

Diisononyl phthalate – Organics Interactions: A Phase Equilibrium Study Using Modified UNIFAC Models

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Abstract—Volatile organic compounds (VOCs) are a series of organic compounds that readily vaporize at room temperature. When emitted into the environment can affect climate change and plants growth, and cause long term human health risks. Absorption abatement technique has been the most preferred to reduce VOCs from contaminated gaseous streams, hence the need for a polymeric solvent with a greater affinity for end-pipe inventory. This phase equilibrium study investigated the ability of diisononyl phthalate (DINP) as an absorbent to 80 selected VOCs at infinite dilution. The solvent-solute(s) interactions were studied using modified UNIFAC Lyngby and Dortmund group contribution methods, with the latter being consistent and reliable, as its results are related to literature. Alkanes, alkanes, aldehydes and cyclo-alkanes with shorter carbon-chain length are highly soluble in DINP, with their solubility decreasing with increasing molecular weight or size, at infinite dilution. Alkynes, ketones, alcohols and carboxylic acids are less soluble in DINP, as a result of their dominating polarity compared to the DINP non-polarity structure. However, results could be improved with further studies and publication of solvent-solute(s) sub-groups interaction parameters, and thus further development of modified UNIFAC Lyngby model. DINP is a good absorbent for short-chained non-polar VOCs.

Keywords—Abatement, absorbent, interactions, phase equilibrium, solubility.

I. INTRODUCTION

THIS study was aimed at studying thermodynamic interactions of 80 volatile organic compounds and diisononyl phthalate (DINP). The activity coefficients of the (VOCs) in (DINP) solvent were computed using both the modified UNIFAC models, Dortmund [1] and Lyngby [2]. The computations were conducted at constant pressure and

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temperature, with the solubility of solutes defined by the activity coefficients behaviour at infinite dilution. Solubility is the property of a solute to dissolve in a liquid solvent to form a homogeneous solution of the solute and solvent. It is defined as the maximum amount of the solute that will dissolve in a given amount of a particular solvent at given conditions. Solubility is influenced by a number of factors such as temperature, pressure, concentration and the nature of the solute and the solvent. Solute mole fractions, concentrations, were varied from infinite dilution to pure component environment, thus the variation of solubility of VOCs in DINP was governed by the nature of solute and solvent interactions. The solubility of the solutes in the solvent are influenced by the intermolecular forces between the organics and the solvent. The three intermolecular forces that affect solubility are dipole-dipole, hydrogen bonding and London dispersion forces. DINP has two ester components on a single aromatic structure, with the other ends of the esters with long, similar alkanes chains; general formula of an ester is RCOOR' . The C-O bond makes the functional group polar provided the hydrocarbon portions, R and R', are shorter chains, though since the esters are joined to long hydrocarbons portions, London dispersion forces are dominant intermolecular force making the overall DINP molecule non-polar.

II. SOLUBILITY OF ALKANES IN DINP

The solubility, in terms of activity coefficients of alkanes are shown in Fig. 1. Modified UNIFAC models were used with parameters extrapolated from the Dortmund Data Bank (DDB).

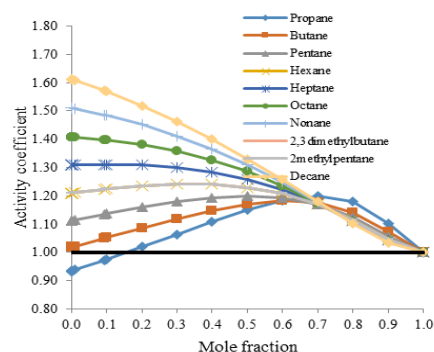


Fig. 1: Variations of activity coefficients with mole fractions of Alkanes in DINP using Dortmund model

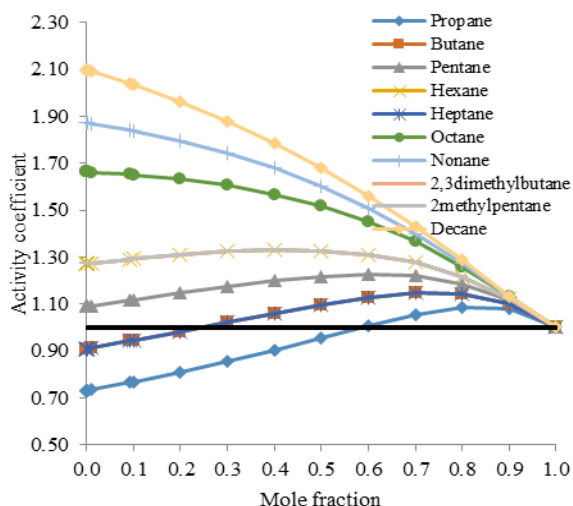


Fig. 2 Variations of activity coefficients with mole fractions of Alkanes in DINP using Lyngby model

