Intermolecular Dynamics between Aromatic Compounds and Ester Polymeric Solvents

Jacques J. Scheepers, Edison Muzenda and Mohamed Belaid

***Abstract*—**This work focused on the interactions that occur between ester solvents and simple aromatic solutes. Solutes were selected from various functional groups in their simplest form, and predictions of activity coefficients at infinite dilution 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. For polar aromatic solutes, solubility decreased with increase in size of the ester solvent molecule and the opposite was found to be true for non-polar solutes. For all aromatic/ ester solvent interactions there was a decrease in activity coefficients with an increase in the degree of ester unsaturation.

***Keywords*—**Activity coefficients, aromatic compounds, esters, solubility, van der Waals.

I. Introduction

THE release of volatile organic compounds (VOCs) into the atmosphere needs to be avoided at all costs where possible in order to limit the effect of these compounds on humans and the environment. Of the VOC abatement technologies available for treatment of industrial end-of-pipe emissions, physical absorption has proven to be particularly useful provided the process is efficiently designed and profitable.

One area of particular concern in absorber design is finding a thermodynamically favourable absorbent, and thus a thorough understanding of solvent-solute interactions is required. Not all VOCs are soluble in water – thus suitable organic solvents are required. There is an increasing drive internationally for the use of 'green' solvents to replace traditional organic solvents. Biodiesel, which is a mixture of fatty acid esters, has been proven to possess all the properties of a good solvent and is above all environmentally friendly [1], [2].

Another area of concern is ensuring that accurate thermodynamic data is selected to model the absorption process. Since VOCs are present in very dilute concentrations in the gaseous waste stream, it is essential to obtain phase equilibrium data in the very dilute region [3]. Since experimental work is often laborious and very time-consuming, it is convenient to predict thermodynamic data such as activity coefficients using a suitable thermodynamic model. Activity coefficients are key parameters required to compute phase equilibrium data for absorption systems.

This work is a continuation of our focus on the use of biodiesel as a suitable solvent for the abatement of volatile organic compounds through physical physical absorption. 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 procedure as well as solvent and thermodynamic model selection have been previously discussed [4]–[8] .

II. Results & Discussion

Infinite dilution activity coefficients were predicted for 12 aromatic compounds 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* [9] 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. Overview

Table I contains infinite dilution activity coefficient data of various aromatic solute/ saturated ester solvent interactions. The twelve aromatic compounds selected represent the simplest form of various functional groups. Table II represents infinite dilution activity coefficients of the same aromatic volatile organic compounds in monounsaturated and polyunsaturated esters. For ease of reference, the work is subdivided into three sections, namely polar, non-polar and miscellaneous aromatic compounds.

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

		Activity Coefficients - Aromatic Solute/ Saturated Ester Interactions											
Ester Solvent	**Desig-nation**	Aceto-phenone	Aniline	Anisole	Benz-aldehyde	Benzoic Acid	Benzo-nitrile	Chloro-benzene	Ethynyl-benzene	Phenol	Phenyl Acetate	Styrene	Toluene
M. Butyrate	1-C4:0	2.056	1.029	0.683	3.386	2.077	1.356	0.921	0.945	0.241	1.468	1.132	1.188
M. Caproate	1-C6:0	1.724	1.071	0.607	2.329	2.253	1.223	0.749	0.911	0.298	1.528	0.931	0.947
M. Octanoate	1-C8:0	1.627	1.179	0.608	1.927	2.507	1.233	0.678	0.930	0.368	1.653	0.854	0.842
M. Decanoate	1-C10:0	1.593	1.300	0.628	1.717	2.760	1.280	0.637	0.959	0.443	1.779	0.813	0.779
M. Laurate	1-C12:0	1.579	1.419	0.652	1.585	2.988	1.335	0.610	0.985	0.519	1.890	0.786	0.736
M. Myristate	1-C14:0	1.570	1.530	0.674	1.491	3.186	1.391	0.588	1.007	0.593	1.984	0.765	0.702
M. Palmitate	1-C16:0	1.563	1.631	0.694	1.418	3.355	1.442	0.570	1.023	0.665	2.061	0.747	0.674
M. Stearate	1-C18:0	1.554	1.723	0.710	1.358	3.496	1.487	0.554	1.035	0.733	2.122	0.731	0.650
M. Arachidate	1-C20:0	1.543	1.804	0.724	1.307	3.612	1.526	0.540	1.042	0.799	2.170	0.716	0.628

