

Alkenes – Ester Polymeric Solvents Thermodynamic Interactions - Part 1

Jacques J. Scheepers and Edison Muzenda

Abstract—This work focused on the interactions between ester solvents and volatile organic compounds of alkene in nature. Infinite dilution activity coefficients of alkenes in various fatty acid ester solvents were predicted in order to study and thermodynamically understand the nature and effect of the bond interactions involved. Activity coefficients were computed using Microsoft Excel model specifically designed for this purpose. The ester solvent chain length and saturation influenced the solubility of alkene organics. Saturated and longer ester chains gave better absorption performance. Alkenes were found to be more soluble than their alkane counterparts of similar carbon count.

Keywords— Activity coefficients, esters, interactions, organics, thermodynamically, solubility

I. INTRODUCTION

It is important to understand the mechanics of volatile organic compounds – ester polymeric solvent interactions for absorber system design for the abatement of volatile organics from contaminated gaseous industrial effluent. 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 were discussed in our previous studies [1], [2]. This work is a continuation of our interest in search for suitable polymeric solvents for the treatment of volatile organic compounds through physical absorption. This current work is aimed at studying the solubility of alkene organics in aliphatic and olefinic tailed ester absorbents (solvents).

II. RESULTS AND DISCUSSION

Activity coefficients were predicted for 13 volatile organic compounds in 15 various methyl esters at 30°C. This temperature lies within an area of interest for most scientific investigations, and is considered a practical temperature for most absorption operations [3]. A mole fraction of 1×10^{-5} was used in all calculations as it lies within the infinite dilution range of 10^{-4} (for mixtures of similar hydrocarbons) and 10^{-7} (for highly associated species) Alessi et al. [4]. Furthermore, preliminary tests of the model showed no change in infinite dilution activity coefficients at mole fraction values lower than 1×10^{-5} for system studied.

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A. Solutes and Solvents Naming

1) For solutes:

'=' represents a double bond. The number preceding the '=' represents the position of the bond.

'n' represents a straight-chained solute.

2) For solvents:

As per van Gerpen *et al* [5] notation, ester solvents are designated after the 'C' by two numbers separated by a colon. The first number represents the number of carbon atoms in the chain including the carboxylic carbon (i.e. the carbon that is double bonded to the oxygen atom) and the second number designates the number of double bonds in the ester molecule. The number attached as prefix to the 'C' refers to the length of the alcohol chain which is attached to the carboxylic group during the esterification reaction. Thus (3-C18:0) refers to the ester propyl stearate, which was formed using propanol. It has 18 carbons in the ester chain, 3 carbons forming the propyl chain, with no double-bonded carbons in the hydrocarbon tail.

B. Aliphatic Tailed Esters – Alkenes Interactions

Table 1 and Fig 1 show infinite dilution activity coefficients for C₃ to C₁₅ 1-alkenes (1=C_N) in various aliphatic hydrocarbon-tailed methyl esters.

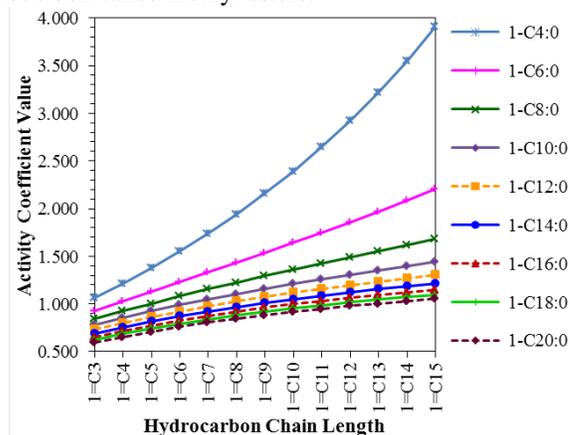


Fig. 1 Activity coefficients for straight-chain alkene solutes in various aliphatic-tailed ester solvents

