase Equilibrium

Prausnitz, Lichtenthaler and de Azevedo [7] have shown that for a closed heterogeneous system at equilibrium, consisting of N phases and m components, the following principles are valid for the system pressure (P), temperature (T) and chemical potential (μ):

$$T^{(1)} = T^{(2)} = T^{(3)} = \dots = T^{(N)} \quad (1)$$

$$P^{(1)} = P^{(2)} = P^{(3)} = \dots = P^{(N)} \quad (2)$$

$$\mu_m^{(1)} = \mu_m^{(2)} = \mu_m^{(3)} = \dots = \mu_m^{(N)} \quad (3)$$

Under isothermal conditions, the change in chemical potential for an ideal gas changing from a standard (reference) state pressure (P^0) to pressure (P) is represented by (4) [7]:

$$\mu_i - \mu_i^0 = RT \ln \frac{P}{P^0}, \quad (4)$$

where μ_i is the chemical potential (i.e. partial molar Gibbs free energy) of component i , and R is defined as the Universal Gas Constant. However (4) represents ideal gas behavior, thus the pressure terms are replaced by fugacity (f) terms to cater for non-ideal gas behavior as in (5) [7]:

$$\mu_i - \mu_i^0 = RT \ln \frac{f_i}{f_i^0}. \quad (5)$$

In (5), the ratio f_i/f_i^0 is referred to as the activity (a_i) of component i in the system. Using the principle defined in (1), (2) and (3) above, (5) is further modified to cater for a system in vapor-liquid equilibrium (VLE), consisting of a liquid phase (L) and vapor phase (V), as

$$\mu_{i,V}^0 + RT \ln \frac{f_{i,V}}{f_{i,V}^0} = \mu_{i,L}^0 + RT \ln \frac{f_{i,L}}{f_{i,L}^0} \quad (6)$$

If the standard states for the two phases are the same,

(i.e. $\mu_{i,V}^0 = \mu_{i,L}^0$) then it follows that the standard state fugacities for each phase are also equal, i.e.

$$f_{i,V}^0 = f_{i,L}^0, \quad (7)$$

thus implying that

$$f_{i,V} = f_{i,L}. \quad (8)$$

Equations (1), (2) and (8) are regarded as the three fundamental equations of phase equilibrium [7]. Using (8), the partial fugacity (\hat{f}_i) of component i can be therefore be expressed as

$$\hat{f}_{i,V} = \hat{f}_{i,L}. \quad (9)$$

B. Phase Equilibrium Ratios for Separation Systems

Phase equilibrium ratios (also known as K -factors, or K -values) are often used in separation technology design. They are of significance in equilibrium-stage computations when the relative volatility of components to be separated needs to be determined. The K -factor is mathematically defined by (10) as follows [8]:

$$K_i \equiv \frac{y_i}{x_i}, \quad (10)$$

where y_i represents the mole fraction in the vapor phase and x_i represents the mole fraction in the liquid phase.

In order to obtain the desired equilibrium ratios, it is often more appropriate to replace the partial fugacities (\hat{f}_i) by expressions which incorporate mole fractions. It is also necessary to cater for the system liquid phase non-ideality – this is often accounted for by the use of activity coefficients (γ). Activity coefficients represent the departure of activities from ideal liquid mole fractions, as in (11) [8]:

$$\gamma_{i,L} \equiv \frac{a_{i,L}}{x_i}. \quad (11)$$

By substituting the activity (a_i) with the partial fugacity ratio described previously in (9), and upon rearranging (11), the mole fraction expression for the partial fugacity in the liquid phase is obtained [8]:

$$\hat{f}_{i,L} = \gamma_{i,L} \cdot x_i \cdot f_{i,L}^0. \quad (12)$$

Equation (12) can also be written using partial fugacity coefficients ($\hat{\phi}_i$), as follows [8]:

$$\hat{f}_{i,L} = \hat{\phi}_{i,L} \cdot x_i \cdot P. \quad (13)$$

Similarly, partial fugacity coefficients can also be used to obtain a mole fraction expression for vapor phase non-ideality as follows [8]:

$$\hat{f}_{i,V} = \hat{\phi}_{i,V} \cdot y_i \cdot P \quad (14)$$

Using (7) and equating (14) to (13), the *equation-of-state* (EoS) form of the K -value is obtained [8], i.e.

$$K_i = \frac{\hat{\phi}_{i,L}}{\hat{\phi}_{i,V}}, \quad (15)$$

which, in combination with appropriate mixing rules, allows one to determine required VLE data using EoS models such as the Soave-Redlich-Kwong EoS and the Peng-Robinson EoS. The EoS approach to obtaining VLE data is often referred to as the φ - φ approach [9] since the real behavior of both phases is described using fugacity coefficients.

By following the same approach as for (15), but equating (14) to (12) instead, one obtains the *activity coefficient* form of the K -value [8], i.e.

$$K_i = \frac{\gamma_{i,L} \cdot \hat{f}_{i,L}}{\hat{\phi}_{i,V} \cdot P} = \frac{\gamma_{i,L} \cdot \phi_{i,L}}{\hat{\phi}_{i,V}}, \quad (16)$$

The above approach is often referred to as the γ - φ approach [9] since activity coefficients are used to describe the real behavior of the liquid phase, and the fugacity coefficients the vapor phase. The activity coefficient approach is used for determining VLE data using excess Gibbs energy models and appropriate vapor pressure data.

