

Intermolecular Dynamics between Alcohols and Fatty Acid Ester Solvents

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Abstract—This work focused on the interactions which occur between ester solvents and alcohol solutes. The alcohols selected ranged from the simplest alcohol (methanol) to C10-alcohols, and solubility predictions in the form of infinite dilution activity coefficients were made using the Modified UNIFAC Dortmund group contribution model. The model computation was set up on a Microsoft Excel spreadsheet specifically designed for this purpose. It was found that alcohol/ ester interactions yielded an increase in activity coefficients (i.e. became less soluble) with an increase in the size of the ester solvent molecule. Furthermore, activity coefficients decreased with an increase in the size of the alcohol solute. The activity coefficients also decreased with an increase in the degree of unsaturation of the ester hydrocarbon tail. Tertiary alcohols yielded lower activity coefficients than primary alcohols. Finally, cyclic alcohols yielded higher activity coefficients than straight-chain alcohols until a point is reached where the trend is reversed, referred to as the ‘crossover’ point.

Keywords—Activity coefficients, alcohols, esters, solubility, van der Waals, UNIFAC.

I. INTRODUCTION

As a result of the relentless drive towards ‘greener’ living, chemical industries are under continued pressure to curb the release of volatile organic compounds (VOCs) into the atmosphere. VOCs adversely affect the environment as well as human health, and thus a suitable technology needs to be employed to reduce or preferably eliminate the release of these compounds by purifying industrial waste gas streams. Physical absorption has been proven to be a reliable technology for treatment of industrial end-of-pipe emissions, provided the process is designed to be efficient and (where possible) profitable.

When designing absorption systems, it is vital that the correct absorbent (solvent) is sourced to ensure maximum efficiency of the separation system – thus a thorough understanding of solvent-solute interactions is required. Most VOCs quickly saturates in water, and therefore organic solvents are required for the 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 [1], [2].

Modeling the absorption process requires accurate thermodynamic data. VOCs are present in very dilute concentrations in industrial gaseous waste streams, and thus phase equilibrium data is often required in the infinitely dilute region [3]. For preliminary design purposes, it is impractical and uneconomical to perform phase equilibrium measurements. It is thus necessary to predict thermodynamic data such as activity coefficient values using suitable thermodynamic models such the Modified UNIFAC Dortmund. Activity coefficients are key parameters which are required to compute phase equilibrium data for absorption systems.

This work continues our focus on the use of biodiesel as a suitable solvent for physical absorption systems. As mentioned previously, an understanding of solute-solvent interactions is vital in determining the suitability of a solvent. It was well known that biodiesel (being essentially non-polar) is unsuited for absorbing alcohols (being polar), thus this work essentially completes our understanding of the behavior of biodiesel in various operating environments. The Modified UNIFAC Dortmund group contribution model, developed by Weidlich and Gmehling [4] in 1987 was selected to compute the required activity coefficient values using a Microsoft Excel spreadsheet designed for this purpose. The phase equilibrium fundamentals, the modified UNIFAC Dortmund group contribution method, relevant previous studies of interest, computational methodology as well as solvent and thermodynamic model selection have been previously described [1], [2], [4]–[9].

II. RESULTS & DISCUSSION

Infinite dilution activity coefficients were predicted for 20 alcohols in 12 various methyl esters at 30°C. This temperature lies within a range which is considered practical for most absorption operations [1]. A mole fraction of 1×10^{-5} was selected to represent infinite dilution conditions, as recommended by Alessi et al. [3]. The notation described by Van Gerpen et al. [10] 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.

A. Aliphatic Tailed Ester/ Alcohol Interactions

Table I shows infinite dilution activity coefficient data of C1 to C10 straight-chain primary alcohol solute/ saturated ester solvent interactions under study. The trends depicted by this data are displayed in Fig. 1.