TABLE I
INTERACTIONS BETWEEN ESTER SOLVENTS WITH SATURATED HYDROCARBON TAILS AND STRAIGHT CHAIN ALKENE SOLUTES

Ester Solvent	Designation	Activity Coefficients - Straight Chain Solute/ Ester Interactions												
		I=C3	I=C4	I=C5	I=C6	I=C7	I=C8	I=C9	I=C10	I=C11	I=C12	I=C13	I=C14	I=C15
M. Butyrate	1-C4:0	1.063	1.216	1.379	1.554	1.741	1.941	2.158	2.392	2.646	2.922	3.222	3.549	3.906
M. Caproate	1-C6:0	0.925	1.028	1.130	1.231	1.332	1.434	1.537	1.642	1.748	1.858	1.970	2.085	2.205
M. Octanoate	1-C8:0	0.841	0.925	1.005	1.081	1.154	1.225	1.293	1.360	1.426	1.491	1.555	1.619	1.683
M. Decanoate	1-C10:0	0.780	0.854	0.924	0.989	1.049	1.107	1.161	1.212	1.262	1.309	1.355	1.399	1.442
M. Laurate	1-C12:0	0.732	0.800	0.864	0.923	0.977	1.027	1.074	1.118	1.159	1.198	1.236	1.271	1.305
M. Myristate	1-C14:0	0.691	0.756	0.816	0.871	0.921	0.967	1.010	1.050	1.087	1.122	1.154	1.185	1.214
M. Palmitate	1-C16:0	0.656	0.718	0.776	0.828	0.876	0.920	0.960	0.997	1.032	1.064	1.094	1.122	1.148
M. Stearate	1-C18:0	0.625	0.685	0.741	0.791	0.837	0.879	0.918	0.954	0.987	1.017	1.046	1.072	1.097
M. Arachidate	1-C20:0	0.598	0.656	0.710	0.759	0.804	0.845	0.882	0.917	0.949	0.978	1.006	1.031	1.055

TABLE II
INTERACTIONS BETWEEN ESTER SOLVENTS WITH UNSATURATED HYDROCARBON TAILS AND STRAIGHT CHAIN ALKENE SOLUTES

Ester Solvent	Designation	Activity Coefficients - Straight Chain Solute/ Ester Interactions												
		I=C3	I=C4	I=C5	I=C6	I=C7	I=C8	I=C9	I=C10	I=C11	I=C12	I=C13	I=C14	I=C15
M. Stearate	1-C18:0	0.625	0.685	0.741	0.791	0.837	0.879	0.918	0.954	0.987	1.017	1.046	1.072	1.097
M. Oleate	1-C18:1	0.644	0.708	0.767	0.822	0.873	0.919	0.963	1.003	1.041	1.076	1.110	1.141	1.171
M. Linoleate	1-C18:2	0.666	0.736	0.801	0.862	0.918	0.971	1.021	1.068	1.113	1.156	1.196	1.235	1.272
M. Linolenate	1-C18:3	0.694	0.770	0.842	0.910	0.975	1.037	1.095	1.152	1.206	1.258	1.309	1.358	1.406

The results show a similar pattern to that of alkane-ester interactions [2] of increasing activity coefficients with increase in hydrocarbon chain length. The increase in activity coefficients is more marked for smaller ester/ alkane interactions compared to the gradual one for longer-chained esters. This can be attributed to the lower net van der Waals dispersion force experienced between the smaller solvent and the relatively larger solute molecules. We previously reported work [2] that the increase in activity coefficients with an increase in carbon chain length was mainly due to a combination of solvent and solute sizes. Alkene/ methyl arachidate interactions resulted in the most favourable phase equilibrium (lowest activity coefficients) as the solvent was the largest saturated ester studied in this work. As the length of the non-polar solvent hydrocarbon chain increases, the number of electrons in the overall molecule increases. This increases the strength of the van der Waals dispersion forces of the solvent molecule. A small non-polar solute molecule will have weak dispersion forces, thus its small electron cloud can easily be distorted by that of the solvent inducing a temporary dipole moment. This in turn results in the low activity coefficients for such interactions and hence the solute can easily be absorbed. The inverse is also true when the solute chain length is increased per solvent molecule size as this increases the energy required to break existing intermolecular solute bonds before intermolecular bonding with the solvent can take place. This is due to the increase in solute van der Waals forces with increase in solute size resulting in higher activity coefficients.