III. MODIFIED UNIFAC DORTMUND GROUP CONTRIBUTION METHOD

When little or no experimental data are available, a class of excess Gibbs energy models (g^E -models) known as group contribution methods (GCMs), is traditionally utilized to predict activity coefficients under specified conditions of temperature and composition [10]. A useful technique for activity coefficient estimation is the UNIFAC method – it is generally regarded as the most successful of the g^E -models [11]. The UNIFAC GCM consists of a combinatorial (C) term, which describes the excess Gibbs energy arising due to differences in molecular size and shape, and a residual (R) term which describes the excess Gibbs energy differences due to molecular interactions [1], i.e.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R. \quad (17)$$

The original UNIFAC model, developed in 1975 by Fredenslund, Jones and Prausnitz [12], had several shortcomings which led to various modifications to the model being proposed. Modified UNIFAC Dortmund is regarded as the more superior of these modifications in most instances [13].

A. Combinatorial Term

The combinatorial term is derived from statistical-mathematical arguments and is computed using the

Stavermann-Guggenheim correction to the original Flory-Huggins expression, i.e.:

$$\ln \gamma_i^C = \ln \frac{\Phi_i^C}{x_i} + 1 - \frac{\Phi_i^C}{x_i} - \frac{z}{2} q_i \left(\ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right). \quad (18)$$

In the above equation, Parameter z is known as the lattice co-ordination number, usually set to a value of 10, and parameter q_i is referred to as the van der Waals molecular surface area for component i . Parameter θ_i , known as the area fraction, is determined by the expression

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \quad (19)$$

where j represents the summation over all components, including component i . Equation (18) differs from the Original UNIFAC expression in that a correction to the volume (segment) fraction term (Φ_i^C) replaces the standard volume fraction term (Φ_i) in the Flory-Huggins part of the combinatorial expression. The standard volume fraction term (which still appears in the Stavermann-Guggenheim correction) is expressed as

$$\Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}, \quad (20)$$

whereas the corrected segment fraction is defined as follows:

$$\Phi_i^C = \frac{r_i^{3/4} x_i}{\sum_j r_j^{3/4} x_j}, \quad (21)$$

The term r_i is known as the van der Waals volume parameter.

B. Residual Term

The residual term is based on the solution-of-groups concept, which is based on the assumption that a fluid's physical properties are the sum of contributions made by the molecule's functional groups [12]. The residual term is expressed as

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}], \quad (22)$$

where $v_k^{(i)}$ is the number of groups of kind k in a molecule of component (i) and is thus always an integer. The residual activity coefficients (Γ_k) and ($\Gamma_k^{(i)}$) are both computed using (23), the superscript i indicating the residual activity coefficient of k in a reference solution containing only molecules of type i .

$$\ln \Gamma_k = Q_k \left\{ 1 - \left(\ln \sum_m \Theta_m \psi_{mk} \right) - \sum_m \left(\frac{\Theta_m \psi_{km}}{\sum_n \Theta_n \psi_{nm}} \right) \right\} \quad (23)$$

Parameter Θ_m , the surface area fraction for group m , is described as

$$\Theta_m = \frac{Q_m x_m}{\sum_n Q_n x_n}, \quad (24)$$

where Q represents the group area parameter and X represents the group mole fraction for group m , calculated as follows:

$$X_m = \frac{v_m^{(j)} x_j}{\sum_n \sum_j v_n^{(j)} x_j}. \quad (25)$$

The group interaction parameter (ψ_{mn}) is determined as follows:

$$\psi_{mn} = \exp\left(-\frac{a_{mn} + b_{mn}T + c_{mn}T^2}{T}\right). \quad (26)$$

IV. PREVIOUS STUDIES ON THE AREA OF INTEREST

Bay, Wanko and Ulrich [3] published activity coefficient data in the dilute region of various VOCs using Gas-Liquid Chromatography (GLC). The results, obtained at temperatures of 30°C, 40°C and 50°C, were compared to estimations obtained from an unspecified UNIFAC type model at 30°C. The results showed low activity coefficients for all the families except for the alcohols, formic acid and acetonitrile. Low activity coefficient values (especially activity coefficient values less than 1) indicate favorable solute-solvent interaction for absorption processes. The authors thus concluded that, barring the exceptions noted above, the high boiling point methyl esters which constitute biodiesel are well suited as absorption solvents.

Bay, Wanko and Ulrich [2] followed up their first publication with a detailed analysis of VLE data on three of the VOCs studied in the previous report, namely benzene, toluene and 1,2-dichloroethane (1,2-DCE). Head Space Gas Chromatography was employed to calculate the activity coefficients of these compounds in European biodiesel, approximating the properties to that of the major constituent methyl oleate. Measurements were carried out for pure biodiesel and varying mole fractions of the three VOCs in biodiesel at temperatures of 30°C, 35°C and 40°C. During the analyses, the mole fraction of the VOCs was kept below 0.008, corresponding to VOC partial pressures of between 20 Pa and 200 Pa in all cases for the purposes of extrapolation to infinite dilution. The experimentally determined activity coefficients of the three VOCs in biodiesel were compared to results calculated with Original UNIFAC, and the Modified UNIFAC Dortmund and Lyngby models.

The authors concluded that the activity coefficients calculated during this trial compared well with the data from the previous work, and showed good agreement with the Original and Modified UNIFAC (Dortmund) predictions.

Spear *et al* [14] investigated the physico-chemical properties of soybean oil methyl esters as a potential replacement to organic solvents in liquid-liquid extraction processes. They determined that the solute behavior during extraction was comparable to that found for traditional solvents, thereby concluding that soybean oil methyl esters may be a suitable 'green' solvent for liquid-liquid extraction processes.