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TABLE I
INTERACTIONS BETWEEN ESTER SOLVENTS WITH SATURATED HYDROCARBON TAILS AND ALCOHOL SOLUTES

| Ester Solvent | Designation | Activity Coefficients - Straight Chain Solute/ Ester Interactions | | | | | | | | | |
|---------------|-------------|---|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| | | MeOH | EtOH | 3C-OH | 4C-OH | 5C-OH | 6C-OH | 7C-OH | 8C-OH | 9C-OH | 10C-OH |
| M. Butyrate | 1-C4:0 | 4.164 | 3.331 | 3.139 | 3.045 | 3.008 | 3.010 | 3.041 | 3.097 | 3.172 | 3.267 |
| M. Caproate | 1-C6:0 | 4.512 | 3.316 | 3.029 | 2.842 | 2.713 | 2.621 | 2.553 | 2.505 | 2.471 | 2.448 |
| M. Octanoate | 1-C8:0 | 4.864 | 3.441 | 3.106 | 2.878 | 2.710 | 2.581 | 2.478 | 2.394 | 2.324 | 2.266 |
| M. Decanoate | 1-C10:0 | 5.181 | 3.592 | 3.228 | 2.975 | 2.785 | 2.635 | 2.513 | 2.411 | 2.324 | 2.249 |
| M. Laurate | 1-C12:0 | 5.456 | 3.739 | 3.354 | 3.085 | 2.881 | 2.718 | 2.584 | 2.471 | 2.373 | 2.288 |
| M. Myristate | 1-C14:0 | 5.692 | 3.872 | 3.473 | 3.193 | 2.979 | 2.808 | 2.666 | 2.546 | 2.441 | 2.349 |
| M. Palmitate | 1-C16:0 | 5.893 | 3.991 | 3.582 | 3.293 | 3.073 | 2.896 | 2.748 | 2.623 | 2.514 | 2.417 |
| M. Stearate | 1-C18:0 | 6.063 | 4.094 | 3.678 | 3.384 | 3.159 | 2.978 | 2.827 | 2.697 | 2.585 | 2.486 |
| M. Arachidate | 1-C20:0 | 6.207 | 4.184 | 3.763 | 3.465 | 3.236 | 3.052 | 2.899 | 2.767 | 2.653 | 2.551 |

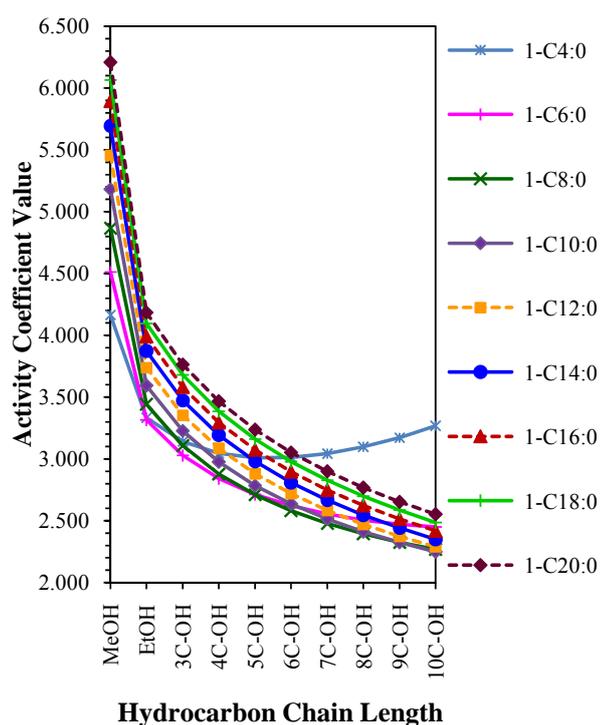


Fig. 1 Interactions between C1 – C10 alcohol solutes and saturated ester solvents