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

		Activity Coefficients - Aromatic Solute/ Unsaturated Ester Interactions											
Ester Solvent	**Desig-nation**	Aceto-phenone	Aniline	Anisole	Benz-aldehyde	Benzoic Acid	Benzo-nitrile	Chloro-benzene	Ethynyl-benzene	Phenol	Phenyl Acetate	Styrene	Toluene
M. Stearate	1-C18:0	1.554	1.723	0.710	1.358	3.496	1.487	0.554	1.035	0.733	2.122	0.731	0.650
M. Oleate	1-C18:1	1.441	1.602	0.687	1.255	2.886	1.315	0.534	0.933	0.691	1.881	0.707	0.643
M. Linoleate	1-C18:2	1.349	1.501	0.673	1.170	2.458	1.182	0.518	0.861	0.656	1.690	0.692	0.641
M. Linolenate	1-C18:3	1.275	1.416	0.667	1.100	2.145	1.077	0.506	0.811	0.627	1.539	0.683	0.643

B. Polar aromatic solutes

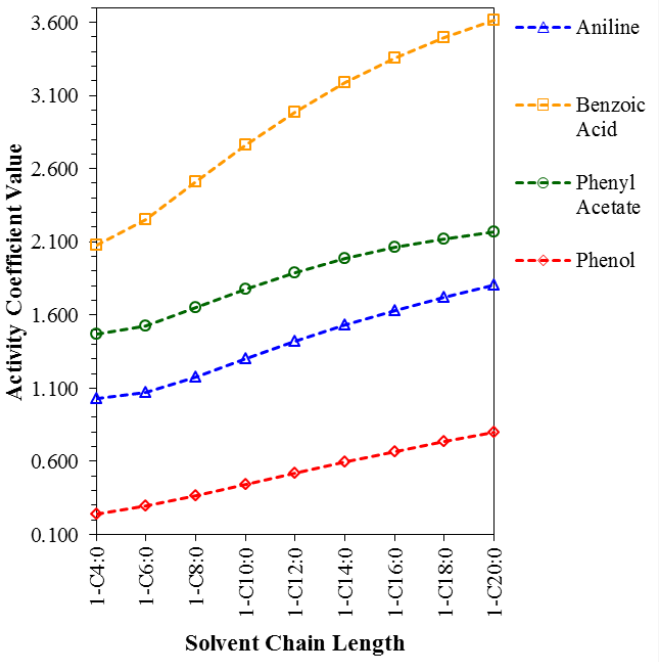

Fig. 1 Interactions between polar aromatic solutes and saturated ester solvents.

Four polar aromatic solutes with the ability to hydrogen-bond with other polar solutes were studied. From Fig.1, activity coefficients increase with an increase in the solvent chain length. The reason for this behavior can be explained as follows – in addition to London dispersion forces and dipole-dipole interactions, esters are capable of hydrogen bonding. This is attributed to the lone electron pairs on the oxygen atoms in the ester chain. Esters do not contain hydrogen atoms attached to the electronegative oxygen atoms and can therefore only act as hydrogen bond (H-bond) acceptors. Thus one of the slightly positive hydrogen atoms contained in each of the above solutes (which can act both as H-bond donors and as H-bond acceptors) can be attracted to one of the lone pairs on one of the oxygen atoms in an ester for a hydrogen bond to be formed. The energy released in these attractions provides the energy required to separate solute molecule from solute molecule and ester molecule from ester molecule to allow mixing. However an increase in ester chain length results in an increase in interference from the non-polar hydrocarbon part of the ester molecules. These chains force themselves between the polar solutes, thereby breaking the hydrogen bonds. The greater the length of the ester hydrocarbon tail, the more evident the above effect becomes, hence the increase in insolubility of the solute with increased solvent chain length.

