# Volatile Organic Compounds- Biodiesel Thermodynamic Interactions: Influence of Temperature

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*Abstract*— **This work investigated the suitability of biodiesel (predominantly Methyl Linolenate, Methyl Palmitate, Methyl Oleate and Methyl Stearate) as an absorbent for the recovery of VOCs from waste gas process streams through absorption. The objective was to predict the vapour liquid equilibria (VLE) data in the form of infinite dilution activity coefficients for five VOC families, in fatty acid methyl ester solvents at varying temperature. The Original Universal Functional Group Activity Coefficient (UNIFAC) model (Fredenslund et al., 1975) [1], Modified UNIFAC (Larsen et al., 1981) [2] and Modified UNIFAC (Bastos et al., 1988) [3] was used to predict the required phase equilibrium. Alkanes, alcohols and acids/ester interactions showed an increase in activity coefficients with increase in temperature. The influence of temperature on the activity coefficients for alkene and amine families was negligible. The solubility of VOCs in biodiesel decreases with increase in ester hydrocarbon unsaturation. The solubility of VOCs increased with increase in ester molecular weight.**

***Keywords*— Activity coefficients, biodiesel, phase equilibrium, Universal Functional Activity Coefficient.**

## I. INTRODUCTION

THE National Environmental Management: Air Quality Act 39 of 2004, has forced all industries to closely monitor any effluents emitted to the environment. Thermodynamic models which are required to predict phase equilibrium data are applied in these situations, as their function is to compute vapour liquid equilibria. It is crucial to use models in the determination of these equilibria since actual measurements are costly and time-consuming. The use of group contribution methods to predict VLE data will provide information which could be used as a design basis for absorption processes to eliminate or control the release of VOCs into the atmosphere.

## II. ABSORPTION

Absorption is a separation method which involves the removal of a compound from a gas stream by contacting the contaminated air with a suitable absorption fluid. The two common absorption systems are; systems where interface transfer is purely by physical processes and those where a chemical reaction occurs between the component being absorbed and the absorbent.

Absorption is a physical process, and it follows the Nerst partition law which states that the ratio of concentrations of some solute species in two bulk phases in contact is constant for a given solute and bulk phase.

$$x_1 \big/ x_2 = K_{N(x,12)} = \mathrm{C}onstant \qquad (1)$$

In equation 1, the partition coefficient $K_N$ depends on the temperature. This equation is valid if the concentrations are low and if the species x does not change its form in any of the two phases. If such a molecule undergoes association or dissociation then this equation still describes the equilibrium of *x* in both phases, but only for the same form [4].

## III. BIODIESEL SOLVENT

Biodiesel is environmentally friendly, has a low volatility and is also a renewable material with low viscosity and good solubility properties [5]. The largest fraction of biodiesel consists of $C_{16}$-$C_{18}$ methyl esters which are readily biodegradable due to their chemical nature and can be domestically produced and obtained at competitive prices [6].

Biodiesel is produced from vegetable oils by converting the triglyceride oils to methyl (or ethyl) esters through a process known as transesterification. The transesterification process reacts alcohol with the oil to release three "ester chains" from the glycerin backbone of each triglyceride. Duffy and Patrick, 1883 [7] were responsible for the transesterification of vegetable oil.

The selection of a suitable scrubbing solvent for a specific waste gas stream composition is influenced by a high absorption capacity for the separating component, a high selectivity with reference to other gases, low toxicity and low volatility.

J Hu, Z Du, Z Tang and E Min, 2004 [8] investigated the suitability of biodiesel as a solvent. They confirmed that the

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small quantities of non-monoalkyl esters (eg. glycerides) in biodiesel have effects on the solvent power of biodiesel. The length of the carbon chain of the fatty acid group of biodiesel has an effect on the solvent power of biodiesel, and the longer the carbon chain, the weaker the solvent power. The unsaturated fatty acid esters have a higher solvent dissolving power than the saturated fatty esters, but the number of double bonds in the unsaturated fatty acid esters has little effect on the solvent power.

## IV. MODEL SELECTION

Infinite dilution activity coefficients play an important role in the analysis and design of separation processes. At infinite dilution the single solute molecule is completely surrounded by the solvent. Hence, infinite dilution activity coefficients, ($\gamma^{\infty}$) are useful as they give a measure of the greatest degree of non-ideality of a mixture [9].

The most successful methods currently used for the calculation of activity coefficients are the group contribution methods, in which the liquid phase is considered to be a mixture of structural groups. The most well-known and accurate of the group contribution methods proposed is the Universal Functional Activity Coefficient (UNIFAC) [10].

The UNIFAC model was first published in 1975 by Fredenslund, Jones and Prausnitz of the University of California [11]. The UNIFAC method is a semi-empirical system for the prediction of non-electrolyte activity estimation in non-ideal mixtures and it makes use of the functional groups present in the molecules that make up the liquid mixture to compute activity coefficients. By utilising interactions for each of the functional groups present in the molecules, as well as some binary interaction coefficients, the activity of each of the solutions can be calculated [12]. In the Original UNIFAC model (Fredenslund); the activity coefficient is expressed as the sum of the combinatorial and residual parts respectively [13].

$$\ln\gamma_i^{\infty} = \ln\gamma_i^{c} + \ln\gamma_i^{r} \qquad (2)$$

In equation (2), $\gamma^{com}$ and $\gamma^{res}$ represent the combinatorial and the residual components respectively. Many modifications have been proposed to the both the residual and combinatorial terms in order to improve the performance of the UNIFAC model in the prediction of VLE, $\gamma^{\infty}$ and excess enthalpies.

### A. Group Contribution Methods

The group contribution method uses the principle that the structures of chemical components are always the same in many different molecules. This coupled with a single, double or triple bonds reinforces that there are only ten atom types and three bond types with which we can build thousands of components. The next more complex building blocks of the components are the functional groups which are themselves built of a few atoms and bonds.

Group contribution methods are used to predict the properties of pure components and mixtures by using group properties. This reduces the amount of data required. Therefore, instead of requiring the properties of millions of components, only the data for a few groups are required.

The group contribution concept has been used to estimate various chemical properties of pure compounds such as densities, heat capacities and critical constants [14]. Since the early applications of group contribution methods, they have been developed and applied to calculate activity coefficients of the components in a liquid mixture. When considering mixtures of molecules in terms of the fundamental groupings of atoms, it should be made clear that the following aspects need to be accounted for; the organization of the molecules in the solution and in the standard state, the restrictions imposed on these interactions by the organization of the groups into molecules and the interaction of various groups which can occur in the solution and in the standard state.

The advantage of GCMs is that it allows for systematic interpolation and extrapolation of VLE data for many chemical mixtures. It also offers an appropriate way of predicting properties of mixtures for which experimental data is insufficient. When considering such mixtures it is not necessary to measure the intermolecular interaction because they can be calculated whenever the appropriate group interaction parameters are known [15]. However, these are found from experimental data not necessarily with the same molecules as those in the investigated mixture, but containing the same functional groups.