V. METHODOLOGY

In order to accomplish the objectives of this work, a Microsoft Excel spread sheet was designed to perform the required computations. Model-specific group interaction parameter tables, and ' R_k '- and ' Q_k ' parameter tables, were established within the spread sheet in order to facilitate ease of computation.

The UNIFAC models in essence encompass the following methodology:

- The suitable reduction of previously obtained experimental activity coefficient data to develop interaction parameters which characterize the interactions between pairs of structural groups, and
- The use of these parameters in predicting activity coefficients for other systems for which no experimentally obtained data is available, but which contain the same functional groups.

The interaction parameters which comprise the UNIFAC models are the energy-interaction parameters R_k (group volume parameter) and Q_k (group area parameter), as well as the group interaction parameters a_{mn} , b_{mn} and c_{mn} .

VI. RESULTS & DISCUSSION

Activity coefficient values were predicted for 41 volatile organic compounds in 18 various methyl-, ethyl-, propyl- and butyl esters at a temperature of 30°C. This temperature was deemed most suitable for the required computations as this temperature lies within an area of interest for most scientific investigations, and is considered a practical temperature for most absorption operations [2]. A mole fraction of 1×10^{-5} was selected as a standard for all calculations, as this mole fraction falls between the infinite dilution region proposed by Alessi, Fermiglia and Kikic of between 10^{-4} (for mixtures of similar hydrocarbons) and 10^{-7} (for highly associated species) [5]. Furthermore, preliminary tests of the model revealed no appreciable change in infinite dilution activity coefficient at mole fraction values lower than 1×10^{-5} for the species tested.

A. General Observations

For the purposes of this work, N appearing in tables and graphs represents the number of carbon atoms in the chain (e.g. for propane with three carbons, $N=3$). As per van Gerpen *et al* [15], ester solvents are designated after the 'C' by two numbers separated by a colon. The first number represents the number of carbon atoms in the chain including the carboxylic

carbon (i.e. the carbon that is double bonded to the oxygen atom) and the second number designates the number of double bonds in the ester molecule. The number attached as prefix to the 'C' refers to the length of the alcohol chain which is attached to the carboxylic group during the esterification reaction. Thus (3-C18:0) refers to the ester propyl stearate, which was formed using propanol. It has 18 carbons in the ester chain (including the carboxylic carbon) and the molecule has 21 carbons in total if one includes the three propyl carbons. There are no double-bonded carbons in the chain.

B. Aliphatic (Saturated Bond) Ester Interactions with Alkanes

Table I presents results computed in this work for the C₃ to C₁₅ straight chain alkanes (*n*-C_N) in various saturated bonded methyl ester solvents.

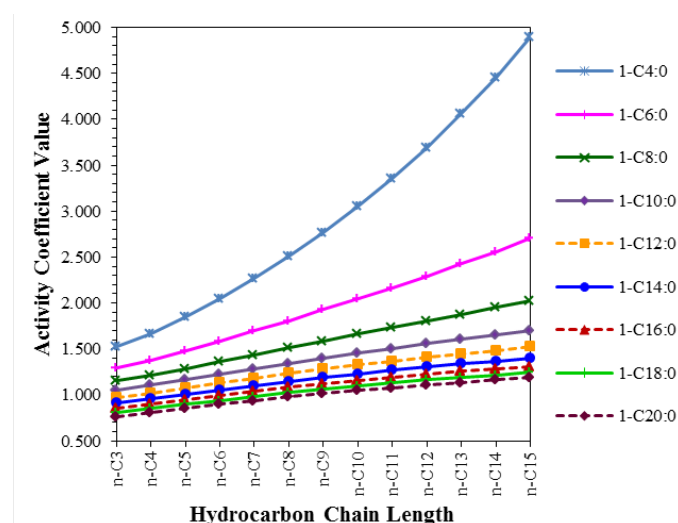


Fig. 1 Activity coefficients for straight-chain hydrocarbons in various aliphatic ester solvents

The results, in Fig. 1, illustrate a clear trend of increasing activity coefficient values with an increase in hydrocarbon

chain length.

The increase in activity coefficient is more marked with the smaller ester/ alkane interactions (especially with methyl caproate), whilst the increase is only gradual with the longer-chained esters. Since none of the esters featured in Fig.1 contain unsaturated (double) bonds, and since aliphatic alkanes are highly unreactive, it can be assumed that the increase in activity coefficient with an increase in carbon chain length is attributable to solvent and solute sizes only. The steep increase experienced in the methyl caproate/ alkane interactions can most likely be attributed to the size of the ester solvent in relation to the size of the alkane solutes. On the other hand, the size of the C16:0 to C20:0 esters are much larger than the solute molecules; hence the increase in activity coefficient with increased hydrocarbon chain length being only slight. As expected, methyl arachidate yielded the lowest activity coefficients, being the largest saturated ester solvent computed in this work.

The solubility of alkanes decreases with an increase in molecular weight due to an increase in van der Waals forces with increasing molecular weight. Furthermore, alkanes are non-polar molecules. Since non-polar solutes are generally only soluble in non-polar solvents, it therefore follows that the carboxyl group of the ester solvent would have little effect on the alkane-ester interactions and the ester solvents could therefore be considered as essentially non-polar. Based on the above analogy, the increase in activity coefficients experienced with increasing solute chain length can be attributed to the fact that increased energy is required to break the existing intermolecular solute bonds before intermolecular bonding with the solvent can take place. This is attributed to the increased surface area exposed to bonding with increased chain length that needs to first be overcome before new bonds can be formed.