Phenol was the most soluble of the four solutes. This is due

to the fact that one of the lone pairs of electrons of the oxygen atom are delocalized across the benzene ring, thereby reducing the polarity of the –OH group. This reduction in the polarity of the hydroxyl group allows phenol to be very miscible with the predominantly non-polar esters. The same principle applies for aniline where the single lone electron pair is delocalized across the benzene ring. This accounts for the relative solubility of aniline in the ester solvents in relation to benzoic acid and phenyl acetate. These two compounds contain two oxygen molecules in their functional groups, making them strongly polar as these molecules possess high dipole moments. These molecules are more soluble in polar solvents such as the alcohol and ether groups.

C. Non-polar aromatic compounds

Fig.2 shows the solubility of relatively non-polar aromatic solutes in the ester solvents studied.

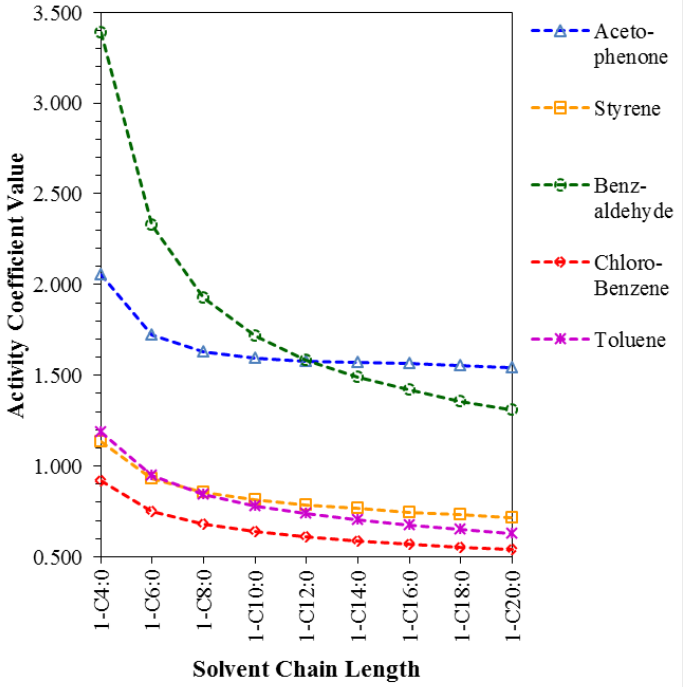

Fig.2 Interactions between non-polar aromatic solutes and saturated ester solvents.

It is evident that, unlike the polar solvents, these solute-solvent interactions display an increase in solubility with an increase in solvent chain length. This can be attributed to an increase in the attractive London dispersion forces with an increase in solvent molecule size, since hydrogen bonding is absent in these interactions and dipole-induced dipole interactions would remain more or less constant.

Chlorobenzene is the most soluble of the five solutes. As with phenol and aniline, there is an interaction between the delocalized electrons in the benzene ring and one of the lone electron pairs on the chlorine atom creating an overlap. This results in a movement of electrons away from the chlorine towards the benzene ring. Whilst chlorine is itself quite electronegative, the polarity of the chlorine-carbon bond is much reduced by the delocalization.

Whilst acetophenone and benzaldehyde can partake in hydrogen bonding in that they have electronegative oxygen atoms, they have no hydrogen bonded to an electronegative atom and can only act as H-bond acceptors. Since the ester solvents are also only H-bond acceptors, no hydrogen bonding can take place and thus the only van der Waals forces dominating in these interactions are London dispersion forces and attractive dipole - induced dipole forces. Both these molecules will possess a high dipole moment due to the presence of their highly electronegative polar oxygen atom. The effect of these molecules' ability to polarize the solvent molecules does however decrease with increasing ester chain length due to the increase in strength of the dispersion forces. It should be mentioned however that these two molecules are much less miscible than the other three aromatic solutes in non-polar ester solvents due to the high polarity of these solutes.

D.Miscellaneous aromatic compounds

The solubility of anisole, benzonitrile and ethynylbenzene is described in Fig.3 below.

