INFLUENCE OF TEMPERATURE ON VOLATILE ORGANIC COMPOUNDS – ESTER SOLVENT INTERACTIONS

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Abstract - The influence of temperature on the solubility of 27 volatile organic compounds (VOCs) representing seven VOC families in biodiesel esters was investigated. Phase equilibrium data in the form of infinite dilution activity coefficients were predicted for a temperature range of 30°C to 50°C using the Modified UNIFAC Dortmund Group Contribution Model. The desired phase equilibrium data were computed using a Microsoft Excel spreadsheet designed for this purpose. It was found that alkane activity coefficients decreased with increasing temperature, but do not approach ideality with increasing temperature. With the exception of the acroleins, activity coefficients of the aldehydes decreased with increasing temperature, approaching ideality. Activity coefficients of organic acids in unsaturated esters tended towards ideality whilst interactions with unsaturated esters deviated from ideality. With the exception of tetrahydrofuran and tetrahydropyran, ether interactions with ester solvents generally tended towards ideality. It was also observed that the activity coefficients of formates and carbonates particularly ethyl formate in biodiesel generally tended towards ideality with increasing temperature. The interactions in this study show that ester/solute interactions yielding activity coefficients greater than 1 favour higher absorption temperatures whilst those with coefficients less than 1 favour lower absorption temperatures.

INTRODUCTION

Due to increasingly stringent environmental legislation imposed by national and international authorities, chemical industries are obligated to employ reliable technologies to remove volatile organic compounds (VOCs) from their process gaseous waste streams before they are released into the atmosphere. Physical absorption processes are a particularly attractive end-of-pipe technology, provided the process is designed to be efficient and where possible, profitable.

The selection of a suitable absorbent has significant influence on the efficiency and profitability of an absorption process. A good understanding of solvent-solute interactions is therefore required to ensure suitable solvent selection for a particular absorption operation. Water is a good absorbent for highly polar VOCs, but mildly polar and non polar VOCs quickly saturate in water. Thus organic solvents are an attractive option for scrubbing non polar solutes from waste gas streams. The various fatty acid esters which comprise biodiesel have been found to possess all the properties of a good solvent, and due to its biodegradability it is environmentally friendly (Bay et al, 2006).

Since VOCs are present in very dilute concentrations in waste gas streams, it is important that the required phase equilibrium data is obtained in the infinitely dilute region in order to accurately model the absorption process (Alessi et al, 1991). For preliminary design purposes, it is impractical and uneconomical to perform phase equilibrium measurements. For these situations, thermodynamic data such as infinite dilution activity coefficients is predicted using suitable thermodynamic models such as the Analytical Solution of Groups (ASOG) or the various Universal Quasi chemical Functional Groups Activity Coefficient (UNIFAC) models.

This work focused on the effect of temperature on the thermodynamics of VOC physical absorption using biodiesel. Biodiesel (being essentially non-polar) is well suited for absorbing non-polar and moderately polar solutes (Bay et al, 2004), (Bay et al, 2006). However the optimum temperature for the absorption process depends on the VOC family group. The Modified UNIFAC Dortmund group contribution model, developed by Weidlich and Gmehling (1987) was selected to compute the required phase equilibrium data.

VOC Treatment Technologies

VOC treatment technologies are broadly classified into two main groups depending on the ultimate fate of the emission being treated; namely destructive technologies and recovery technologies.
Destructive technologies are employed when the VOC is odorous or toxic. The VOCs are either destroyed (using oxidisers or flares) or the chemical structure of the VOC is modified into more benign compounds using bio-reactor processes. Oxidiser operations are limited to VOC concentrations of less than 25% of the lower explosive limit (Moretti, 2002). For treatment of such VOCs flares and bio-reactors should be used. Halogenated VOCs cannot be abated using flares or bio-reactors (Moretti, 2002). Oxidisers equipped with post-oxidation acid gas treatment scrubbers should be used for the destruction of such VOCs.

VOC recovery technologies are used to recover valuable VOCs in the waste streams which can be either recycled or converted into other useful compounds. Separation processes are inevitably used in VOC recovery, the main separation processes employed being adsorption, condensation, membrane separation or absorption. Membrane separation is not as efficient as the other recovery technologies and is thus often used as a pre-concentrator step prior to further recovery using condensation or adsorption, or destruction using appropriate oxidation technologies.

Absorption

Absorption, also known as wet scrubbing, is a diffusion-controlled, mass transfer process between a soluble gas and a solvent which are in contact with each other. When the gaseous and liquid phases are in intimate contact with each other, a concentration gradient is established between the two phases in the laminar region of the fluid flow, consequently diffusion takes place (Cheremisinoff, 2002). The VOCs, having a higher concentration in the gaseous phase, are transferred across the gas/liquid interface into the liquid phase which has a low VOC concentration. The diffusion of the solute into the scrubbing solvent takes place with or without a chemical reaction.