TABLE I
ACTIVITY COEFFICIENTS OF STRAIGHT CHAIN HYDROCARBONS IN ALIPHATIC ESTERS

Ester Solvent	Designation	Straight Chain Solutes												
		<i>n</i> -C ₃	<i>n</i> -C ₄	<i>n</i> -C ₅	<i>n</i> -C ₆	<i>n</i> -C ₇	<i>n</i> -C ₈	<i>n</i> -C ₉	<i>n</i> -C ₁₀	<i>n</i> -C ₁₁	<i>n</i> -C ₁₂	<i>n</i> -C ₁₃	<i>n</i> -C ₁₄	<i>n</i> -C ₁₅
M. Butyrate	1-C4:0	1.521	1.669	1.847	2.047	2.266	2.505	2.766	3.049	3.358	3.694	4.061	4.461	4.898
M. Caproate	1-C6:0	1.293	1.379	1.478	1.585	1.695	1.809	1.926	2.045	2.169	2.296	2.427	2.562	2.702
M. Octanoate	1-C8:0	1.152	1.216	1.289	1.364	1.439	1.514	1.588	1.661	1.734	1.806	1.878	1.950	2.022
M. Decanoate	1-C10:0	1.051	1.105	1.165	1.227	1.287	1.345	1.401	1.456	1.508	1.559	1.609	1.657	1.705
M. Laurate	1-C12:0	0.972	1.021	1.075	1.129	1.182	1.232	1.279	1.324	1.367	1.408	1.447	1.485	1.521
M. Myristate	1-C14:0	0.907	0.953	1.004	1.054	1.102	1.147	1.190	1.230	1.268	1.304	1.337	1.369	1.399
M. Palmitate	1-C16:0	0.853	0.897	0.945	0.992	1.038	1.080	1.120	1.157	1.192	1.225	1.255	1.284	1.311
M. Stearate	1-C18:0	0.807	0.849	0.895	0.941	0.984	1.025	1.063	1.098	1.131	1.162	1.191	1.218	1.243
M. Arachidate	1-C20:0	0.766	0.808	0.852	0.896	0.938	0.978	1.014	1.048	1.080	1.110	1.137	1.163	1.187

C. Olefinic Ester Interactions with Alkanes

Table 2 presents results for the C₃ to C₁₅ straight chain alkanes in 1-C18:1 (methyl oleate), 1-C18:2 (methyl linoleate)

and 1-C18:3 (methyl linolenate) unsaturated bonded methyl ester solvents. The results, depicted graphically in Fig. 2, show that methyl stearate (1-C18:0) performed best (i.e. interactions with respective straight chain alkanes yielded

lowest activity coefficients) of methyl oleate, methyl linoleate and methyl linolenate. Methyl oleate, possessing only one double bond, performed better than the other unsaturated esters.

TABLE II
ACTIVITY COEFFICIENTS OF STRAIGHT CHAIN HYDROCARBONS IN OLEFINIC ESTERS

Ester Solvent	Designation	Straight Chain Solutes												
		n-C ₃	n-C ₄	n-C ₅	n-C ₆	n-C ₇	n-C ₈	n-C ₉	n-C ₁₀	n-C ₁₁	n-C ₁₂	n-C ₁₃	n-C ₁₄	n-C ₁₅
M. Stearate	1-C18:0	0.807	0.849	0.895	0.941	0.984	1.025	1.063	1.098	1.131	1.162	1.191	1.218	1.243
M. Oleate	1-C18:1	0.857	0.905	0.957	1.008	1.058	1.105	1.149	1.191	1.230	1.267	1.303	1.336	1.368
M. Linoleate	1-C18:2	0.914	0.968	1.028	1.088	1.146	1.202	1.255	1.306	1.355	1.401	1.446	1.489	1.531
M. Linolenate	1-C18:3	0.978	1.042	1.112	1.183	1.252	1.319	1.385	1.448	1.510	1.570	1.628	1.685	1.740

Thus a clear trend of increasing activity coefficients with an increase in unsaturation (i.e. double bonds) present in the ester hydrocarbon chain is observed.

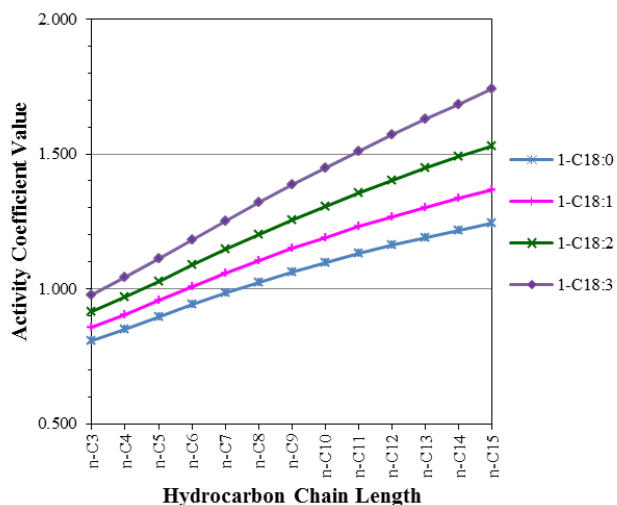


Fig. 2 Activity coefficients for straight-chain hydrocarbons in isomers of C18 ester solvents

The reason for the poorer absorption capacity of the unsaturated bonded esters in relation to the saturated bonded esters is likely due to the conformation of the unsaturated *cis*- or *trans*- double-bonds. This would affect the surface area of the solvent presented for bond interaction to occur, making it smaller in relation to the saturated straight-chain counterparts.