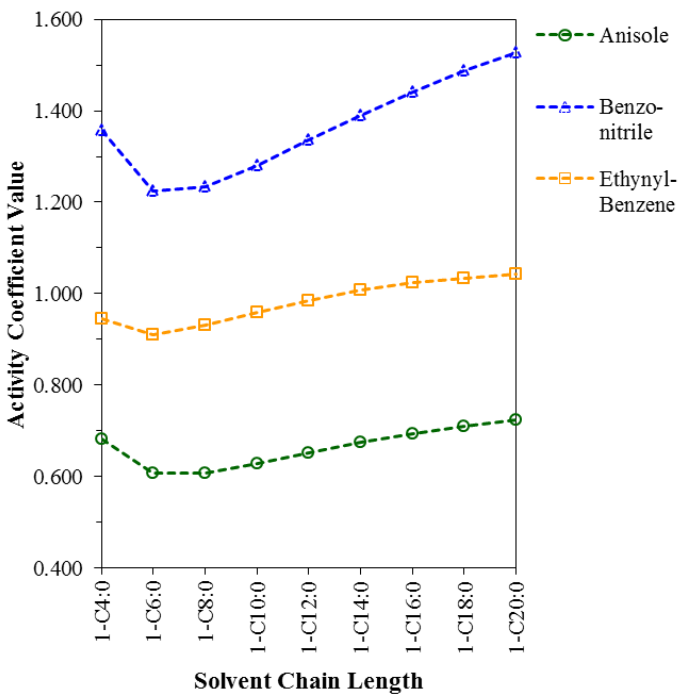

Fig.3 Interactions between miscellaneous aromatic solutes and saturated ester solvents.

It can be seen from Fig.3 that all three solute-solvent interactions experienced a marked decrease in activity coefficients followed by an increase in activity coefficients with increasing solvent chain length. It is presumed that the initially high activity coefficients could be attributed to the small size of the methyl butyrate solvent. Being small, it is possible that the methyl butyrate molecule would find it

difficult to orientate itself in such a way that a strong mutual attraction could take place between itself and the predominantly linear solvents. This is especially true if one considers the weak London forces the solvent molecule would possess. Methyl caproate on the other hand possesses a large enough London force to cause a more significant dipole-induced dipole to occur between the solvent and solute molecules. Since the solute molecules are all linear in nature, it is assumed that the increase in activity coefficients is due to the increased difficulty in aligning themselves with increasing solvent chain lengths for maximum bond interactions to occur. In other words, the longer the solvent chain length, the more loosely the solutes will arrange themselves with the solvent molecules.

Anisole was the most soluble of the three molecules in the ester solvents. Its alkane tail allows for miscibility in non-polar solvents even though its electronegative oxygen atom allows for miscibility in polar solvents (it is an H-bond acceptor). The miscibility of anisole in non-polar solvents is attributed to the shielding effect afforded to the oxygen atom by the alkyl and aryl groups. Benzonitrile, on the other hand, was the least soluble due to the high polarity exerted by the unshielded lone nitrogen electron pairs, which can facilitate hydrogen bonding.

E. Interactions between unsaturated esters and aromatic solutes

Thermodynamic interactions for interactions unsaturated ester solvents and aromatic solutes are shown in Fig.4, Fig.5 and Fig.6.