### B. Original UNIFAC model (Fredenslund et al., 1975)

In this model, the infinite dilution activity coefficient is expressed as the sum of the combinatorial and residual contributions:

$$\ln\gamma_i^{\infty} = \ln\gamma_i^{c} + \ln\gamma_i^{r} \qquad (3)$$

In equation (3), $\ln\gamma_i^{c}$ is the combinatorial part accounting for differences in the size and shape of the molecules and $\ln\gamma_i^{r}$ is the residual that accounts mainly for the effects arising from energetic interactions between groups present in solution.

For the combinatorial part:

$$\ln\gamma_i^{c} = \ln\frac{\phi_i}{x_i} + 1 - \frac{\phi_i}{x_i} - \frac{z}{2}q_i\left(\ln\frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i}\right) \quad (4)$$

In equation (4), $\theta_i$, $\phi_i$ is the molar weighted segment and area fractional components for the i^th^ molecule in the total system, *z* being the coordination number respectively, which is found to be relatively insensitive to change and is quoted as a constant having the value of 10. $r_i$ and $q_i$ are calculated from the group surface area and volume contributions; These parameters are calculated as follows:

$$\phi_i = \frac{x_i r_i}{\sum_j x_j r_j} \qquad (5)$$

$$r_i = \sum_k v_k^i R_k \qquad (6)$$

$$q_i = \sum_k v_k^i Q_k \qquad (7)$$

$$\theta_i = \frac{x_i q_i}{\sum_j x_j q_j} \qquad (8)$$

For the residual component of the activity $\gamma_i^r$ , is due to energetic interactions between groups present in the system. The residual component of the activity for the $i^{th}$ molecule containing *n* unique functional groups can be written as follows:

$$\ln \gamma_i^r = \sum_k v_k^i (\ln \Gamma_k - \ln \Gamma_k^i) \qquad (9)$$

$$\ln \Gamma_k = Q_k \left[ 1 - \ln\left( \sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{mk}}{\sum_n \theta_n \psi_{nm}} \right] \qquad (10)$$

In equation (10), $\Gamma_k$ is the activity of an isolated group in a solution consisting only of molecules of type *i.* The formulation of the residual activity ensures that the condition for the limiting case of a single molecule in a pure component solution is abided by ensuring that the activity is equal to 1. $\theta_m$ is the summation of the area fraction of group *m*, over all the different groups and is somewhat similar in form, but not the same as $\theta_i$. $\psi_{mn}$ is the group interaction parameter and is a measure of the interaction energy between groups. $X_n$ is the group mole fraction, which is the number of groups.

In equation (11), $\theta_m$ being the group parameter shown as:

$$\theta_m = \frac{Q_m x_m}{\sum_n Q_n x_n} \qquad (11)$$

In equation (12), $x_m$ is the group mole fraction shown as:

$$x_m = \frac{\sum_j v_m^i x_j}{\sum_{j,n} v_n^i x_j} \qquad (12)$$

In equation (13), $\psi_{mn}$ the group interaction parameter is determined by:

$$\psi_{mn} = \exp\left[ \frac{-a_{mn}}{T} \right] \qquad (13)$$

Thus $a_{mn}$ still represents the net energy of interaction between groups *m* and *n* and has the units of SI Kelvin. These interaction energy values are obtained from experimental data and are usually tabulated [16].

### *C. Modified UNIFAC (Larsen et al., 1981)*

This model is the result of two modifications that have been done with respect to the original UNIFAC model. Larsen presented a modified version of the UNIFAC (Lyngby modified UNIFAC) in which the Staverman-Guggeheim combinatorial part was changed to a Flory-Huggings combinatorial part with a modified volume fraction. He also introduced temperature dependant group interaction parameters. This model allows for the simultaneous presentation of VLE and excess enthalpies. It was also capable of presenting liquid-liquid equilibria using the modified UNIFAC-VLE parameters with the same quality as the original UNIFAC with LLE based parameters, confirmed in 1982 by Magnusses [17]. The combinatorial term and the group interaction parameters of the residual part were modified according to equations (14) and (15):

$$\ln \gamma_i^{comb} = \ln\left( \phi_i / x_i \right) + 1 - \left( \phi_i / x_i \right) \qquad (14)$$

In equation (14), $\phi_i$ the segment fraction of component *(i)* is determined by:

$$\phi_i = \frac{x_i r_i^{2/3}}{\sum x_j r_j} \qquad (15)$$

And second, the interaction parameter in the residual part

$$\psi_{mn} = \exp\left\{ - \left[ \frac{a_{mn} + b_{mn}(T - T_0) + c_{mn} + (T \ln T_0/T + T - T_0)}{T} \right] \right\} \qquad (16)$$

In equation (16), $T_0$ is taken as a reference temperature equal to 298.15K (25°C)

## V. MODIFIED UNIFAC (BASTOS ET AL., 1988)

The Modified UNIFAC (Bastos et al., 1988) only modifies the combinatorial part of the Original UNIFAC from Fredenslund et al. [18]

$$\ln \gamma_i^c = \ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i} - \frac{z}{2} q_i \left( \ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \qquad (17)$$

In equation (17), $\psi_i$ is determined from:

$$\psi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j} \qquad (18)$$

## VI. METHODOLOGY

In order to facilitate prompt computations, Microsoft Excel spreadsheets were used. Minimal manual input was required with most of the required inputs being obtained by formulae which included lookup references. Tables which included, Component Identification, Original UNIFAC Group Interaction Parameters (GIP), Modified UNIFAC Group Interaction Parameters (GIP), Van der Waals parameters, and '$R_k$' and '$Q_k$' parameter tables, were generated in order to facilitate the computation procedure.

The selected VOCs were added to a table where each selected VOC was broken down into the constituent functional groups (in terms of type and quantity) which encompassed the compound in question. The '$R_k$' and '$Q_k$' parameters and Component identification table was sorted in ascending order in terms of sub-groups to facilitate the 'Vlookup' function. For the GIP tables, a cross-reference table was set up in ascending order in terms of both parameters '$\Psi_{nm}$' and '$\Psi_{mn}$' numerical identities in order to facilitate the 'Vlookup' and 'Hlookup' functionality.

## VII. RESULTS & DISCUSSION

This work discusses infinite dilution activity coefficients for 25 volatile organic compounds in four methyl esters namely methyl linolenate, methyl oleate, methyl stearate and methyl palmitate. The influence of temperature on activity coefficients was studied at a temperature range of 298 K to 398K. Previous studies indicate that a temperature of approximately 308K is favourable for the absorption of organic compounds in polymeric solvents [20].

### A. Alkanes

From Figs. 1 and 2, it is evident that most of the ester/alkane interactions show an increase in activity coefficient as the temperature increased. 1-2 Dibromoethane yielded the lowest activity coefficients as the temperature increased.