An absorption process can either be physical, irreversible chemical reaction or reversible chemical reaction. Irreversible chemical reactions between the solute and a component in the scrubbing solvent result in the product compound exerting a negligible equilibrium vapour pressure of the solute over the solution (Kohl and Nielsen, 1997). The reaction products do not readily decompose to release the solute and are usually restricted to the destruction of gaseous compounds. Reversible reactions involve a chemical reaction between the solute being absorbed and the scrubbing solvent, forming a loosely bound compound that exerts a finite equilibrium vapour pressure of the absorbate over the solution (Kohl and Nielsen, 1997). Physical absorption processes utilise solubility differences of the waste stream components in the scrubbing agent and thus do not involve chemical reactions (Kohl and Nielsen, 1997). Physical scrubbing is preferred when VOC recovery is required. The VOC is recovered by regeneration of the solvent, allowing the solvent to be reused in the process.

Contact between gas and solvent occurs predominantly via a counter-current flow pattern, however cross-current flow is sometimes employed (Cheremisinoff, 2002). The VOC to be treated must be soluble in the scrubbing liquor (Cheremisinoff, 2002). Water is a common solvent for scrubbing hydrophilic VOCs, as long as an azeotrope is not formed. Heavy hydrocarbon absorbents such as mineral oils or other non-volatile petroleum oils are commonly used as scrubbing solvents for hydrophobic VOCs (Moretti, 2002). When absorption is used for VOC control, packed towers are preferred as they give higher mass-transfer performance and are usually more cost effective than impingement plate towers. However, impingement plate towers are used when internal cooling is required or when inadequate wetting of the packing due to low liquid flow rates is a possibility (Cheremisinoff, 2002).

Scrubbers can handle a wide variety of waste gas flow rates and can also process flammable and explosive gases with low risk. Unfortunately spent solvent disposal could itself be a source of environmental pollution (Moretti, 2002), hence the need for solvent regeneration in scrubber systems. Furthermore only VOCs that are soluble in the absorbent are recoverable, thus further treatment of insoluble VOCs may be required.

Phase Equilibrium

In order to design separation processes, the phase equilibrium ratios ($K_i$), also known as distribution coefficients or $K$-factors, are often required (Gmehling, 1995). The $K$-factor for vapour-liquid equilibrium is mathematically defined as in (1) (Seader and Henley, 2005):

$$K_i \equiv \frac{y_i}{x_i} \quad (1)$$
In (1), \((y_i)\) and \((x_i)\) represent the vapour mole fraction and liquid mole fraction of component \((i)\) respectively. \(K\)-values are used in vapour-liquid equilibrium computations when the relative volatility of components to be separated needs to be determined.

The liquid phase non-ideality of a system is often accounted for by the use of activity coefficients \((\gamma)\). Activity coefficients represent the departure of activities from ideal liquid mole fractions, and are represented mathematically as a ratio of the activity \((a)\) of component \((i)\) in the system over its liquid mole fraction, as in (2) (Seader and Henley, 2005):

\[
\gamma_i, (L) \equiv \frac{a_i(L)}{x_i}
\]  

(2)

The activity of a component is defined as the ratio of the fugacity over the fugacity at a defined standard state i.e.\((f/f_0)\). Thus (2) is represented in terms of its partial fugacity coefficient in the liquid phase by substitution of the activity term as in (3), thereby obtaining the mole fraction expression for the partial fugacity in the liquid phase \((\hat{f}_{i,(L)})\), where \((f_{i,(L)}^0)\) represents the fugacity in the standard state (Seader and Henley, 2005):

\[
\hat{f}_{i,(L)} = \gamma_{i,(L)} \cdot x_i \cdot f_{i,(L)}^0
\]  

(3)

Since fugacity and pressure are related, the pure-component fugacity of component \((i)\) can be described as a fraction of pressure (Seader and Henley, 2005), i.e.

\[
\varphi_i = \frac{\hat{f}_i}{P}
\]  

(4)

In (4), \((\varphi_i)\) is referred to as the pure-component fugacity coefficient. For an ideal gas the fugacity coefficient ratio reduces to a value of 1. For a mixture, the partial fugacity coefficients are defined for the liquid and vapour phase as in (5) and (6) (Seader and Henley, 2005):

\[
\hat{f}_{i,(V)} = \gamma_{i,(V)} \cdot y_i \cdot P
\]  

(5)

and

\[
\hat{f}_{i,(L)} = \gamma_{i,(L)} \cdot x_i \cdot P
\]  

(6)

Thus by re-arranging (6), a second expression for the partial fugacity in the liquid phase is obtained (Seader and Henley, 2005).