The results show an inverse pattern to that displayed by the alkane/ ester [6] and alkene/ ester [7] interactions, in that activity coefficients decrease with an increase in alcohol solute chain length, but increase with an increase in solvent hydrocarbon tail chain length. This trend is caused by the polarity of the solute molecule in relation to that of the solvent molecule. The carbonyl group in the methyl esters makes this molecule slightly polar for the smaller methyl esters such as methyl butyrate and methyl caproate. Since the alcohol molecules are also polar, the interactions between the smaller esters and alcohols results in a higher solubility. However the size of the molecule also has an impact on solute/ solvent interactions as is evident from Fig. 1 for methyl butyrate. In this instance the solute molecule gradually becomes larger

than the solvent molecule resulting in decreased solubility with an increase in solute size.

As the length of the hydrocarbon tail of the solvent increases, the solvent becomes increasingly non-polar. The hydroxyl group in the alcohol molecule has an extremely high dipole moment, making alcohols extremely polar, hence the high activity coefficient values experienced between these two chemical species. As the solvent hydrocarbon tail increase in length, the interactions between alcohol and solvent become more unlike, resulting in decreased solubility. Furthermore, there are two forces dominating intermolecular attractions in alcohol/ ester interactions – dipole-induced dipole and hydrogen bonding. Thus the larger the solvent molecule becomes, the lower the ability the solvent and solute have to interact to form hydrogen bonds with each other, and thus the solute molecules will tend to hydrogen bond with each other instead of bonding with the solvent molecules. Furthermore, there is an increase in London dispersion forces with an increase in solvent size due to an increase in the number of electrons in the molecule. It therefore becomes increasingly difficult for the polar solute molecules to induce a dipole on the solvent molecule as its size increases. All of the above factors result in increased activity coefficients with an increase in the solvent hydrocarbon chain length.

Methanol (MeOH) has no hydrocarbon tail, resulting in the high polarity of this molecule, and hence the extremely high activity coefficient values experienced between MeOH/ ester interactions. As the length of the alcohol chain increases, the polarity of the hydroxyl group is increasingly shielded by the non-polar tail resulting in a decrease in the overall polarity of the solute molecule. Therefore the activity coefficients of alcohol/ ester interactions decrease with an increase in alcohol hydrocarbon chain length.

B. Olefinic Tailed Ester/ Alcohol Interactions

The infinite dilution activity coefficient data of C1 to C10 straight-chain primary alcohol solute/ unsaturated ester solvent interactions is tabulated in Table II. The trends for C2 to C10 solutes are displayed in Fig. 2.

TABLE II
 INTERACTIONS BETWEEN ESTER SOLVENTS WITH UNSATURATED HYDROCARBON TAILS AND ALCOHOL SOLUTES

| Ester Solvent | Designation | Activity Coefficients - Straight Chain Solute/ Ester Interactions | | | | | | | | | |
|---------------|-------------|---|-------|-------|-------|-------|-------|-------|-------|-------|--------|
| | | MeOH | EtOH | 3C-OH | 4C-OH | 5C-OH | 6C-OH | 7C-OH | 8C-OH | 9C-OH | 10C-OH |
| M. Stearate | 1-C18:0 | 6.063 | 4.094 | 3.678 | 3.384 | 3.159 | 2.978 | 2.827 | 2.697 | 2.585 | 2.486 |
| M. Oleate | 1-C18:1 | 5.626 | 3.949 | 3.558 | 3.283 | 3.074 | 2.906 | 2.767 | 2.648 | 2.545 | 2.455 |
| M. Linoleate | 1-C18:2 | 5.257 | 3.826 | 3.461 | 3.207 | 3.015 | 2.862 | 2.736 | 2.629 | 2.537 | 2.456 |
| M. Linolenate | 1-C18:3 | 4.944 | 3.723 | 3.385 | 3.152 | 2.978 | 2.841 | 2.730 | 2.636 | 2.557 | 2.488 |