The activity coefficients of the halogenated hydrocarbons are relatively unaffected by the changes in temperature - as reflected by their "flat" graphs (very small variations in activity coefficient as the temperature increased). 1-2 Dibromoethane had lower activity coefficients than 1-2 dichloroethane. This is due to the uneven distribution of the chlorine molecules around1-2 dichloroethane, which results in the localisation of the negative charges around these atoms, thus rendering the 1-2 dibromoethane molecule to be more polar. This localisation of negative charge has a hindering effect on the solubility of the 1-2 dibromoethane molecules in FAMEs, which can be attributed to increased repulsive Van der Waals forces. Therefore, the charge distribution of the 1-2 dibromoethane molecule is more balanced and the polarity is favourable for absorption when compared to the 1-2 dichloroethane molecule. The chlorine molecule has a higher electronegativity when compared to the bromine molecule. The outer electrons of the chlorine molecule are also closer to the nucleus therefore a higher bond disassociation energy has to be overcome for the molecules to interact. Thus, 1-2 dibromoethane yielded lower activity coefficients than 1-2 dichloroethane throughout the temperature range.

The infinite dilution activity coefficients increased with an increase in non-polar hydrocarbon chain length, with heptane having higher activity coefficients than hexane across the temperature range. This can be attributed to an increase in the Van der Waals forces between solute-solute interactions as the molecular weight is increased. Therefore, increased energy is required to break the solute-solute bonds to allow for bonding of the solvent to occur.

The esters with a lower carbon count (shorter chained esters) had higher activity coefficients when compared to the esters with a higher carbon count (longer chained esters) across the temperature range. Therefore, as the solvent increases in size the surface area proportionately increases, which affects the intensity of the London dispersion forces of the solvent molecule, thus resulting in an increased attraction for the solute molecules as the solvent size was increased. This was also due to the number of available sites for solute/solvent interaction to occur which was favourable with the longer chained esters. This is evident as methyl stearate had lower activity coefficients than methyl palmitate with both being saturated esters with no double bonding.

Methyl oleate-alkane interactions yielded lower activity coefficients than methyl linolenate/alkane interactions and the activity coefficients decreased even lower with methyl stearate, with all three esters containing 19 carbon atoms. Therefore, the activity coefficient values increase with an increase in the amount of unsaturated double bonds in the ester hydrocarbon chain across the temperature range. Thus, the solubility decreased with the increase in the degree of solvent unsaturation for the alkane family. This is due to the thermal stability of saturated esters which have higher melting points than unsaturated esters. Saturated esters have a more "linear" structure due to the single bonds (C-C) in the hydrocarbon tail, so they pack closely together. Unsaturated esters have "kinks" due to the double bonds between the carbons (C=C), therefore they do not pack together as closely. This causes the unsaturated esters to break-up more easily when the temperature is increased despite having double bonded carbon atoms which have a higher bond dissociation energy than that of single bonded carbons. Thus, less energy is required to cause separation between the molecules.

### B. Alkenes

Figs 4-3 and 4-4 show negligible influence of temperature of VOCs – biodiesel interactions. Alkenes are less soluble than akanes with thiophene being the most soluble. Thiophene ($C_4H_4S$) is a heterocyclic compound which consists of a five membered ring. Thiophene is considered to be an aromatic although the degree of aromaticity is less than that of benzene. The electron pairs on the sulphur (C-S-C) are significantly delocalised and readily available for bonding. The molecule also has a small surface area and is flat with a bond angle of 93 degrees at the sulphur and 114 degrees at the two carbons, which makes it possible for ease of interaction with the solvent, therefore accounting for the lower activity coefficients.

From Figs 3 and 4, it is evident that naphthalene had the highest activity coefficient and varied to a small degree with an increase in temperature. The naphthalene molecule can be viewed as a fusion of a pair of benzene rings, although unlike the benzene molecule the carbon-carbon (C-C) bonds are not the same length. This coupled with the high boiling temperature of 170-230 $^{o}$C, accounts for the stability in the studied temperature range.

The naphthalene thermal stability was because of the benzene molecule, where the double bonds of the solutes tend to polarize the double bonds of the solvent molecules. In benzene there are three pi bonds located in the hexagonal ring in an alternate manner. These pi bonds get delocalised in the ring and make the molecule thermally stable. An increase in the number of double bonds in the solvent results in decreased polarizability, therefore the solubility decreases with an increase in the degree of solvent unsaturation.

Saturated esters have a more “linear” structure due to the single bonds (C-C) in the hydrocarbon tail, so they pack closely together. Unsaturated esters have “kinks” due to the double bonds between the carbons (C=C), therefore they do not pack together closely. This naturally causes the unsaturated esters to break-up more easily despite having double bonded carbon atoms which have a higher bond dissociation energy than that of single bonded carbons. Thus, less energy is required to cause separation between the molecules.

Esters with a lower carbon count had higher activity coefficients when compared to the esters with a higher carbon count across the temperature range. This means that as the solvent increases in size the surface area will proportionately increase, which will affect the intensity of the London dispersion forces of the solvent molecule, therefore resulting in an increased attraction for the solute molecules as the solvent size was increased. This was also due to the number of available sites for solute/solvent interaction to occur which was more favourable with the longer chained esters.

### C. Amines

The amine family showed little variation in activity coefficient as the temperature was increased. This is represented by the relatively “flat” graphs, Figs 4-5 and 4-6. With regards to the amine family, triethanolamine was the most suitable and the effect of temperature was negligible. Triethanolamine ($C_6H_{15}NO_3$) is a viscous organic compound that is both a triol and a tertiary amine. The activity coefficients for tertiary amines (Trimethylamine) were lower than that of the secondary mines (Dimethylamine), indicating that tertiary amines are more soluble in ester solvents. This was due to the hydrogen bonding that was readily available in tertiary amines for interactions with ester solvents. In the case of triethanolamine the hydrogen bonding ability is increased due to the presence of the hydroxyl groups. In the triethanolamine molecule the (N-OH) bond is a much weaker bond with a bond disassociation energy of 201kJ/mol. Due to the low electronegativity of the nitrogen atom, the hydrogen molecule is available for bonding with the solvent. Nitrogen has a half filled p-orbital containing three electrons, which is more stable than oxygen’s electron configuration, which has an incomplete p-orbital containing four electrons. Therefore, less energy was required to break the solute-solute bonds, allowing for solute-solvent bonds to form, thereby accounting for the lower activity coefficients.

The number of double bonds in the solvent resulted in decreased polarizability, therefore the solubility decreased. Saturated esters have a more “linear” structure due to the singlebonds (C-C) in the hydrocarbon tail, and therefore pack closely together. Unsaturated esters have “kinks” due to the double bonds between the carbons (C=C), therefore they do not pack together closely. Therefore the unsaturated esters break-up more easily despite having double bonded carbon atoms which have a higher bond dissociation energy than that of single bonded carbons. Thus, less energy is required to cause separation between the molecules.