\[
\hat{f}_{i,(L)} = \varphi_{i,(L)} \cdot x_i \cdot P
\]  

(7)

Similarly, re-arranging (5) yields an expression for the partial fugacity in the vapour phase (Seader and Henley, 2005).

\[
\hat{f}_{i,(V)} = \varphi_{i,(V)} \cdot y_i \cdot P
\]  

(8)

By making \((x_i)\) and \((y_i)\) the subjects of the formula of (7) and (8), substituting into (1), and taking into account that the partial fugacity of component \((i)\) in the vapour phase is equal to the partial fugacity of component \((i)\) in the liquid phase (Prausnitz et al, 1999), the equation-of-state (EoS) form of the \(K\)-value is obtained (Seader and Henley, 2005), as in (9).
\[ K_i = \frac{\phi_i^{L(L)}}{\phi_i^{L(V)}} \]  

Equation (9), in combination with appropriate mixing rules, is used to determine the required VLE (Vapor-Liquid Equilibrium) data using EoS models such as the Soave-Redlich-Kwong EoS (Soave, 1972) and the Peng-Robinson (Peng and Robinson, 1976) EoS. This approach is often referred to as the \( \phi-\phi \) approach (Schmid and Gmehling, 2010) since the real behaviour of both phases is described using fugacity coefficients. Similarly the substitution of (3) and (8) into (1) yields the activity coefficient form of the \( K \)-value (Seader and Henley, 2005) as in (10).

\[ K_i = \frac{Y_i^{L(L)} \cdot f_i^0}{\phi_i^{L(V)} \cdot P} = \frac{Y_i^{L(L)} \cdot \phi_i^{L(L)}}{\phi_i^{L(V)}} \]  

The above approach is often referred to as the \( \gamma-\phi \) approach (Schmid and Gmehling, 2010) since activity coefficients are used to describe the real behaviour of the liquid phase, whilst fugacity coefficients describe the vapour phase. The activity coefficient approach is used for determining VLE data using excess Gibbs energy models and appropriate vapour pressure data.

Both approaches can be used to determine thermodynamic properties of multi component non-electrolyte mixtures using only binary information (Gmehling, 1995). In most cases, the required binary data are incomplete or missing and therefore predictive methods which use the activity coefficient approach are often required to obtain the missing data for preliminary design purposes (Gmehling, 1995). EoS models are incapable of modelling even moderately polar systems (Prausnitz et al, 1999). Unfortunately, the activity coefficient approach requires the use of a standard fugacity and is thus unable to describe the behaviour of supercritical compounds (Gmehling, 1995). In such instances only EoS models can be used unless data is available for the use of a Group Contribution Equation-of-State model.

**The Modified Unifac Dortmund Model**

The Modified UNIFAC Dortmund predictive procedure, a group contribution thermodynamic model, is based on the Original UNIFAC model which was published by Fredenslund, Jones and Prausnitz (1975). The model combines the solution-of-groups concept as described by Wilson (1962) with the UNIQUAC model developed by Abrams and Prausnitz (1975). The UNIQUAC model is itself based on an extension of Guggenheim’s quasi-chemical theory of liquid mixtures (Abrams and Prausnitz, 1975), and was slightly adapted for use with the group contribution model.

The Modified UNIFAC Dortmund was developed because the Original UNIFAC model possessed weaknesses which affected its accuracy. Firstly inaccurate predictions were made for enthalpies of mixing because the binary interaction parameters are not temperature dependent in terms of the Gibbs excess energy (Weidlich and Gmehling, 1987). Secondly poor results were obtained for infinite dilution activity coefficients and excess enthalpies for systems with compounds very different in size. This is because the VLE data base used for fitting group interaction parameters was of limited concentration range (5 - 95 %) and is therefore not from the dilute region (Gmehling, 1995).

Modified UNIFAC Dortmund consists of a combinatorial term (which describes the excess Gibbs energy arising due to differences in molecular size and shape) and a residual term (which describes the excess Gibbs energy differences due to molecular interactions). This is defined in terms of activity coefficients as in (11) (Fredenslund et al, 1975).

\[ \ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \]  

The combinatorial term (\( \ln \gamma_i^C \)) consists of a Flory-Huggins combinatorial along with a Staverman-Guggenheim correction factor. The combinatorial term was altered for Modified UNIFAC Dortmund in order to account for systems with compounds very different in size by the introduction of a modified group volume fraction parameter (\( \phi_i' \)) into the Flory-Huggins part of the combinatorial term. The group volume fraction parameter (\( \phi_i \)) remained unchanged for the Staverman-Guggenheim portion of the combinatorial term. These changes culminated in the combinatorial expressions described in (12) (Weidlich and Gmehling, 1987).
\[
\ln \gamma_i^C = \ln \Phi_i' + 1 - \Phi_i' - 5q_i \left( \ln \frac{\Phi_i}{\theta_i} + 1 - \frac{\Phi_i}{\theta_i} \right) \quad (12)
\]