Figs. 1 and 2 show the variation of activity coefficients with mole fraction of alkanes in DINP using modified UNIFAC Dortmund and modified UNIFAC Lyngby models respectively. The activity coefficients at infinite dilution increase with an increasing alkane chain length (or molecular weight). Alkanes are non-polar, and the longer the chain the greater the non-polarity. At lower molecular weight (or shorter chain) the London dispersion forces dominate allowing the solute and solvent to interact, thus dissolving the solute. The hydrocarbon portions on the esters molecule of DINP interact more with the shorter alkane solutes. The intermolecular attractive forces between the alkanes-DINP molecules are very strong. In these solutions the organic compounds cannot easily escape from the liquid phase into the gas phase where the intermolecular forces between the alkanes-alkanes molecules are weaker. The strong intermolecular forces are a result of the non-polar ends being attracted to non-polar alkanes and less repulsion between C=O of the ester molecule and the shorter chained alkanes, C-H bonds. The Dortmund model has a broader database than Lyngby, Dortmund parameters were used for both models. As the alkane chain length increases, the surface area of the molecule increases thereby increasing the van der Waals forces. Activity coefficients at infinite dilution increases, indicating a decrease in solubility, as the required bond breaking energy is increased in longer or heavier alkanes. The intermolecular forces become weaker and weaker resulting in slight repulsion of the molecules, hence higher infinite dilution activity coefficients of alkanes for longer chains. The affinity of the solute for the absorbent solvent is decreased as a slight rise in van der Waals force is experienced with heavier alkanes. Due to longer hydrocarbons portions on the ends of the esters, DINP is slightly non-polar and should be able to absorb shorter chained alkanes.

III. SOLUBILITY OF ALKANES IN DINP

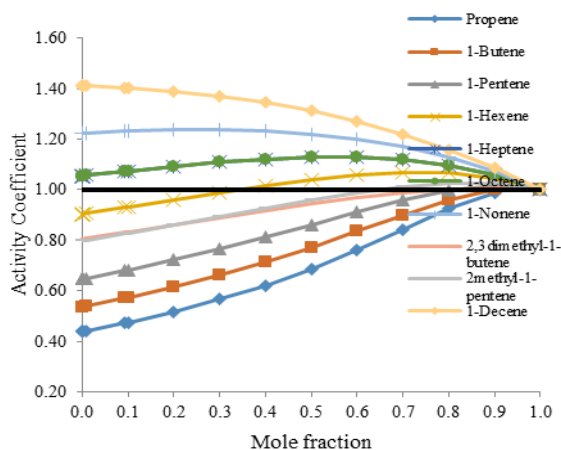


Fig. 3 Variations of activity coefficients with mole fractions of Alkenes in DINP using Dortmund model

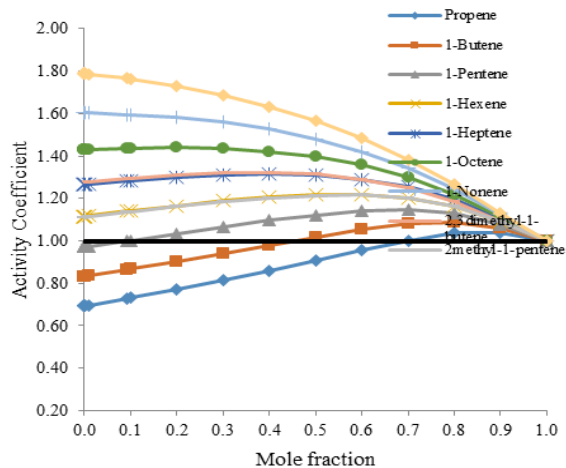


Fig. 4 Variations of activity coefficients with mole fractions of Alkenes in DINP using Lyngby model

Figs. 3 and 4 show the variation of activity coefficient with mole fraction of alkenes in DINP using modified UNIFAC Dortmund and modified UNIFAC Lyngby models respectively. Alkenes are non-polar, due to lower electronegativity difference between their intramolecular bonds; C=C and C-H. At lower molecular weights (<C7 for Dortmund and <C6 for Lyngby), infinite dilution activity coefficients are below 1. The strong intermolecular forces exist between alkenes-DINP due to the hydrocarbon portions on DINP interacting with low molecular weight (short chained) alkenes. DINP is a good absorbent for low molecular weight alkenes. Non-polar alkenes dissolve in non-polar solvent (DINP). As the alkenes molecular weight increases, the activity coefficients at infinite dilution also increases, thus decreasing solubility of alkenes in DINP. The increase in molecular weight (lengthened chains) increases the surface area, thus the van der Waals forces being larger, therefore, more energy is required to break bonds of larger alkenes

making then insoluble in DINP. Weak alkenes-DINP interactions are experienced with longer alkene chains.