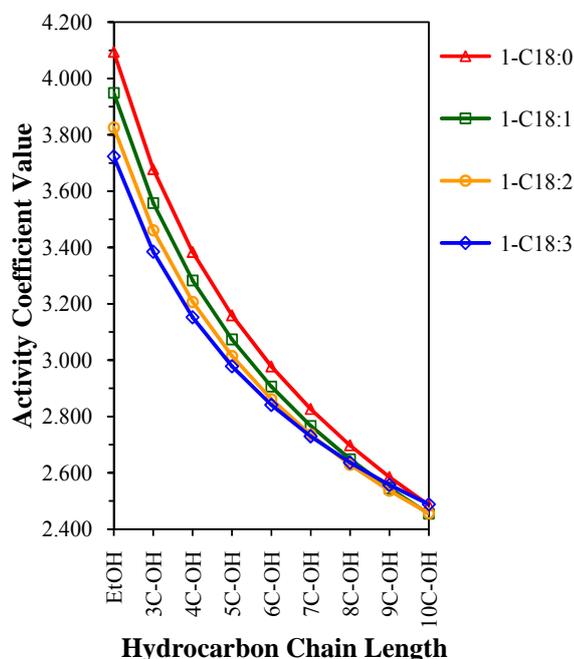


Fig. 2 Interactions between C2 – C10 alcohol solutes and unsaturated ester solvents

It is evident from Fig. 2 that activity coefficients decrease with an increase in the degree of ester solvent hydrocarbon tail unsaturation for the lower carbon chain alcohols. The trend becomes less marked with an increase in alcohol chain length until the point is reached at nonanol (9C-OH) and decanol (10C-OH) interactions where the trends converge.

It is suspected that the polar head of the lower alcohols such as ethanol (EtOH) and propanol (3C-OH) tend to interact with the unsaturated bonds in the solvent hydrocarbon tail by inducing bond interactions with the double bonds as the unsaturated bonds are not as stable as saturated bonds. An increase in the degree of unsaturation results in an increase in interactions with the alcohol molecules while the alcohol molecule is small and more reactive, due to the high polarity of the solute molecule. As the alcohol solute increases in size it becomes more unreactive as the solute cannot reach the double bond sites to interact with the solvent due to the hindrance of the solute's stable hydrocarbon tail, resulting in the convergence experienced.

C. Location of the Alcohol Functional Group

Fig. 3 illustrates the interactions of primary, secondary and

tertiary C4 alcohols.

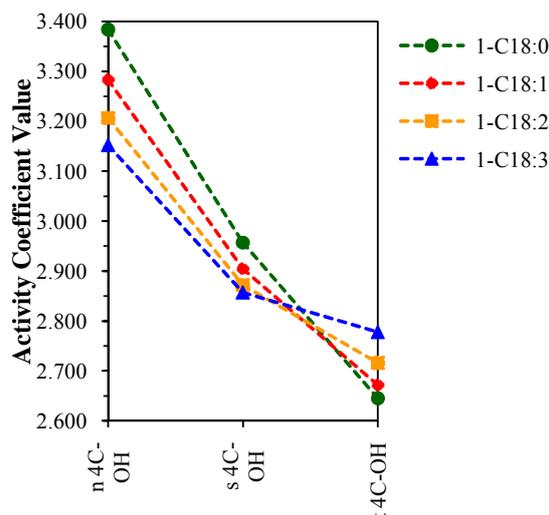


Fig. 3 Comparison of interactions of primary, secondary and tertiary C4 alcohols

It is evident that, unlike the branching of alkane/ ester interactions [6], the effect of branching and the resultant location of the alcohol functional group has a definite impact on solute/ solvent interactions. It can be seen that activity coefficients decrease with an increase in the degree of branching, since tertiary alcohols yield lower activity coefficients than primary and secondary alcohols. This is due to the fact that an increase in branching serves to increasingly shield the degree of polarity of the hydroxyl group.