C. Olefinic Tailed Ester – Alkenes Interactions

Fig. 2 shows the solubility of C₃ to C₁₅ 1-alkenes in 1-C18:1 (methyl oleate), 1-C18:2 (methyl linoleate) and 1-C18:3 (methyl linolenate) unsaturated methyl esters. The phase equilibrium indicate that alkene - methyl stearate (1-C18:0) interactions gave the best solubility (absorption) scenario.

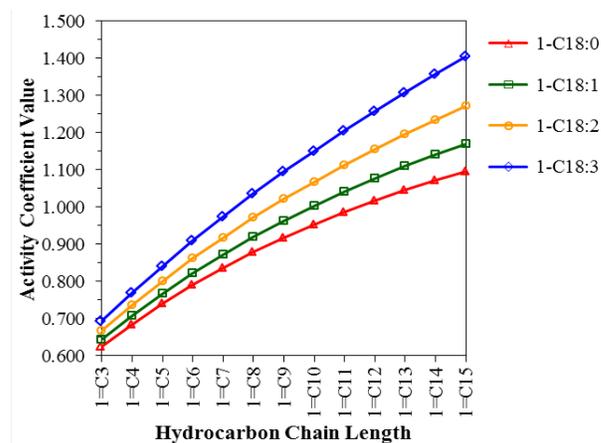


Fig. 2 Activity coefficients for straight-chain alkene solutes in various olefinic-tailed ester solvents

An increase in the number of unsaturated bonds in the solvent molecule resulted in decrease in solubility Fig. 2. This trend can possibly be explained by the differences in shape of the solvent molecules. For saturated esters, the amount of van

der Waals dispersion force presented to the solute molecule is at a maximum. However as *cis*- or *trans*-bonds appear in the hydrocarbon tail, the solvent molecule develops 'kinks'. The kinks cause the remaining part of the solvent tail to be directed further away from the solute, hence resulting in a diminished dispersion force being exerted by that portion of the tail on the neighboring solvent or solute molecule. In the case of solvents studied here, Fig. 2, only *cis*-bonding occurs. The kinking effect is increased with increase in ester solvent *cis*-bonds. The solvent becomes hook-shaped while solvent molecules become more loosely packed.

D. Effects of Alcohol Feedstock in Ester Preparation

The interactions of alkenes with esters formed from C₁-, C₂-, C₃- and C₄-alcohols is shown in Fig. 3. Infinite dilution activity coefficients decrease with increase in alcohol-bonded chain length. Thus butyl esters were predicted to have the best absorption performance compared to absorbents prepared from lower alcohols. Propyl stearate (3-C18:0) with 21 carbons yielded identical activity coefficients as methyl arachidate which also has 21 carbons. Thus the improved performance is purely a function of the increase in solvent chain length as a result of increased van der Waals dispersion forces.

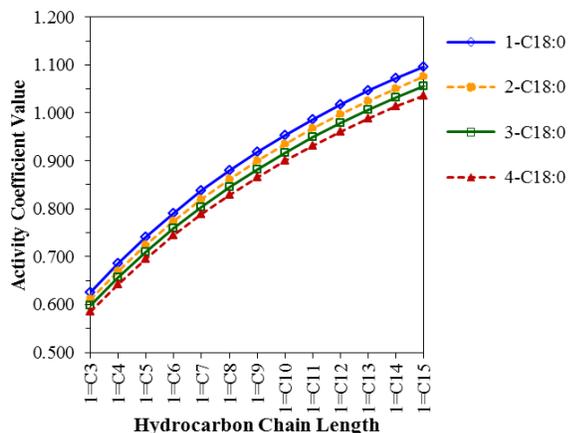


Fig. 3 Activity coefficients for straight-chain alkene solutes in C18 ester solvents produced from different alcohols

E. Comparison between Ester/Alkane and Ester/Alkene Interactions

A comparative study of ester/straight-chain alkane and ester/ straight-chain alkene interactions is presented in Fig.4.