Amine - methyl stearate is the most soluble among the amine family of VOCs, Fig. 4.6. VOCs solubility increases with increase in esters molecular weight. As the solvent increases in size, the surface area also increases affecting the intensity of the London dispersion forces of the solvent molecule, thus enhancing solute solubility. The number of available sites for solute / solvent interaction increase with increase in solvent molecular weight.

Amines are bulky molecules and this increases the surface area available for solute–solvent London dispersion interactions to occur. Trimethylamine is more soluble than triethylamine due to its smaller size and is also a H-bond acceptor, and therefore has a higher degree of polarizability.

## VIII. CONCLUSION

This paper presents the vapour liquid equilibrium data for 25 volatile organic compounds in four biodiesels using the using the Original UNIFAC: Fredenslund et al, 1975; Modified UNIFAC: Bastos et al, 1988 and lastly the Modified UNIFAC (Larsen et al., 1981). The UNIFAC procedure can reliably predict phase equilibrium data within the temperature range and is time and cost saving. Biodiesel is a good absorption medium for volatile organic compounds considered in this work because of the low activity coefficients.

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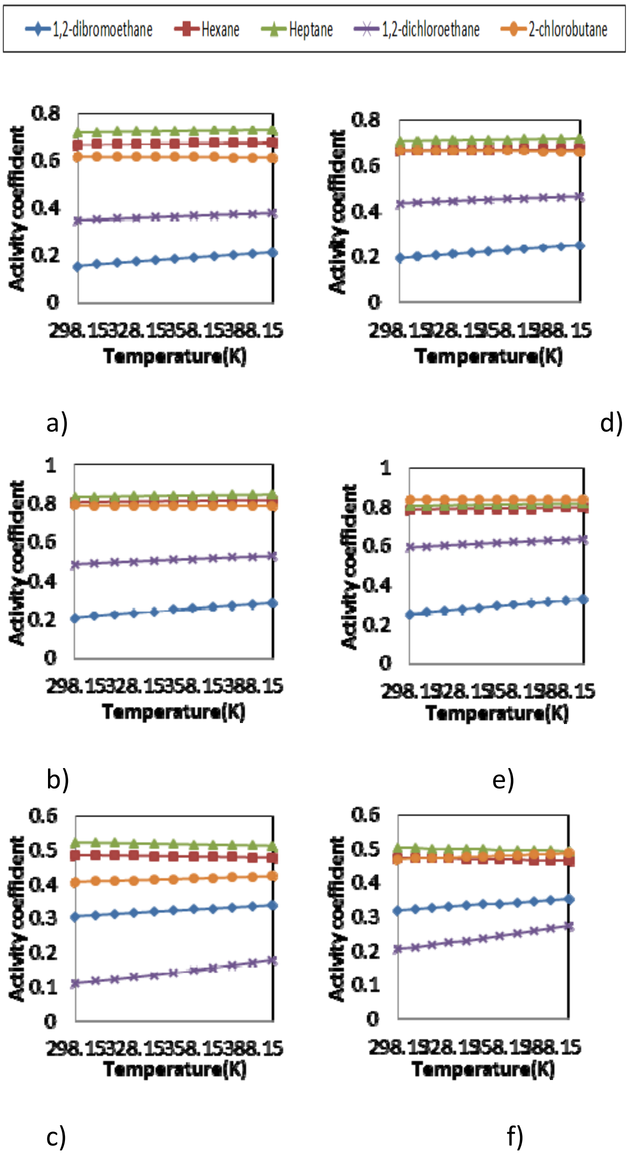

Fig.1. Variation of activity coefficients with temperature for the Alkane family in Methyl Palmitate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Linolenate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

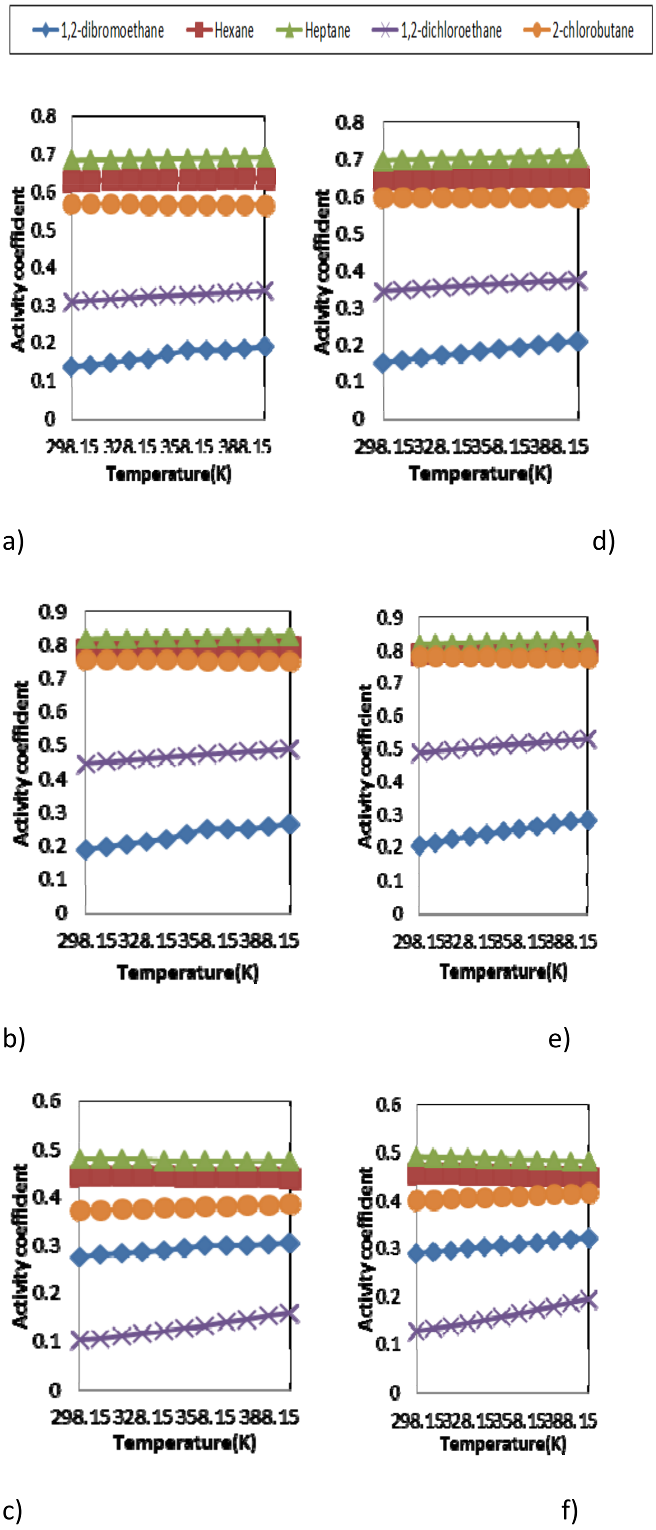

Fig.2. Variation of activity coefficients with temperature for the Alkane family in Methyl Stearate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Oleate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