Bay, Wanko and Ulrich [2] assumed that the properties of European biodiesel would be similar to those of methyl oleate, constituting approximately 60% of the total blend. This assumption was made in order to predict activity coefficient values to test the validity of their experimental values. Based on the above findings, the accuracy of this assumption could be queried pending the fraction of zero- to single- to double- to triple-unsaturated bonded esters in the biodiesel composition.

D. Effects of Alcohol Feedstock in Ester Preparation

The interactions of esters formed with C₁-, C₂-, C₃- and C₄-alcohols are shown in Table 3 and Fig. 3.

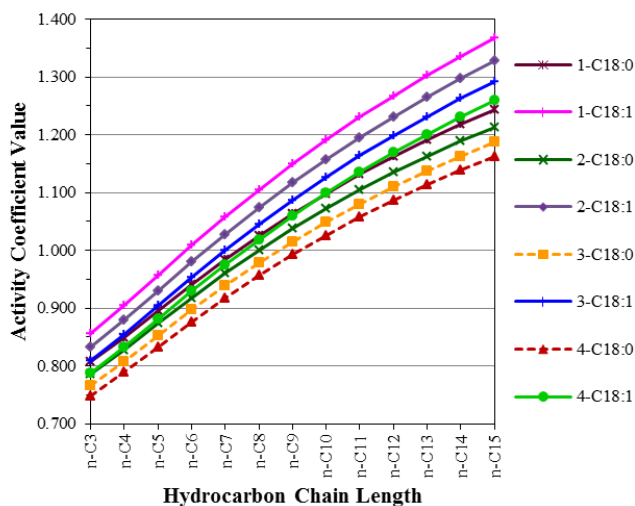


Fig. 3 Activity coefficients for straight-chain hydrocarbons in C18 ester solvents produced from different alcohols

A trend of decreasing activity coefficients with increase in alcohol-bonded chain length was noted, thus butyl esters performed best as an absorbent solvent than esters prepared with the lower alcohols. The improved performance is purely a function of the increase in solvent chain length as it was observed that propyl stearate (3-C18:0), possessing 21 carbons yielded identical activity coefficients as methyl arachidate which also possesses 21 carbons. This observation confirms that the location of the carboxyl group in the total ester chain length has no influence on solvent-solute bond interactions. It should be noted that, as a weakness, UNIFAC cannot account for isomeric effects [16]. However, since vapor-liquid equilibrium behavior is usually only significant when vapor pressure differences are experienced [16], it can be assumed that isomeric effects on activity coefficients are negligible.

TABLE III
ACTIVITY COEFFICIENTS OF STRAIGHT CHAIN HYDROCARBONS IN ESTERS FORMED FROM VARIOUS ALCOHOLS

Ester Solvent	Designation	Straight Chain Solutes												
		n-C ₅	n-C ₆	n-C ₇	n-C ₈	n-C ₉	n-C ₁₀	n-C ₁₁	n-C ₁₂	n-C ₁₃	n-C ₁₄	n-C ₁₅		
M. Stearate	1-C18:0	0.807	0.849	0.895	0.941	0.984	1.025	1.063	1.098	1.131	1.162	1.191	1.218	1.243
M. Oleate	1-C18:1	0.857	0.905	0.957	1.008	1.058	1.105	1.149	1.191	1.230	1.267	1.303	1.336	1.368
E. Stearate	2-C18:0	0.786	0.828	0.873	0.918	0.960	1.000	1.038	1.072	1.105	1.135	1.163	1.189	1.214
E. Oleate	2-C18:1	0.832	0.879	0.929	0.980	1.028	1.074	1.117	1.157	1.195	1.231	1.265	1.297	1.328
P. Stearate	3-C18:0	0.766	0.808	0.852	0.896	0.938	0.978	1.014	1.048	1.080	1.110	1.137	1.163	1.187
P. Oleate	3-C18:1	0.809	0.855	0.904	0.954	1.001	1.045	1.087	1.127	1.164	1.199	1.231	1.263	1.292
B. Stearate	4-C18:0	0.748	0.789	0.833	0.876	0.918	0.956	0.992	1.026	1.057	1.087	1.114	1.139	1.163
B. Oleate	4-C18:1	0.787	0.832	0.881	0.929	0.975	1.019	1.060	1.098	1.135	1.169	1.201	1.231	1.259

E. Ester Interactions with Branched Alkanes

It is evident from the results in Table 4 that the location of branches on the parent chain has negligible effect on solute-solvent interaction. Interactions with compounds with two branches linked to the same carbon (e.g. neopentane, 2,2-

dimethylhexane) yielded generally slightly lower activity coefficients than straight-chained compounds with similar carbon values (e.g. n-pentane, n-octane) and staggered-branch counterparts (e.g. isopentane, 2,5-dimethylhexane).