The residual term \(\ln \gamma_i^R\) remained unchanged from the Original UNIFAC and is expressed as in (13) (Fredenslund et al., 1975).

\[
\ln \gamma_i^R = \sum_k \Gamma_k^{(i)} \left[ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (13)
\]

In (13), \(\Gamma_k\) is the residual activity coefficient of the group \((k)\), whilst \(\Gamma_k^{(i)}\) represents the residual activity coefficient of group \((k)\) in a reference solution which contains only molecules of type \((i)\). The group residual activity coefficients \(\Gamma_k\) and \(\Gamma_k^{(i)}\) are determined according to (14) (Fredenslund et al., 1975).

\[
\ln \Gamma_k = Q_k \left[ 1 - \ln \sum_m \theta_m \psi_{mk} - \sum_m \left( \frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right) \right] \quad (14)
\]

In the combinatorial term, the volume (or segment) fraction parameter \((\theta_i)\) of component \((i)\) is determined according to (15) (Fredenslund et al., 1975) and the modified volume fraction parameter \((\theta_i')\) is defined as in (16) (Weidlich and Gmehling, 1987). The area fraction \((\theta_i)\) is computed according to (17) (Fredenslund et al., 1975).

\[
\Phi_i = \frac{r_i x_i}{\sum_j \eta_j x_j} \quad (15)
\]

\[
\Phi_i' = \frac{r_i^{3/4}}{\sum_j r_j^{3/4} x_j} \quad (16)
\]

\[
\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (17)
\]

The pure-component area parameter \((q_i)\) is calculated as in (18) whilst the pure-component volume parameter \((r_i)\) is computed using (19) (Fredenslund et al., 1975). The group area parameters \((Q_k)\) and the group volume parameters \((R_k)\) are obtained from published tables. The parameter \((v_k^{(i)})\) is the number of groups of kind \((k)\) in a molecule of component \((i)\) and is always an integer (Abrams and Prausnitz, 1975).

\[
q_i = \sum_k v_k^{(i)} Q_k \quad (18)
\]

\[
r_i = \sum_k v_k^{(i)} R_k \quad (19)
\]

In the residual term, the group area fraction \((\theta_m)\) is defined as in (20) (Fredenslund et al., 1975).

\[
\theta_m = \frac{Q_m X_m}{\sum_n Q_m X_m} \quad (20)
\]

The summation covers all the different groups. Parameter \((X_m)\), the mole fraction of group \((m)\) in the mixture, is calculated as in (21) (Fredenslund et al., 1977).
\[ X_m = \frac{\sum_j v_m^{(j)} X_j}{\sum_j \sum_n v_n^{(j)} X_j} \]  

(21)

The modified group interaction parameter which, unlike that of the Original UNIFAC was made to be temperature dependant, was expressed as in (22) (Weidlich and Gmehling, 1987).

\[ \Psi_{mn} = \exp \left[ - \frac{a_{mn} + b_{mn} T + c_{mn} T^2}{T} \right] \]  

(22)

Temperature Dependence Of Activity Coefficients

The removal efficiency of a given VOC from a waste gas stream by absorption is influenced by the temperature at which the absorption system is operated. The influence of temperature on solubility can be observed by studying the variation of infinite dilution activity coefficients with temperature. Carlson and Colburn (1942) used (23) to describe the temperature dependence of activity coefficients.

\[ \frac{d \ln \gamma_i}{dT} = - \frac{L_i}{RT^2} \]  

(23)

In (23), \((L_i)\) is the relative partial molal enthalpy of component \((i)\) referenced to the pure liquid enthalpy at the same temperature \((T)\), with units (cal./ mole), and \((R)\) is the universal gas constant. \((L_i)\) is practically described as the amount of heat absorbed upon the addition of one mole of component \((i)\) to an infinite quantity of solution (Carlson and Colburn, 1942).

According to Carlson and Colburn (1942), systems of organic component mixtures which deviate positively from Raoult’s Law have positive values for molal enthalpy \((L)\), whilst those which deviate negatively from Raoult’s Law possess negative values for \((L)\). This led to the observation that organic liquid systems, possessing either positive or negative deviations from Raoult’s Law, would thus approach Raoult’s Law as a limit with increasing temperature. This would result in activity coefficients \((\gamma_i > 1)\) decreasing with an increase in temperature whilst activity coefficients \((\gamma_i < 1)\) would increase with increasing temperature (Carlson and Colburn, 1942). This hypothesis was supported by Schiller and Gmehling (1992), who stated that for almost all substances, activity coefficients approach ideality (i.e. a value of 1) with increasing temperature. Lower activity coefficients translate to increased solubility which favours the absorption process, but hinders solvent regeneration.