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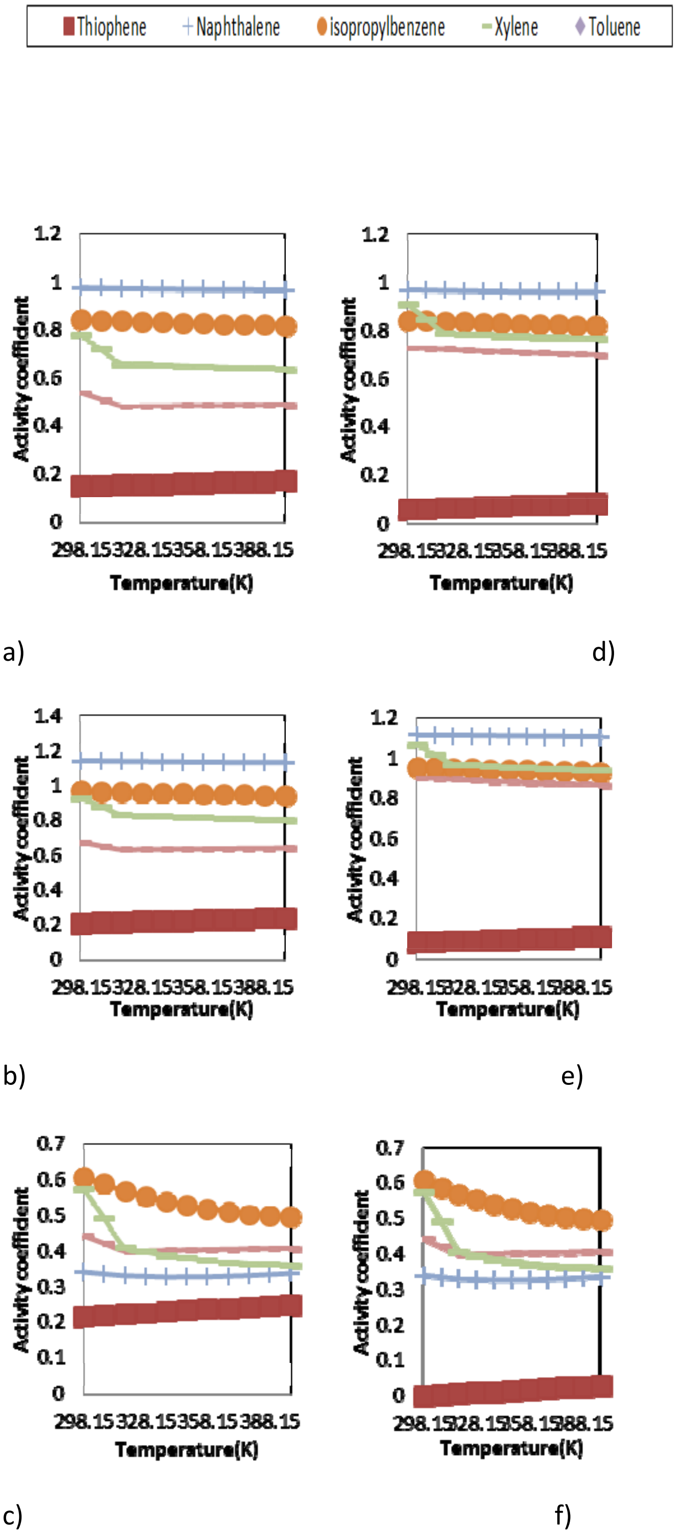

Fig.3. Variation of activity coefficients with temperature for the Alkene family in Methyl Palmitate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Linolenate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

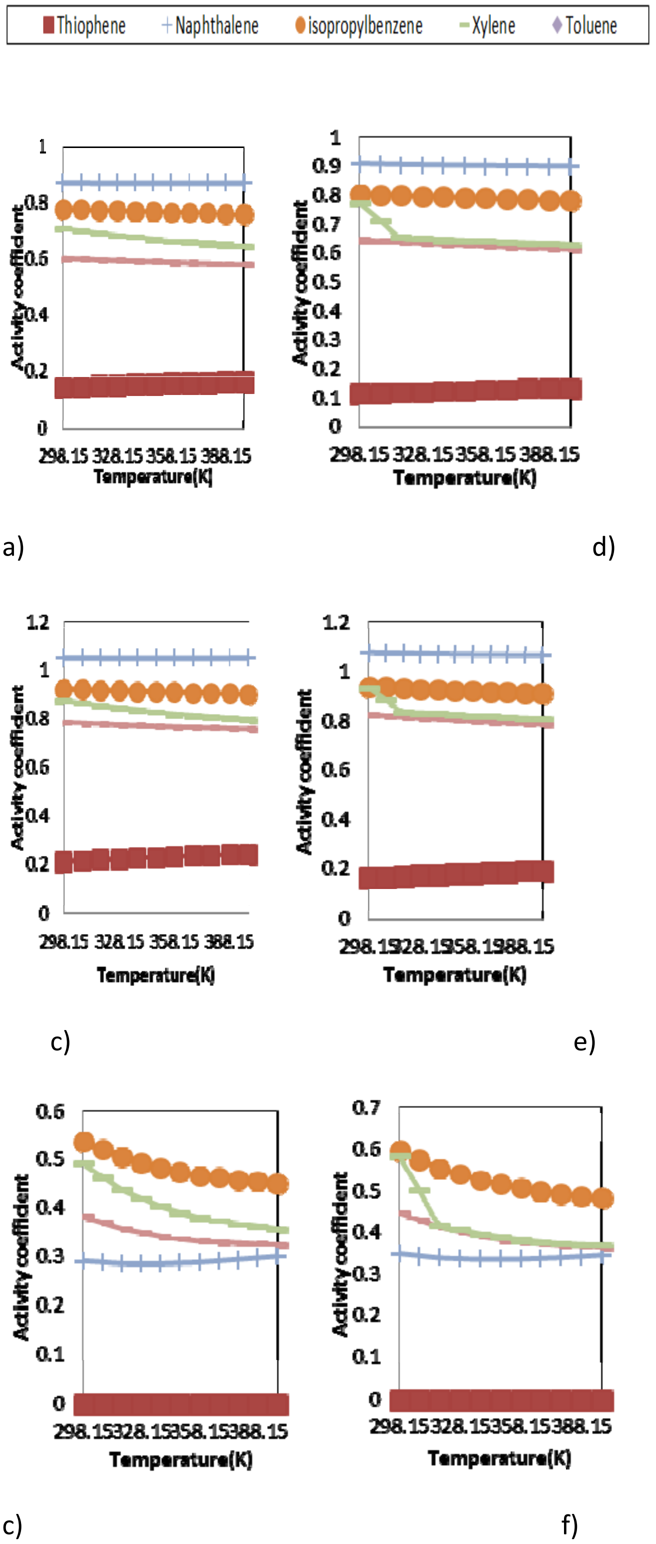

Fig.4. Variation of activity coefficients with temperature for the Alkene family in Methyl Stearate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Oleate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