The crossover experienced between *sec*-butanol and *tert*-butanol can be explained by an increase in the degree of non-polarity with an increase in branching, where *tert*-butanol/ solvent interactions behave more like alkane/ ester interactions [6]. With alkane/ ester interactions the activity coefficient increases with an increase in bond saturation due to an increase in the degree of bending of the solvent molecule. This decreases the effective area of the solvent's London forces for interaction to occur.

D. Comparison between Straight-Chain and Cyclic Solute Interactions

The various cyclic alcohol/ ester interactions studied are shown in Table III as well as Figs. 4 and 5.

TABLE III
 INTERACTIONS BETWEEN ESTER SOLVENTS WITH UNSATURATED HYDROCARBON TAILS AND ALCOHOL SOLUTES

| Ester Solvent | Designation | Activity Coefficients - Ester/ Cyclic Alcohol Solute Interactions | | | | | | | |
|---------------|-------------|---|----------|----------|----------|----------|----------|----------|-----------|
| | | cy 3C-OH | cy 4C-OH | cy 5C-OH | cy 6C-OH | cy 7C-OH | cy 8C-OH | cy 9C-OH | cy 10C-OH |
| M. Caproate | 1-C6:0 | 4.581 | 3.592 | 3.034 | 2.672 | 2.416 | 2.225 | 2.077 | 1.959 |
| M. Laurate | 1-C12:0 | 4.681 | 3.670 | 3.090 | 2.709 | 2.434 | 2.225 | 2.058 | 1.922 |
| M. Stearate | 1-C18:0 | 4.929 | 3.897 | 3.307 | 2.918 | 2.639 | 2.426 | 2.256 | 2.116 |
| M. Oleate | 1-C18:1 | 4.694 | 3.760 | 3.233 | 2.890 | 2.648 | 2.466 | 2.323 | 2.208 |
| M. Linoleate | 1-C18:2 | 4.495 | 3.653 | 3.187 | 2.891 | 2.687 | 2.539 | 2.427 | 2.341 |
| M. Linolenate | 1-C18:3 | 4.325 | 3.572 | 3.166 | 2.919 | 2.757 | 2.647 | 2.571 | 2.519 |

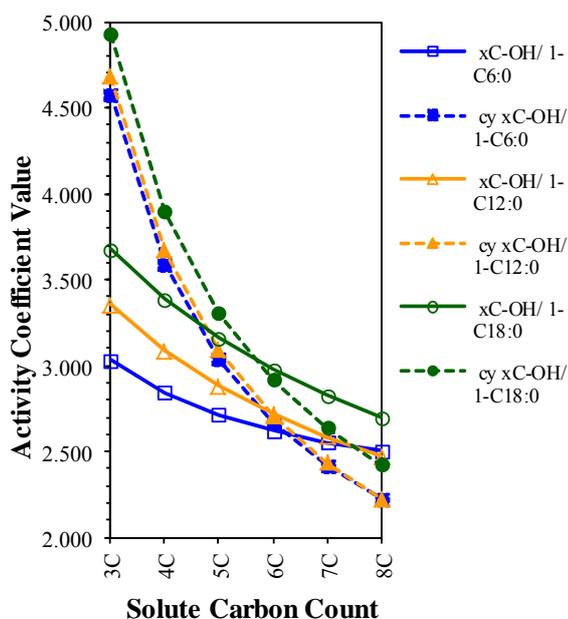


Fig. 4 Comparison between straight-chain and cyclic alcohols in saturated ester solvents