Model Validation

All of the VOC/ester solvent interactions investigated in this study were computed using a Microsoft Excel spreadsheet specifically developed for this purpose, using the formulae as described by Weidlich and Gmehling (1987). In order to verify the accuracy of the model, data was simulated using the model and compared to experimental results of commercial European biodiesel obtained by Bay et al (2004). According to Bay et al (2004), a minimum of 80% of European biodiesel is comprised of the unsaturated C18:1, C18:2 and C18:3 esters, C18:1 ranging from 54 – 63% of total biodiesel composition and C18:2 ranging from 18 – 24% of total biodiesel composition. Results of infinite dilution activity coefficients of selected solutes were therefore obtained for C18:1 and C18:2 using the Modified UNIFAC Dortmund computation for the purposes of comparison and these are shown in Table I.
Table 1: Model Validation

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<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td></td>
<td>Commercial Biodiesel</td>
<td>C18:1</td>
<td>% Deviation</td>
<td>C18:2</td>
<td>% Deviation</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.625</td>
<td>0.611</td>
<td>-2.3</td>
<td>0.603</td>
<td>-3.6</td>
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<tr>
<td>Toluene</td>
<td>0.645</td>
<td>0.643</td>
<td>-0.3</td>
<td>0.641</td>
<td>-0.6</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.355</td>
<td>1.008</td>
<td>-25.6</td>
<td>1.088</td>
<td>-19.7</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.469</td>
<td>1.058</td>
<td>-28.0</td>
<td>1.146</td>
<td>-22.0</td>
</tr>
<tr>
<td>Octane</td>
<td>1.62</td>
<td>1.105</td>
<td>-31.8</td>
<td>1.202</td>
<td>-25.8</td>
</tr>
<tr>
<td>Methanol</td>
<td>4.466</td>
<td>5.626</td>
<td>26.0</td>
<td>5.257</td>
<td>17.7</td>
</tr>
<tr>
<td>Ethanol</td>
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<td>3.949</td>
<td>-3.6</td>
<td>3.826</td>
<td>-6.6</td>
</tr>
<tr>
<td>1-Propanol</td>
<td>3.209</td>
<td>3.558</td>
<td>10.9</td>
<td>3.461</td>
<td>7.9</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.927</td>
<td>0.964</td>
<td>4.0</td>
<td>1.051</td>
<td>13.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.407</td>
<td>1.472</td>
<td>4.6</td>
<td>1.384</td>
<td>-1.7</td>
</tr>
<tr>
<td>Butanone</td>
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<td>1.364</td>
<td>-9.9</td>
<td>1.287</td>
<td>-15.0</td>
</tr>
<tr>
<td>Diethylether</td>
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<td>0.622</td>
<td>-21.5</td>
<td>0.654</td>
<td>-17.5</td>
</tr>
<tr>
<td>Tert-Butylmethylether</td>
<td>0.777</td>
<td>0.599</td>
<td>-22.9</td>
<td>0.629</td>
<td>-19.0</td>
</tr>
</tbody>
</table>

It was observed that the model was very accurate in predicting activity coefficients for aromatic compounds and cyclohexane and was also reasonably accurate in predicting the phase equilibrium involving ketones and the alcohols (barring methanol). The model was least accurate for alkane and ether interactions. Thus the Dortmund UNIFAC model can be utilized for predicting phase equilibrium data for preliminary design and feasibility studies.

RESULTS AND DISCUSSION

In this work, 27 VOCs representing 7 VOC family groups were studied. In order to evaluate the temperature dependence of activity coefficients at infinite dilution, activity coefficients were computed at temperatures of 30, 35, 40, 45 and 50°C. Whilst the general temperature range of interest for absorption operations is between 30°C – 40°C (Bay et al., 2006), the temperature range was extended for scientific inquiry. A solute mole fraction of 1 × 10⁻⁵ was used in these computations, representing infinite dilution conditions as recommended by Alessi et al. (1991).

Four C18 ester solvents with varying degrees of solvent unsaturation were selected for this study as these comprise the major component of conventional biodiesel feedstocks. The notation described by Van Gerpen et al. (2004) was adopted to describe the characteristics of the ester solvent chain, with the prefix ‘1-’ being used to identify the solvent as a methyl ester.

Alkanes

Activity coefficients for the C18 ester solvent/alkane interactions at the various temperatures are shown in Figure 1. For ester/alkane interactions a gentle decrease in activity coefficients with increasing temperature with no approach towards ideality was observed.