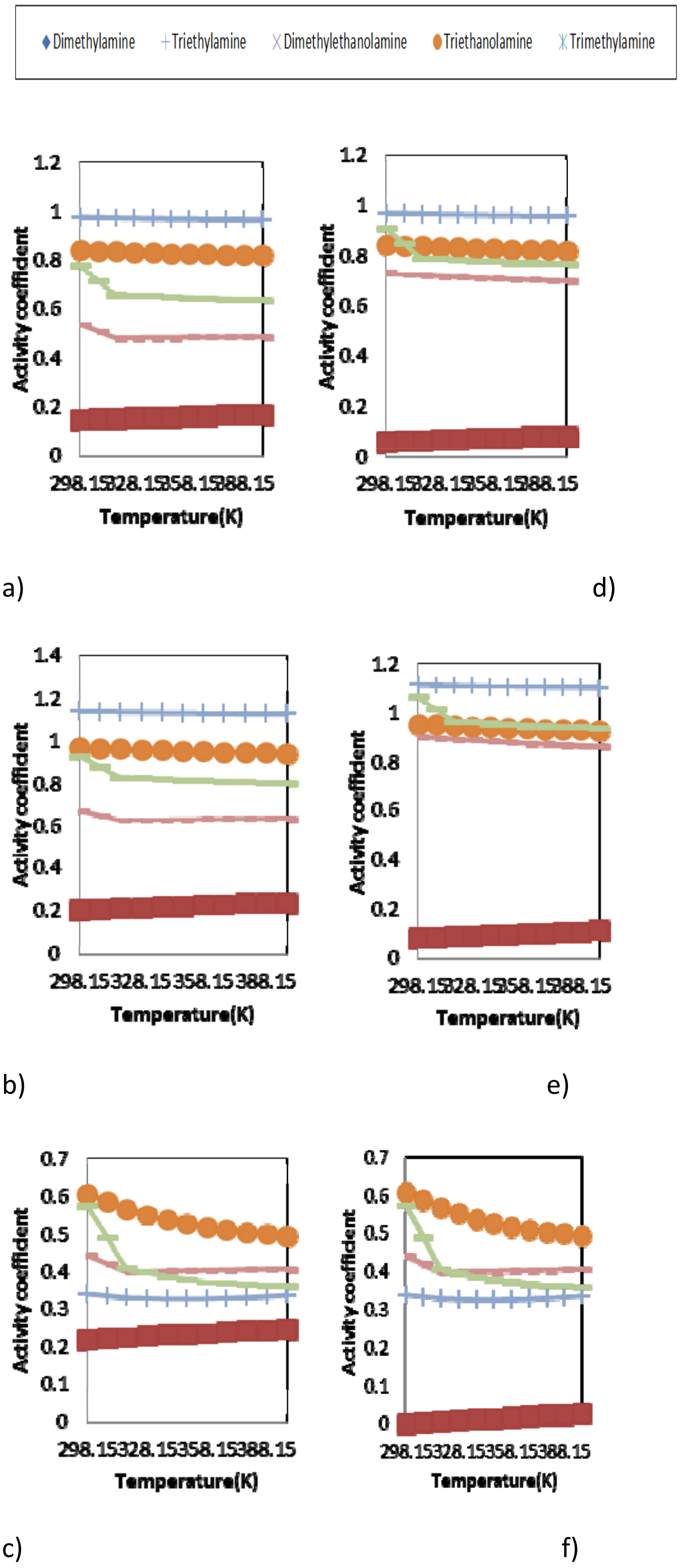

Fig. 5. Variation of activity coefficients with temperature for the Amine family in Methyl Palmitate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Linolenate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

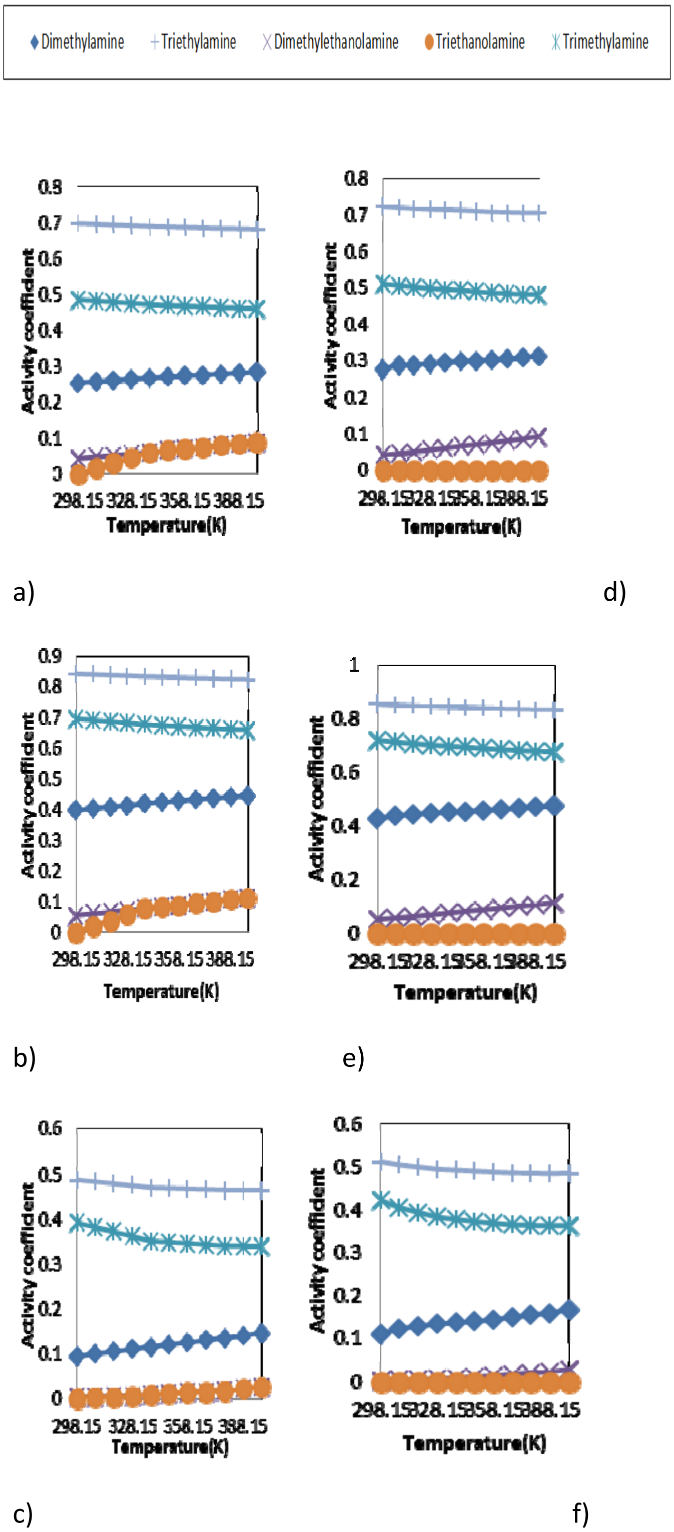

Fig. 6. Variation of activity coefficients with temperature for the Amine family in Methyl Stearate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Oleate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