It can be seen from Fig. 4 that a comparison of cyclic alcohol/ ester solvent interactions with straight-chain alcohol/ ester interactions yielded lower activity coefficients for the smaller straight-chain alcohol interactions than the cyclic alcohol interactions. However a point was attained where the straight-chain alcohol interactions yielded higher activity coefficients than the cyclic alcohol interactions. This point (the 'cross-over' point) was also observed for alkane/ ester interactions [6] and alkene/ ester interactions [8]. However the trend is the opposite of that experienced for alkanes and alkenes, where smaller cyclics yielded lower activities than their straight-chain counterparts initially. Furthermore, unlike alkanes and alkenes [6], [8] the crossover occurred at the same point, namely at around the C6 chain length. The higher activity coefficients for smaller cyclic alcohols in comparison to their straight-chain counterparts can be explained by the shorter bond angle of the smaller cyclic carbons. For example, the bond angle between the methylene groups of cyclopropanol is 60° , whilst that of cyclobutanol is 88° instead of the straight-chained bond angle of 109.5° . The result of this is that the hydroxyl group is completely exposed

(thrust outward), making it much more polar than its corresponding straight-chained counterpart. Even cyclohexanol, whose methylene groups possess a bond angle of 109.5° , has a puckered appearance where two of the methylene groups are thrust upward or downward at any one time making the hydroxyl group attached to these methylene groups more polar than its straight-chain counterparts. However, as the cyclic alcohol expands in size these effects are reduced and the polarity of the hydroxyl group is hidden by the cyclic chains to a point where its activity coefficients are lower than those of its straight-chain counterparts.

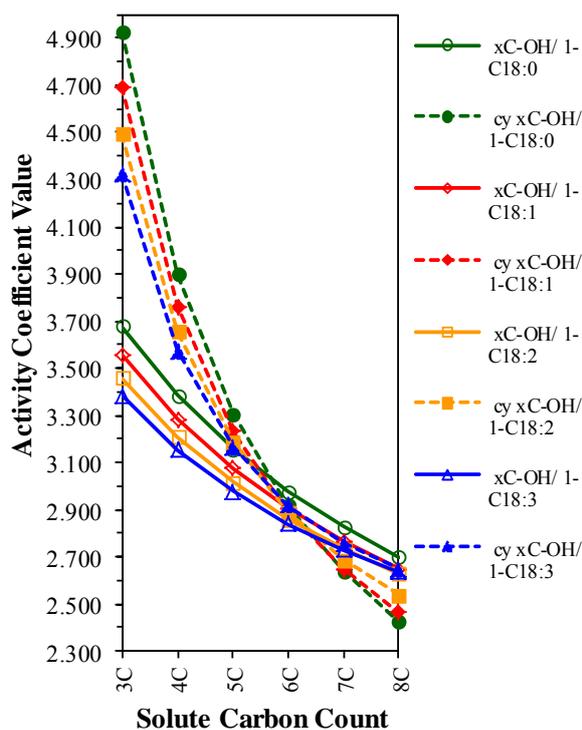


Fig. 5 Comparison between straight-chain and cyclic alcohols in unsaturated ester solvents

Fig. 5 shows a comparison between straight-chain and cyclic alcohols in olefinic esters. Cross-over only occurred for 1-C18:0, 1-C18:1 and 1-C18:2 alcohol/ ester interactions for the carbon range studied. It was observed that the cyclic alcohols crossed over themselves at C6 where 1-C18:0,

having previously a higher activity coefficient, eventually possessed the lowest activity coefficient of the C18 esters. 1-C18:3, having possessed the lowest activity coefficient of the C18 esters for the smaller cyclic alcohols, eventually possessed the highest activity coefficient for the higher cyclic alcohols. In similar fashion, 1-C18:1 and 1-C18:2 also experienced cross-over. The reason for the cross-over between the alcohol/ C18 ester interactions was described earlier in this paper when the straight-chain alcohol/ olefinic ester solvent interactions were discussed.

It is unclear what impacts the trends between cyclic alcohols and straight-chain alcohols – it could be either the polarity of the hydroxyl group, or the impact of hydrogen bonding. Unfortunately this cannot be tested on ketones, which are also polar but do not form hydrogen bonds, since UNIFAC cannot model cyclic ketones.

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