TABLE IV
ACTIVITY COEFFICIENTS OF BRANCHED HYDROCARBON SOLUTES IN VARIOUS ESTERS

Ester Solvent	Designation	Pentanes		Dimethyl hexanes		Trimethyl hexanes		Diethyl hexanes	
		Isopentane	Neopentane	2,2-Dimethyl Hexane	2,5-Dimethyl Hexane	2,2,5-Trimethyl Hexane	2,3,5-Trimethyl Hexane	3,3-Diethyl Hexane	3,4-Diethyl Hexane
M. Caproate	1-C6:0	1.478	1.477	1.809	1.809	1.926	1.926	2.046	2.045
M. Laurate	1-C12:0	1.075	1.073	1.231	1.232	1.278	1.279	1.324	1.324
M. Stearate	1-C18:0	0.895	0.894	1.024	1.025	1.062	1.063	1.097	1.098
M. Oleate	1-C18:1	0.957	0.955	1.103	1.105	1.148	1.149	1.190	1.191
M. Linoleate	1-C18:2	1.028	1.026	1.200	1.202	1.254	1.255	1.305	1.306
M. Linolenate	1-C18:3	1.112	1.109	1.317	1.319	1.383	1.385	1.446	1.448
E. Stearate	2-C18:0	0.873	0.872	0.999	1.000	1.037	1.038	1.072	1.072
E. Oleate	2-C18:1	0.929	0.928	1.072	1.074	1.116	1.117	1.156	1.157
P. Stearate	3-C18:0	0.852	0.851	0.977	0.978	1.013	1.014	1.048	1.048
P. Oleate	3-C18:1	0.904	0.902	1.044	1.045	1.086	1.087	1.126	1.127
B. Stearate	4-C18:0	0.833	0.831	0.955	0.956	0.992	0.992	1.025	1.026
B. Oleate	4-C18:1	0.881	0.879	1.018	1.019	1.059	1.060	1.097	1.098

This effect can possibly be attributed to the compounds with branching from the same carbon being more compact (thus possessing weaker London dispersion forces) than the straight chain and staggered chain counterparts. As described earlier stronger dispersion forces require more energy to break existing bond interactions in order to form new bonds.

F. Ester Interactions with Cycloalkanes

It was found that activity coefficients for ester-cycloalkane interactions increased with an increase in the size of the cycloalkane per ester type. These results are presented in Table 5 and Fig. 4 (a), (b) and (c). Comparisons of cycloalkane-ester solvent interactions with their straight chain counterparts revealed lower activity coefficients for the smaller cycloalkanes than the straight chained compounds.

However a point was attained where the cycloalkane-ester interactions yielded higher activity coefficients than the straight chain counterparts. This point (referred to in this work as the *cross-over point*) differed from solvent to solvent, with methyl caproate attaining cross-over with cyclopentane and methyl stearate attaining cross-over with cyclooctane as examples. Thus the length of the ester affected the location of the crossover point – this point was reached at lower molecular size for smaller esters than for the larger esters such as butyl stearate. Bond saturation also impacted the cross-over, with 1-C18:2 and 1-C18:3 achieving the cross-over at a molecular size of about C₆, 1-C18:1 reaching the point at approximately C₇ and 1-C18:0 reaching the cross-over at C₈. The maximum crossover point attained in this work was C₈, thus implying that cycloalkanes larger than this value (i.e.

molecules larger than cyclohexane) are more difficult to absorb. This phenomenon could be attributed to the bond

angle of the larger cycloalkanes, which is more ideal than that of the smaller cycloalkanes up to cyclohexane.

TABLE V
ACTIVITY COEFFICIENTS OF CYCLOALKANE SOLUTES IN VARIOUS ESTERS

Ester Solvent	Designation	Cycloalkane Solutes							
		Cyclopropane	Cyclobutane	Cyclopentane	Cyclohexane	Cycloheptane	Cyclooctane	Cyclononane	Cyclodecane
M. Caproate	1-C6:0	1.126	1.318	1.482	1.627	1.758	1.879	1.991	2.096
M. Laurate	1-C12:0	0.758	0.889	1.000	1.094	1.177	1.249	1.314	1.371
M. Stearate	1-C18:0	0.602	0.714	0.809	0.893	0.967	1.033	1.092	1.146
M. Oleate	1-C18:1	0.625	0.751	0.863	0.964	1.058	1.145	1.226	1.304
M. Linoleate	1-C18:2	0.653	0.795	0.927	1.051	1.170	1.285	1.397	1.506
M. Linolenate	1-C18:3	0.684	0.847	1.003	1.156	1.308	1.459	1.611	1.766
E. Stearate	2-C18:0	0.584	0.693	0.787	0.869	0.942	1.007	1.066	1.120
E. Oleate	2-C18:1	0.605	0.727	0.836	0.935	1.026	1.110	1.190	1.265
P. Stearate	3-C18:0	0.567	0.674	0.766	0.847	0.919	0.984	1.042	1.096
P. Oleate	3-C18:1	0.586	0.705	0.811	0.908	0.996	1.079	1.157	1.230
B. Stearate	4-C18:0	0.551	0.656	0.747	0.826	0.898	0.962	1.020	1.073
B. Oleate	4-C18:1	0.569	0.685	0.788	0.882	0.969	1.050	1.126	1.198

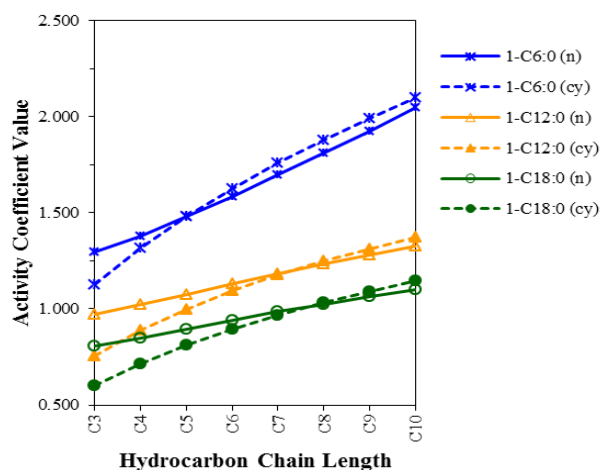


Fig. 4 (a) Comparison of activity coefficients for cycloalkanes and straight chain hydrocarbons in saturated methyl ester solvents