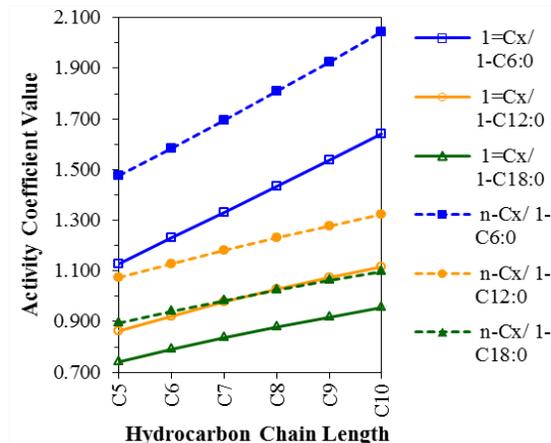


Fig. 4 Activity coefficients of straight-chain alkenes and alkanes in selected aliphatic-tailed ester solvents

The results for the comparison between ester/cyclic alkane and ester/ cyclic mono-alkene interactions for C5 to C10 solutes are shown in Table III and Fig.5.

TABLE III
COMPARISON BETWEEN ESTER/ CYCLIC MONO-ALKENE AND ESTER/ CYCLIC ALKANE INTERACTIONS

		Activity Coefficients - Ester/ Cyclic Solute Interactions ^a					
Ester Solvent	Designation	cy1=C5	cy1=C6	cy1=C7	cy1=C8	cy1=C9	cy1=C10
		M. Caproate	1-C6:0	1.270	1.368	1.458	1.542
M. Laurate	1-C12:0	0.849	0.913	0.968	1.018	1.062	1.102
M. Stearate	1-C18:0	0.689	0.747	0.798	0.844	0.886	0.924
		cy-C5	cy-C6	cy-C7	cy-C8	cy-C9	cy-C10
M. Caproate	1-C6:0	1.482	1.627	1.758	1.879	1.991	2.096
M. Laurate	1-C12:0	1.000	1.094	1.177	1.249	1.314	1.371
M. Stearate	1-C18:0	0.809	0.893	0.967	1.033	1.092	1.146

^aAlkane data (cy-C_x) obtained from [14]

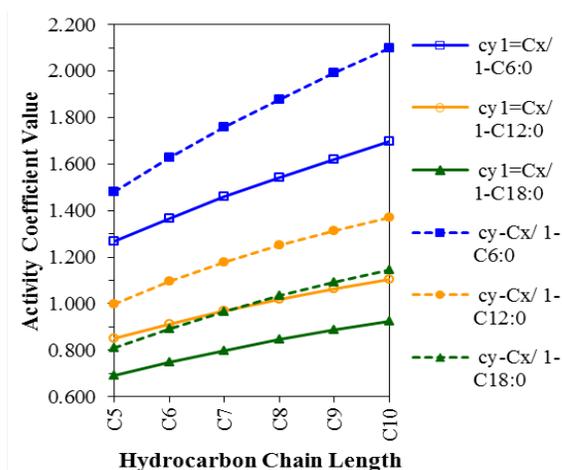


Fig. 5 Activity coefficients of cyclic mono-alkenes and cycloalkanes in selected aliphatic-tailed ester solvents

It is clear from both sets of data that alkenes (1=C_x and cy1=C_x) yielded much lower activity coefficients than their

respective alkanes (n-C_x and cy-C_x). The difference becomes less marked with an increase in ester chain length. The same explanation can be used for the solute-solvent interaction as for the solvent-solute interaction, namely that the presence of a double-bond in the solute causes a kink in the solute molecule. This kink results in part of the solute molecule being positioned further away from the solvent molecule which leads to diminished van der Waals dispersion forces being exerted by that portion of the solute on the solvent molecule. There is therefore a greater net difference in dispersion forces between the solvent and solute molecules resulting in a greater electron cloud distortion of the solute molecule which in turn results in increased forces of attraction. Alkenes are therefore more easily attracted to the ester solvent than their respective alkane counterparts, hence the lower activity coefficients.

III. CONCLUSION

This work investigated and discussed the interactions of 15 methyl esters of various chain lengths with alkene VOCs. The solubility of C₃ to C₁₅ 1 – alkenes in aliphatic and olefinic hydrocarbon – tailed methyl esters was studied. Ester chain length and saturation was found to influence the phase equilibrium. Straight chain alkenes and cyclic mono alkenes yielded lower infinite dilution activity coefficients compared to their respective alkane counter parts. Absorption was also found to increase with increase in alcohol-bonded chain length.