The decrease in activity coefficients with increasing temperature can be attributed to the increased energy available to break the weak London forces between solute-solute bonds, increasing the ease in which solute-solvent attractions can occur.
Activity coefficients decreased with an increase in the degree of ester solvent unsaturation. Since London forces are the only forces that interact between solute and solvent, the shape of both the solute and the solvent are of importance. Alkanes are generally straight chains but this is not the case for the solvent. For methyl stearate (1-C18:0) the solvent molecule is straight, thus maximum contact points are presented between solute and solvent resulting in the strongest London interactions; resulting in very low activity coefficients. With the addition of double bonds in the solvent tail, the shape of the solvent molecule becomes increasingly bent. This results in a decrease in the amount of contact points between the solute and the solvent, weakening the strength of London forces.

**Ketones**

The interactions between ketones with C18 ester solvents are shown in Figure 2. It was found that activity coefficients decrease with an increase in temperature. The interactions show an approach towards ideal
behaviour with temperature. Since ketones are moderately polar, it is assumed that the additional energy provided by the increase in temperature increases the kinetic energy of the solute molecules. The increased kinetic energy serves to disrupt Keesom dipole-dipole forces between solute-solute interactions. This allows for increasing London intermolecular interactions as well as Debye induced dipole interactions between solute and solvent, thereby reducing activity coefficients with increasing temperature.

![Figure 2](Image)

Figure 2. Temperature dependence of ketones in C18 ester solvents, (a) ethylmethyl ketone; (b) 2-heptanone; (c) 4-heptanone; (d) methyl vinyl ketone

Unlike alkanes which are nonpolar, activity coefficients decrease with an increase in the degree of solvent unsaturation for polar interactions. This can be perhaps be attributed to the Debye induced dipole interactions. Double bonds are more polarisable than single bonds; thus the ease in which the solute molecules can induce a dipole (hence increasing the strength of attraction between solute and solvent) increases with an increase in the number of double bonds in the solvent molecule.
Aldehydes

Activity coefficients for the interactions between aldehydes and C18 ester solvents are shown in Figure 3.

Figure 3. Temperature dependence of aldehydes in C18 ester solvents, (a) hexanal; (b) crotonaldehyde; (c) acrolein; (d) methacrolein

It was observed that hexanal and crotonaldehyde tend towards ideality with increasing temperature. The activity coefficients of these compounds in C18 ester solvents decreased with an increase in temperature. This is possibly due to the increasing interruptions of Keesom interactions between the solute molecules due to the increase in kinetic energy imparted to the solute molecules as a result of the increase in temperature of the system. This would allow for increased solute-solvent interactions in the form of London interactions and Debye interactions. As with the ketones, activity coefficients for these compounds decreased with an increase in the degree of solvent unsaturation.
The interaction of acrolein and methacrolein differed from those of the other aldehydes. For these interactions, activity coefficients increased almost exponentially with an increase in temperature. It can be concluded that these compounds do not tend towards ideality with increasing temperature. Acroleins are aldehydes that contain a C=C double bond. It’s not certain as to what governs the behaviour of these compounds, because in Modified UNIFAC Dortmund models acroleins are modelled as special functional groups. It is possible that an increase in kinetic energy of the solute molecules with increasing temperature could result in a decrease in Debye forces due to the decrease in time available to induce a dipole in the solvent molecule; hence the increase in activity coefficients with increasing temperature. It was furthermore observed that, unlike the other aldehydes, activity coefficients for acrolein interactions increased with an increase in ester bond unsaturation. It is assumed that the effect of the carbonyl group is shielded to some extent due to the compact shape of the acrolein molecule, allowing the molecule to behave more like a non polar molecule. This assumption could be substantiated by the much lower activity coefficients experienced with acrolein interactions with ester solvents.

**Organic Acids**

The interactions of organic acids with C18 ester solvents are shown in Figure 4. Organic acids are hydrogen bond (H-bond) donors, hence the high activity coefficients observed with ester organic acid interactions. As is typical with polar solutes, solubility of organic acids in esters improved with increasing degree of solvent unsaturation. With the exception of acrylic acid it was found that activity coefficients decreased for saturated ester/solute systems but increased for unsaturated ester/solute interactions.

![Figure 4](image-url)
The decrease in activity coefficients for saturated ester interactions can perhaps be attributed to the increase in kinetic energy of the system which assists in breaking solute-solute hydrogen bonds thereby increasing the London and Debye interactions between solute and solvent.

The increase in activity coefficients for unsaturated ester interactions is probably a result of a decrease in the ability of the hydrogen bonds to polarize the solvent double bonds through Debye interactions with increasing temperature. The decreased ability to polarize the solvent double bonds is possibly due to the reduced contact time between solute and solvent molecules. The reduced contact time is brought about by the increased movement of the solute molecules arising from the added kinetic energy to the system with an increase in temperature. This results in weaker London interactions, which require more energy, dominating instead of the induced dipole interactions, hence the decrease in solubility.