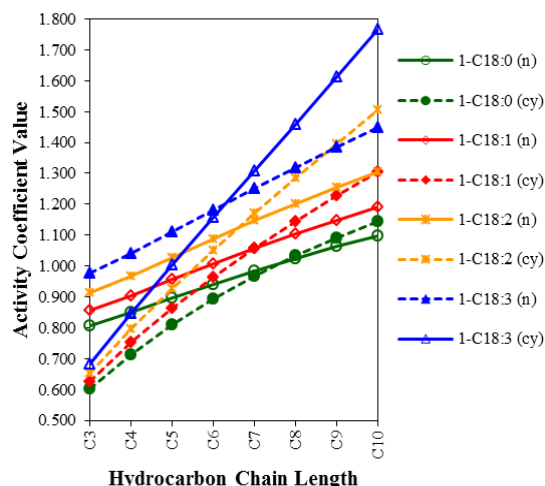


Fig. 4 (b) Comparison of activity coefficients for cycloalkanes and

straight chain hydrocarbons in isomers of C18 methyl ester solvents

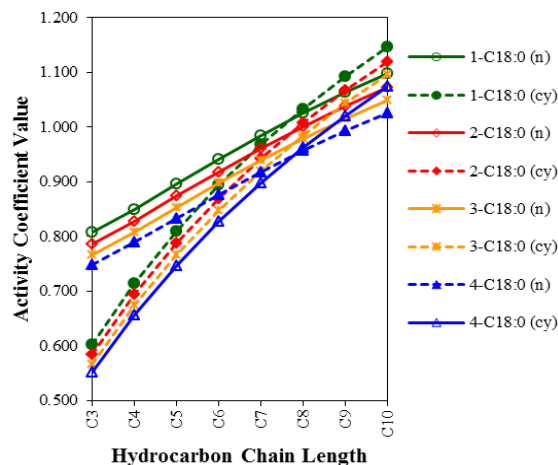


Fig. 4 (c) Comparison of activity coefficients for cycloalkanes and straight chain hydrocarbons in methyl ester solvents formed from different alcohols

The large carbon bond angles in the smaller cycloalkanes make them more reactive and thus intermolecular bonds are easier to break. The larger molecules possess increased van der Waals dispersion forces as they are not as influenced by their carbon bond angles and thus more energy is required to break these bonds. Furthermore, as the cycloalkane molecule increases in size, it becomes more difficult for the molecule to arrange itself spatially in the lattice in order to facilitate the bonding process with the ester solvent; hence the increase in activity coefficient values over their straight-chained counterparts.

G. Ester Interactions with Cycloalkyl Radicals

The interactions of esters with singular straight chain

cycloalkyl radicals are tabulated in Table 6. Activity coefficients for these interactions generally increase with an increase in the size of the alkyl chain, and decrease with an increase in the size of the ester molecule. Furthermore, as expected aliphatic esters yielded lower activity coefficients than their olefinic counterparts. For the purposes of this work, cyclohexane was used as the parent structure.

TABLE VI
ACTIVITY COEFFICIENTS OF STRAIGHT-CHAIN CYCLOALKYL SOLUTES IN VARIOUS ESTERS

Ester Solvent	Designation	Straight-chain Branched Cycloalkyls						
		Methyl-cyclohexane	Ethyl-cyclohexane	Propyl-cyclohexane	Butyl-cyclohexane	Pentyl-cyclohexane	Hexyl-cyclohexane	Heptyl-cyclohexane
M. Caproate	1-C6:0	1.691	1.835	1.979	2.125	2.273	2.424	
M. Laurate	1-C12:0	1.122	1.189	1.251	1.309	1.363	1.414	
M. Stearate	1-C18:0	0.914	0.968	1.017	1.062	1.103	1.141	
M. Oleate	1-C18:1	0.985	1.046	1.102	1.154	1.202	1.248	
M. Linoleate	1-C18:2	1.071	1.142	1.208	1.270	1.329	1.385	
M. Linolenate	1-C18:3	1.176	1.259	1.339	1.415	1.488	1.558	
E. Stearate	2-C18:0	0.890	0.942	0.990	1.034	1.074	1.112	
E. Oleate	2-C18:1	0.955	1.014	1.068	1.118	1.165	1.209	
P. Stearate	3-C18:0	0.867	0.919	0.965	1.008	1.048	1.084	
P. Oleate	3-C18:1	0.927	0.984	1.037	1.086	1.132	1.174	
B. Stearate	4-C18:0	0.847	0.897	0.943	0.985	1.024	1.059	
B. Oleate	4-C18:1	0.902	0.957	1.009	1.057	1.101	1.142	

It was interesting to note (with the exception of methyl caproate-cycloalkyl interactions) that the cycloalkyl molecule-ester interactions generally yielded lower activity coefficients than the cycloalkanes of similar carbon number. As an example, ethylcyclohexane in butyl oleate yielded an activity coefficient of 0.957 in comparison to that of 1.050 experienced for cyclooctane in butyl oleate.