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Impacts of Native and Exotic *Prosopis* Species on Native Plants in Aridlands of the UAE

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Abstract—Two *Prosopis* congeners are present in the eastern coast of the United Arab Emirates (UAE): *P. cineraria* is native, but *P. juliflora* is exotic invasive. The impacts of the two species on the associated native plants were assessed. In each of twenty plots, density of the associated species was assessed in nine quadrats distributed beneath, at the margin and outside the canopy of a *Prosopis* individual. The results indicated a significant depressive effect for *P. juliflora* canopy, but significant positive effects for *P. cineraria* canopy on many of the associated plants. The depressive effect of *P. juliflora* was more obvious on the annual compared with perennial plants, especially grasses. The results indicated that both *Prosopis* species have facilitative effects in relation to the available nutrients, but the allelopathic effects of the litters of *P. juliflora* may override its potential positive effects on soil fertility.

Keywords— community structure, desert habitats, invasive plants, native plants, species diversity.

I. INTRODUCTION

Desert trees play a vital role in enhancing the biodiversity in many desert ecosystems of the arid regions. They are considered as keystone species as they support the life of many other faunal and floral species [1]. Desert trees could influence their understory vegetation in many ways, resulting in a broad range of detrimental or beneficial outcomes. Their beneficial effects on the environment beneath their canopies include the reduction in the extremes of environmental temperatures [2-3], provision of suitable amounts of photosynthetically active radiation to understory plants [4], improved soil texture and nutrient content [5-8], increased soil moisture [9] and protection against herbivory [10-12]. Conversely, desert trees can also have negative effects on seedling survival and establishment in their understory community. The negative impacts of the trees could be through light deprivation, competition for water and nutrients, or leaching of allelopathic compounds [5- 7, 13, 14]. Detrimental and beneficial mechanisms do not act in isolation from each other in nature. The relative importance of these two processes in a particular plant community determines the structure of that community [15].

Prosopis juliflora and *P. cineraria* are among few trees growing in the arid deserts of the UAE and currently growing

together in the same habitats. They constitute a major ecological feature in the Northern Emirates of the UAE. *Prosopis cineraria* is a slow growing tree native to the dry and arid regions of Arabia and India and is beneficial for the growth and development of other species [16]. It is rarely, if ever, seen as weedy species and has not successfully been introduced into other parts of the world [17]. *P. juliflora*, however, is an exotic species from Central and South America and grows luxuriantly on sandy soils with high groundwater table in the UAE. It has been introduced on a large scale in the artificial forests of the UAE because of its faster growth and soil-binding capacity. Recently, it has escaped plantations and come to dominate many plant communities, and is considered a weed. It is highly aggressive and coppices so well that it crowds out native vegetation [18, 19]. The aim of the present study was to assess the impacts of two *Prosopis* species: the exotic invasive *P. juliflora* and the native *P. cineraria* on understory vegetation in the Eastern deserts of the UAE.

II. MATERIALS AND METHODS

A. Study area

A study site was selected in Fujairah at the eastern coast of the UAE to have a reasonable degree of physiognomic homogeneity and with homogenous distribution and densities of both *P. juliflora* and *P. cineraria*. The studied individuals of the two species were selected to cover the medium and large sizes. In some communities of *P. cineraria* that were invaded by *P. juliflora*, the invader was found to negatively affect the growth and vigor of the native *P. cineraria*. These places were excluded from the study.

B. Impacts on associated flora

A total of 20 stands were located randomly around the two *Prosopis* species (10 stands for each). A *Prosopis* tree (*P. juliflora* or *P. cineraria*) was localized near the center of each stand to serve as a focal point. The area of each stand was 225 m² (15 x 15 m). In each stand, nine 1 m² quadrats were distributed on three transects; 3 quadrats beneath; 3 at the margin; and 3 beyond the canopy of the studied *Prosopis*. A species list was compiled in each stand. The absolute density (number of plants of a certain species rooted within 100 m²) was estimated for each associated plant species. Certain other community attributes were also estimated, including species number, species richness (average number of species per stand), and species evenness (estimated by Shannon-Weaver index).

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