Acrylic acid is identical to propionic acid with regards to the number of carbon atoms in its structure, the difference between the two molecules being the presence of terminal double-bonded carbons in acrylic acid. Acrylic acid differs from the other acids in that activity coefficients still decrease with increasing temperature for the unsaturated ester interactions of methyl oleate (1-C18:1) and methyl linoleate (1-C18:2). The difference in behaviour is possibly brought about by the presence of the double bond, which allow for improved London attractive forces between solute and solvent molecules – thus these interactions behave similarly to those of the saturated ester-solute interactions. The shape of methyl linolenate (1-C18:3) is too bent for the London forces to be of much influence with increasing temperature.

**Ethers**

Figure 5 shows the interactions between ethers and C18 ester solvents.
Figure 5. Temperature dependence of ethers in C18 ester solvents, (a) diethyl ether; (b) methyl-n-butyl ether; (c) di-n-propyl ether; (d) ethoxyethanol; (e) butoxyethanol; (f) tetrahydrofuran; (g) tetrahydropyran; (h) dimethoxy methane

It was found that, with the exception of tetrahydrofuran, tetrahydropyran and dimethoxy methane, ethers tended towards ideality with an increase in temperature.

The increase in activity coefficients for the standard ethers can possibly be attributed to a decrease in contact time for London interactions to occur between solute and solvent. This is due to the increase in kinetic energy provided to the solute molecule with increasing temperature. For the standard ethers, it was observed that the location of the ether oxygen atom in the chain influenced the interactions. Terminal ethers are more soluble in ester solvents than internal ethers. For example, diethyl ether (with four carbon atoms in its chain) was less soluble than methyl-n-butyl ether (possessing five carbon atoms). This is possibly because diethyl ether solutes, being symmetrical, can pack closer together resulting in more energy being required to break these intermolecular bonds to form solute-solvent bonds than is the case for methyl-n-butyl ether.

The activity coefficients of tetrahydrofuran and tetrahydropyran decreased with an increase in temperature, deviating from ideality. It is possible that solute-solute bonds are much stronger for cyclic ethers than is the case for straight ethers, as was evidenced by the higher boiling point for tetrahydrofuran (56°C) than that of diethyl
ether (36°C). The addition of energy to the system with increasing temperature increased the motion of the solute molecules, allowing the intermolecular solute-solute bonds to break easier for solute-solvent interaction to occur. This resulted in increased solubility with an increase in temperature.

The interactions of esters with tetrahydrofuran show that solvents with low degrees of unsaturation (1-C18:1 and 1-C18:2) yielded lower activity coefficients than the saturated ester (1-C18:0) and the highly unsaturated ester (1-C18:3). This could possibly be linked to the exposure of the oxygen atom by the bond angle of the ether ring. The oxygen weakly polarizes the unsaturated solvents and this effect markedly decreases with an increase in the kinking of the solvent chain, hence the increase in activity coefficients from 1-C18:1 to 1-C18:3. However London forces dominate more than the polarization of the 1-C18:3 ester because of its highly bent shape, hence the lower activity coefficients of the saturated ester over the 1-C18:3 esters.

It was observed that ester interactions with ethoxyethanol and butoxyethanol yielded much higher activity coefficients than the other ethers. This can perhaps be attributed to the presence of a terminal hydroxyl group attached to these ethers, making them highly polar because they are H-bond donors. It was found that, unlike the other ethers, activity coefficients generally decreased with an increase in the degree of solvent unsaturation.

For dimethoxy methane – ester solvents interactions, the presence of solvent double bonds had a negative effect on solute-solvent interactions. This is likely due to the increased bending (due to kinking) of the solvent molecule with an increase in bond unsaturation. The strength of London forces decrease with increasing bond unsaturation. Thus the ability of the solvent’s London forces to attract the solute molecules decreases with an increase in bond unsaturation. This combined with an increase in the motion of solute molecules with an increase in temperature results in decreased contact time with the solute with increasing temperature, hence the reduced solubility in 1-C18:3. As previously discussed, an increase in temperature aids the breaking of the solute-solute interactions; but due to the strength of the solvent’s London forces in unsaturated ester/ dimethoxy methane interactions, the solvent is still able to capture the solute molecules. This contributes to the decreasing trend observed for unsaturated ester/ dimethoxy methane interactions.

**Formates**

Figure 6 shows the interactions of formates with C18 ester solvents. Formates are also esters, but instead of possessing an alkyl group before the carbonyl group like the other esters, they have only a hydrogen atom flanking the carbonyl group on one side with the alkoxy group flanking the other side. Being polar molecules due to the presence of the carbonyl group, activity coefficients for formate-solvent interactions generally decreased with an increase in bond unsaturation.