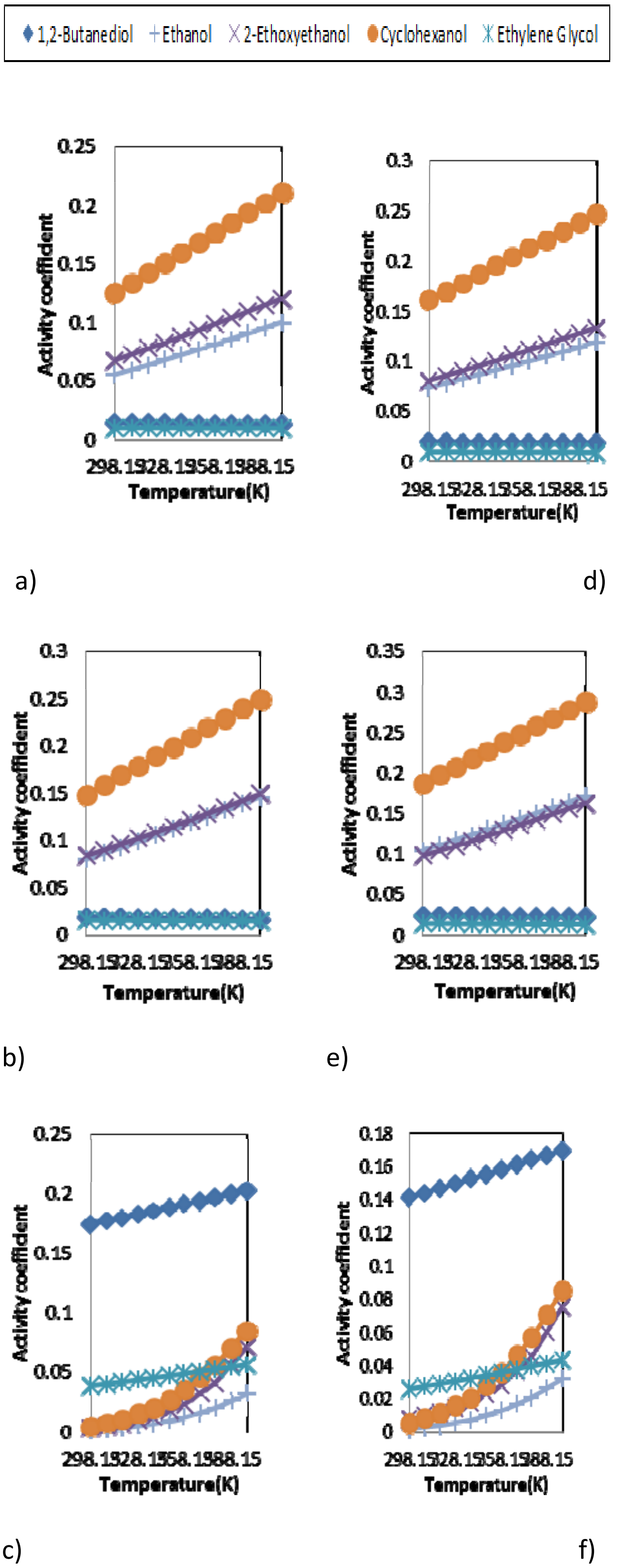

Fig. 7. Variation of activity coefficients with temperature for the Alcohol family in Methyl Palmitate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Linolenate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

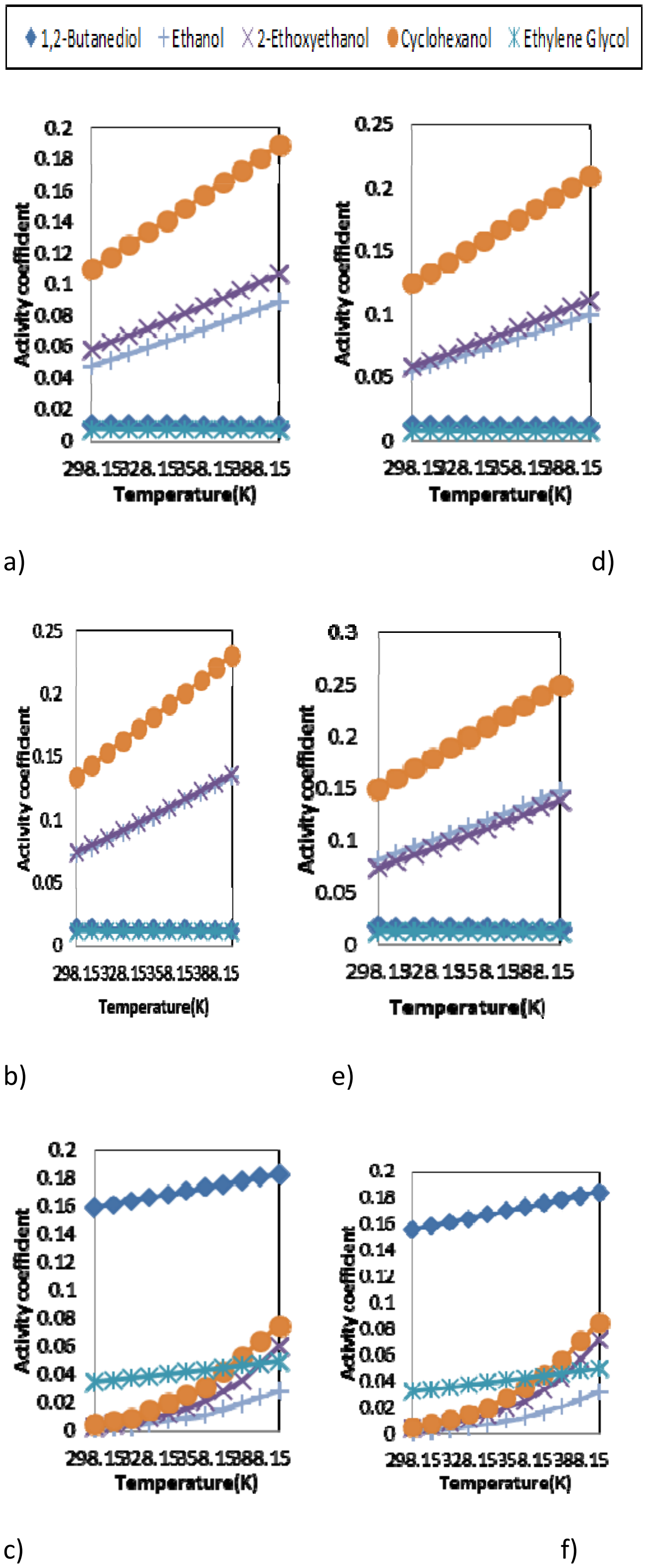

Fig. 8. Variation of activity coefficients with temperature for the Alcohol family in Methyl Stearate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Oleate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