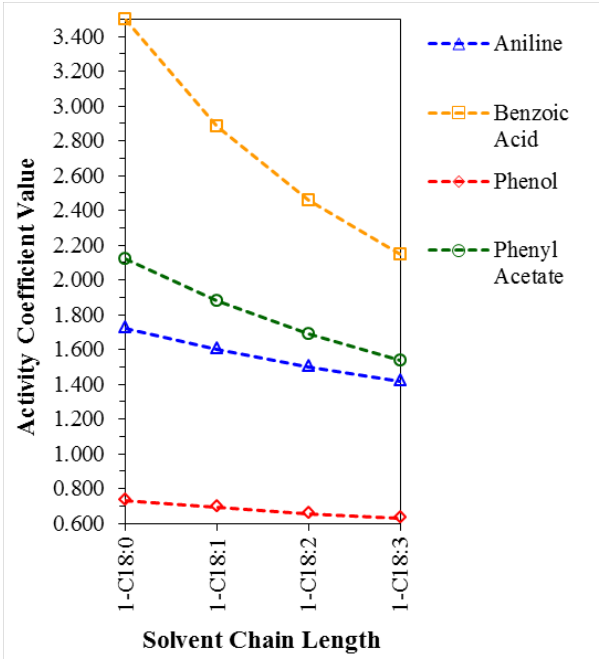

Fig.4 Interactions between unsaturated esters and polar aromatic compounds

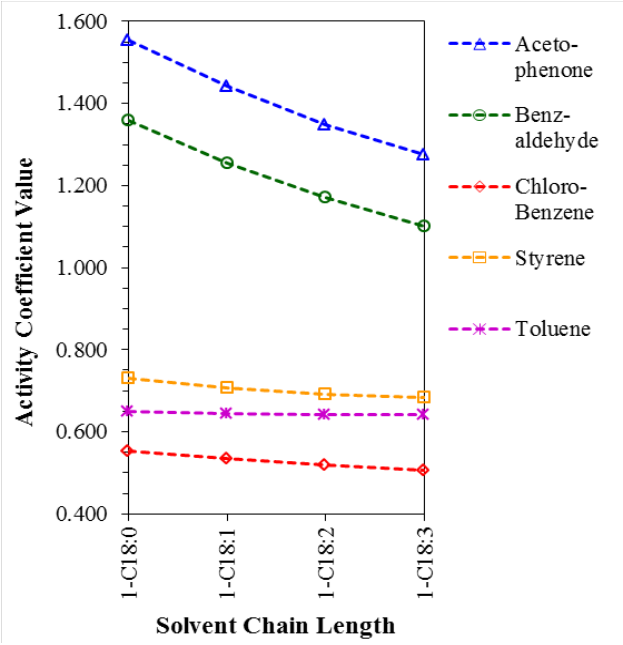

Fig.5 Interactions between unsaturated esters and non-polar aromatic compounds

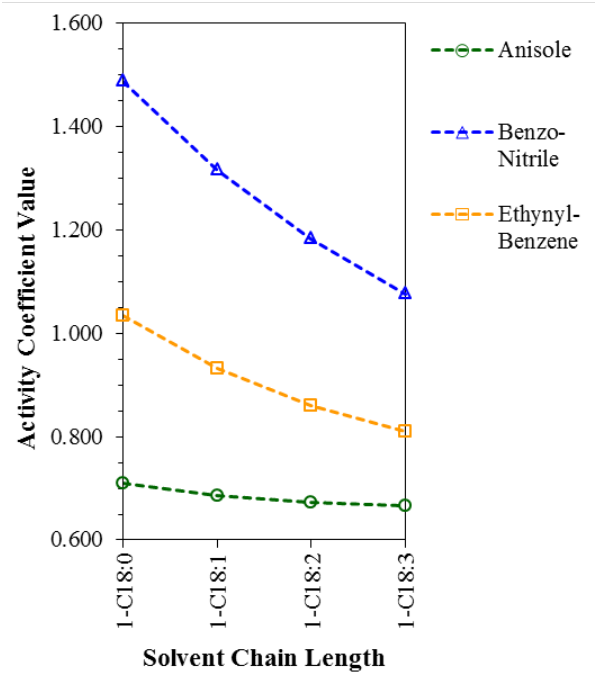

Fig.6 Interactions between unsaturated esters and miscellaneous aromatic compounds

All of the ester/ aromatic interactions experienced a decrease in activity coefficient with an increase in the degree of solvent unsaturation. This was not the case with the alkanes and alkenes studied [6]–[8], where an increase in activity coefficient was experienced with an increase in solvent unsaturation. The latter case is the more logical behavior because the more closely packed the solute and solvent are, the better the van der Waals interactions. Saturated solvents

are much straighter than the unsaturated solvents, which lends to closer packing. The fact that aromatic compounds are more soluble in increasingly unsaturated ester solvents could perhaps be attributed to an increase in the freedom to move around in a more loosely packed solvent structure. This freedom of movement would allow the aromatic molecules to rearrange themselves in such a way as to experience maximum van der Waals interactions, especially since the benzene ring is planar in structure.

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