The most notable observation of ester solvent/ formate solute interactions was that ethyl formate definitely tended towards ideality with an increase in temperature and was in fact the only interaction studied that clearly showed this behaviour. 1-C18:0 and 1-C18:1 solvent interactions with ethyl formate decreased with increasing temperature. The decrease of 1-C18:0 activity coefficients with increasing temperature (being further away from a value of 1) were more marked than that of 1-C18:1, whose activity coefficient values were very close to 1. Activity coefficients of 1-C18:2 and 1-C18:3 interactions with ethyl formate increased with increasing temperature. The activity coefficients of 1-C18:3 (being lower than those of 1-C18:2) increased more rapidly than those of 1-C18:2.
The activity coefficients of butyl formate in C18 esters increased with increasing temperature, approaching ideality. The rate of activity coefficient increase increased with an increase in bond unsaturation. For example – 1-C18:0/ solute interactions was negligible whilst that of 1-C18:3/ solute interactions was quite substantial, resulting in a convergence of 1-C18:0 and 1-C18:3 trends at 50°C. The reason for the convergence observed for butyl formate is possibly due to the influence of Debye forces. At lower temperatures there is little kinetic energy present in the system and the solute molecules have more time to induce a dipole on the solvent molecule through bond polarization. Mutual solute-solvent attraction occurs and thus there is an increase in solubility with an increase in the number of solvent double bonds that can be polarized through Debye interactions. With an increase in temperature, a decrease in Debye interactions results as the solutes move around more rapidly due to the lack of time for the solutes to polarize the solvent double bonds. Thus only London forces between solute and solvent molecules dominate at higher temperatures, and solvent molecular shape dominates these interactions. Since the shape of the solvent molecule becomes increasingly bent with increasing double bonds, its contact points with the solute decrease and the strength of London forces diminishes, resulting in decreased solubility with increasing bond saturation – thus the trends of the unsaturated solvent 1-C18:0 and 1-C18:3 converge.

Figure 6. Temperature dependence of formates in C18 ester solvents, (a) ethyl formate; (b) butyl formate.
Carbonates

The interactions of organic carbonates with C18 ester solvents with increasing temperature are shown in Figure 7.

Organic carbonates are esters of carbonic acid, consisting of a carbonyl group flanked by two oxygen atoms bonded to the central carbon atom. It was found that activity coefficients decreased with increasing temperature, thereby approaching ideality. The decreasing trend in activity coefficients with increasing temperature is most likely due to an increase in kinetic energy which assists the breaking of strong solute-solute bonds, thus facilitating an increase in the likelihood of solute-solvent bonding to occur. Being polar molecules, it was evident that ester/carbonate activity coefficients decreased with an increase in ester solvent unsaturation.

There is minimal shielding of the carbonyl group of dimethyl carbonate, since only a methane group is attached to each of the two oxygen atoms. Thus dimethyl carbonate is highly polar as is evidenced by the high activity coefficients obtained for C18 ester/dimethyl carbonate interactions. Diethyl carbonate has an additional methylene group positioned between the methyl group and the oxygen atom on either side of the carbonyl group, resulting in much lower activity coefficients for its interactions with the C18 esters.

CONCLUSIONS

It was observed that activity coefficients of ester/solute interactions generally tended towards ideality with increasing temperature, with the exception of the alkanes, tetrahydrofuran and tetrahydropyran, methacrolein and, generally, the organic acid/unsaturated ester interactions. The general guideline when selecting a suitable temperature for VOC absorption would therefore be that ester/solute interactions with activity coefficients greater than 1 would favour higher absorption temperatures whilst those interactions with activity coefficients less than 1 would favour lower absorption temperatures. For the alkanes, tetrahydrofuran and tetrahydropyran, high-temperature absorption is preferred whilst for methacrolein lower temperature absorption would be preferred.

The work of Bay et al (2004), (2006) showed that biodiesel is a ‘green’ solvent that is well suited for the absorption of non-polar to mildly polar VOCs. However, their work was based on biodiesel as a blend of esters of varying chain lengths. This work has extended the research into biodiesel as a solvent by increasing the range of VOC family groups investigated and has further shown specific esters in the biodiesel mixture influence interactions with selected VOC solutes. This work has also shown how temperature could affect the efficiency of an absorption system using biodiesel as an absorbent. Biodiesel unfortunately has the disadvantage that it is susceptible to oxidative stresses caused by temperature and exposure to ultra-violet light due to the presence of unsaturated double bonds in its hydrocarbon tail structure (Bay et al, 2006). This could reduce the absorption
affinity of the solvent, resulting in the need for periodic solvent replacement. Lab scale absorption work to study the influence of oxidative stresses on biodiesel is thus recommended.

REFERENCES