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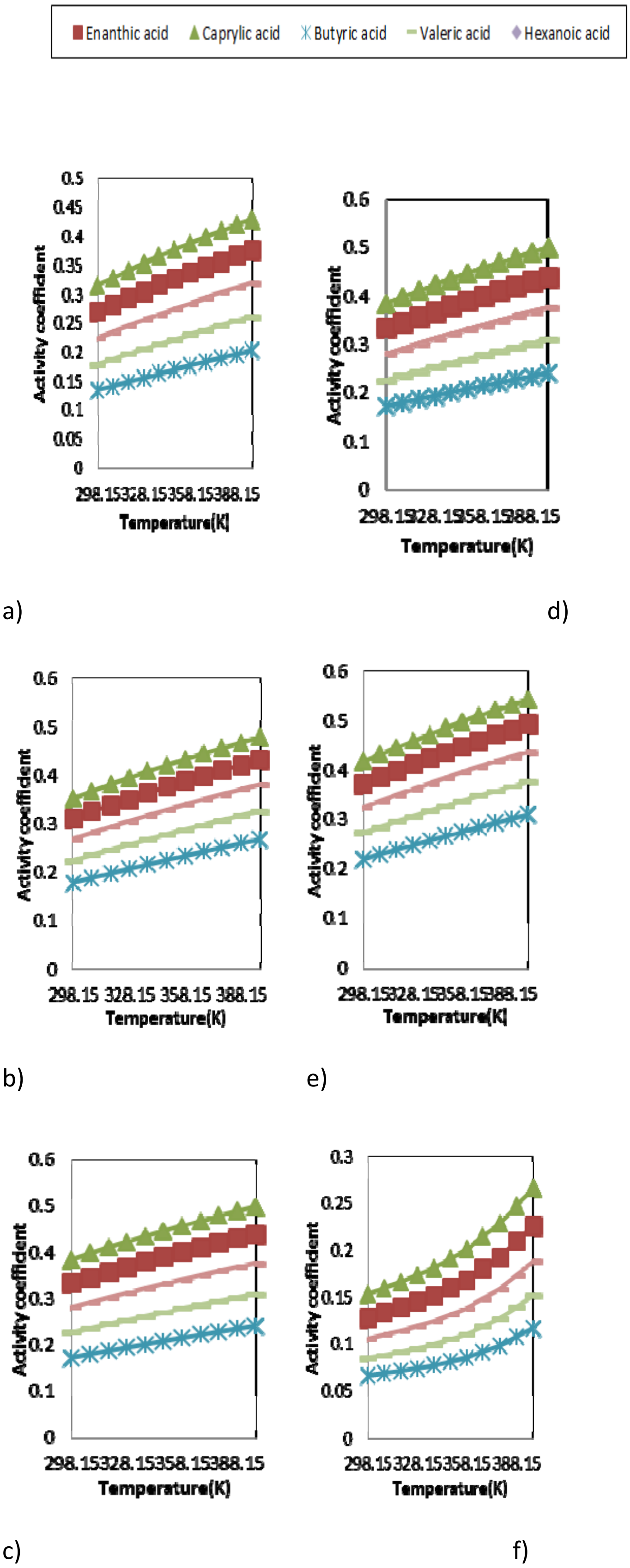

Fig. 9. Variation of activity coefficients with temperature for the Carboxylic Acid family in Methyl Palmitate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Linolenate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

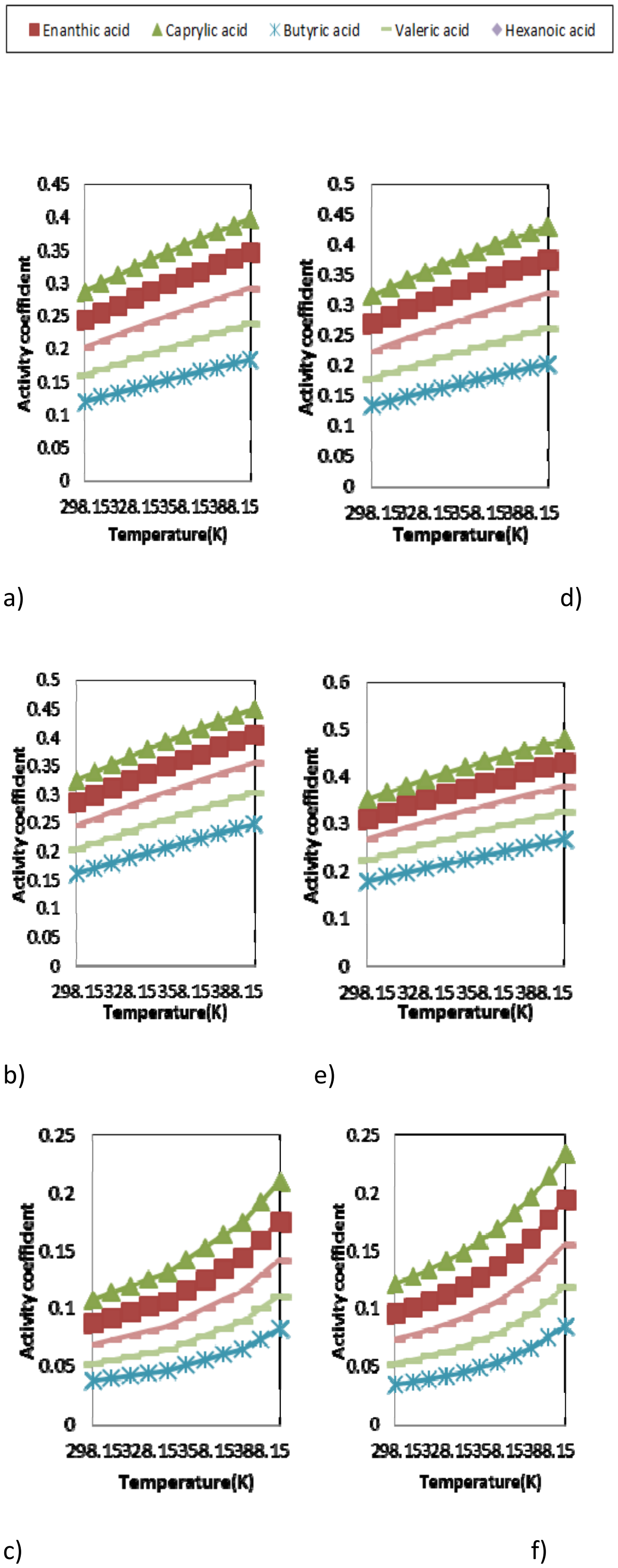

Fig. 10. Variation of activity coefficients with temperature for the carboxylic acid family in Methyl Stearate for a) Original UNIFAC; b) Modified UNIFAC Bastos; c) Modified UNIFAC Larsen; Methyl Oleate for d) Original UNIFAC; e) Modified UNIFAC Bastos; f) Modified UNIFAC Larsen

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