TABLE VII
ACTIVITY COEFFICIENTS OF MULTIPLE-BRANCHED CYCLOALKYL SOLUTES IN VARIOUS ESTERS

Ester Solvent	Designation	Dimethyl cyclohexanes		Diethyl cyclohexanes		Trimethyl cyclohexanes	
		1,1-Dimethyl-cyclohexane	1,3-Dimethyl-cyclohexane	1,1-Diethyl-cyclohexane	1,3-Diethyl-cyclohexane	1,1,3-Trimethyl-cyclohexane	1,3,5-Trimethyl-cyclohexane
M. Caproate	1-C6:0	1.770	1.757	2.010	2.047	1.828	1.825
M. Laurate	1-C12:0	1.216	1.150	1.313	1.275	1.238	1.178
M. Stearate	1-C18:0	1.014	0.936	1.090	1.035	1.031	0.958
M. Oleate	1-C18:1	1.115	1.006	1.206	1.119	1.130	1.026
M. Linoleate	1-C18:2	1.239	1.091	1.352	1.223	1.254	1.111
M. Linolenate	1-C18:3	1.392	1.195	1.533	1.353	1.405	1.214
E. Stearate	2-C18:0	0.989	0.911	1.064	1.008	1.006	0.932
E. Oleate	2-C18:1	1.082	0.975	1.171	1.084	1.098	0.995
P. Stearate	3-C18:0	0.967	0.888	1.041	0.983	0.983	0.909
P. Oleate	3-C18:1	1.053	0.947	1.139	1.053	1.068	0.967
B. Stearate	4-C18:0	0.946	0.867	1.019	0.960	0.962	0.887
B. Oleate	4-C18:1	1.026	0.921	1.110	1.025	1.040	0.940

This is most likely because the cycloalkyl molecule is more compact, and thus more solute surface area is presented for bonding to the solvent after initial intermolecular bonds have been broken. The effect of multiple branching off cycloalkanes was also investigated using cyclohexane as the parent molecule. It was noted that solvent-solute interactions with cycloalkyl branches off the same cyclohexane carbon (e.g. 1,1-dimethylcyclohexane and 1,1,3-trimethylcyclohexane) yielded higher activity coefficients than cycloalkyl branches off different cyclohexane carbons (e.g. 1,3-dimethylcyclohexane, 1,3,5-trimethylcyclohexane). These results are presented in Table 7. This can be attributed to the fact that two alkyl branches off the same cyclo-carbon could present a high bond strain on the cycloalkane portion, which could increase its repulsive forces.

H. Comparisons between Various Ester-alkane Interactions

A performance comparison between ester interactions with various different types of alkanes of similar size is shown in Fig. 5 (a), (b) and (c).

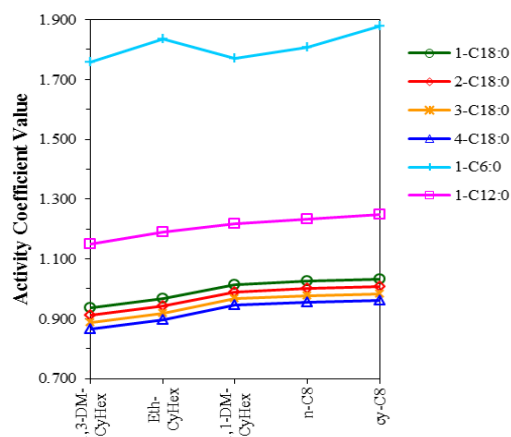


Fig. 5 (a) Comparison of activity coefficients for various C₈ alkanes in saturated methyl ester solvents

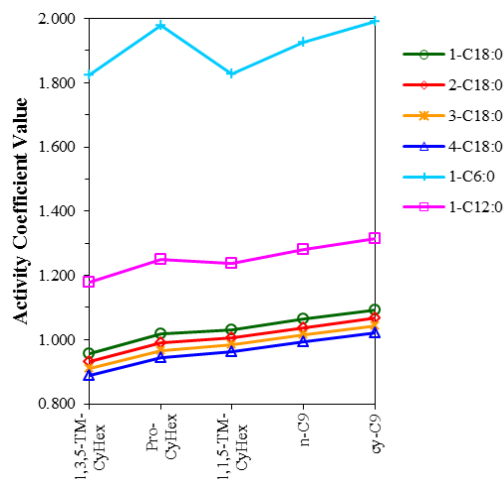


Fig. 5 (b) Comparison of activity coefficients for various C₉ alkanes in saturated methyl ester solvents

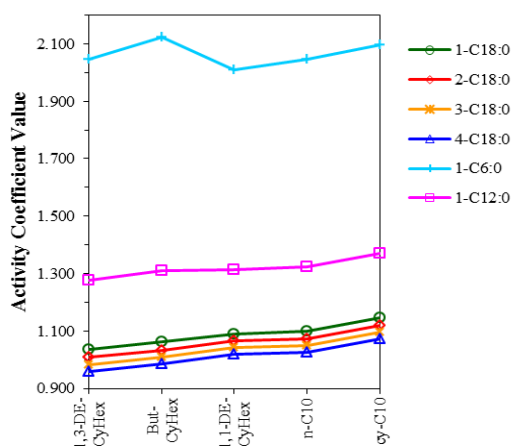


Fig. 5 (c) Comparison of activity coefficients for various C₁₀ alkanes in saturated methyl ester solvents

With the exception of methyl caproate interactions, a definite trend emerges. It can be seen that multiple branched cyclic structures off different cyclo-carbons possess the lowest activity coefficients in their respective ester solvent. This is followed by the singular chain cycloalkyl-ester interaction, which is in turn followed by multiple branched cyclic structures off the same cyclo-carbon. Straight-chained alkane-ester interactions possess the second-highest activity coefficients followed by their cyclic counterparts for the higher carbon number cyclic structures.

VII. CONCLUSION

The interactions between alkanes and ester solvents have led to an increased understanding of the bond dynamics between these two chemical species. It would be interesting to observe the effects of alkene- and alkyne-ester interactions in a similar manner. It would be ideal if these results are experimentally verified, especially to ascertain whether the

impact of isomerism in ester-alkane interactions is indeed negligible.

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