IV. SOLUBILITY OF ALKYNES IN DINP

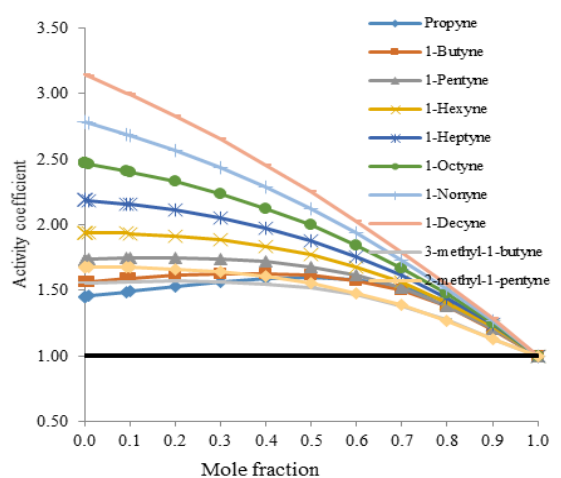


Fig. 4 Variations of activity coefficients with mole fractions of Alkynes in DINP using Dortmund model

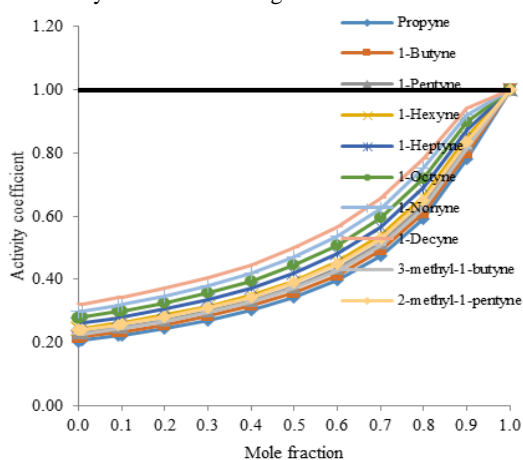


Fig. 5 Variations of activity coefficients with mole fractions of Alkynes in DINP using Lyngby model

Figs. 5 and 6 show the variation of activity coefficients with mole fraction of alkynes in DINP using modified UNIFAC Dortmund and modified UNIFAC Lyngby models respectively. Alkynes are more non-polar than alkanes and alkenes due to $C\equiv C$ bond in their structure. Alkynes are expected to be highly soluble in DINP than alkanes and alkenes. The solubility decreases with increasing carbon chain lengths due to increased surface area resulting in higher van der Waals forces weakening the alkynes-DINP interactions. The results in Fig. 5 are less reliable due to the unavailability of temperature dependence parameters between the alkyne ($C\equiv C$) and aromatic-ester (AC-CCO) functional groups parameters from the DDB. Therefore, solubility of alkynes in DINP in this paper requires further revision.

V. SOLUBILITY OF ALCOHOLS IN DINP

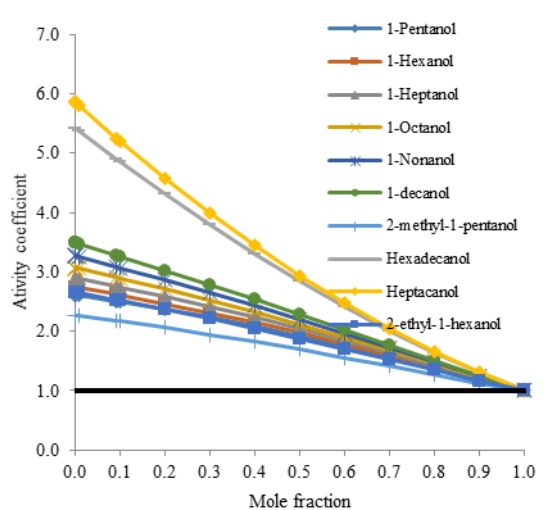


Fig. 6 Variations of activity coefficients with mole fractions of Alcohols in DINP using Dortmund model

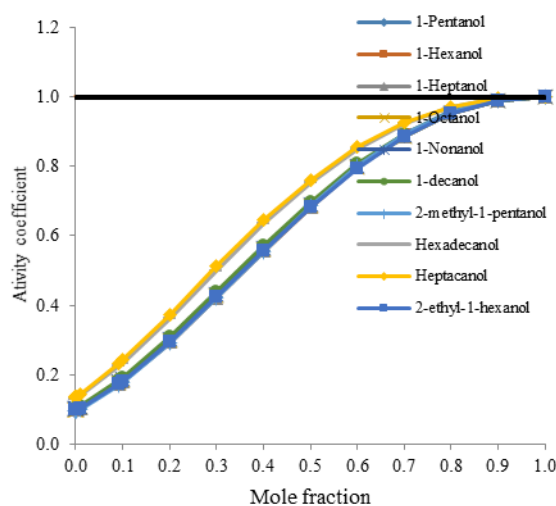


Fig. 7 Variations of activity coefficients with mole fractions of Alcohols in DINP using Lyngby model

The non-polar ends of the DINP are not strong enough to break the C-O bond and the hydrogen bond of the alcohols, hence higher activity coefficients at infinite dilution. The greater the number of carbons in an alcohol molecule the higher the activity coefficients at infinite dilution, as the surface area increases so does the van der Waals forces making it even more difficult to dissolve alcohol molecules in DINP. As alcohol molecules interact, hydrogen bonding also occur between O and H, increasing the energy required to break the alcohol bonds, thus hindering the affinity of alcohols in non-polar solvents.

The Lyngby model suggests that at infinite dilution alcohols are highly soluble in DINP, as indicated by the low activity coefficients. This could be attributed to the lack of interaction

parameters for the Lyngby procedure.

DDB.

VI. SOLUBILITY OF ALDEHYDES IN DINP

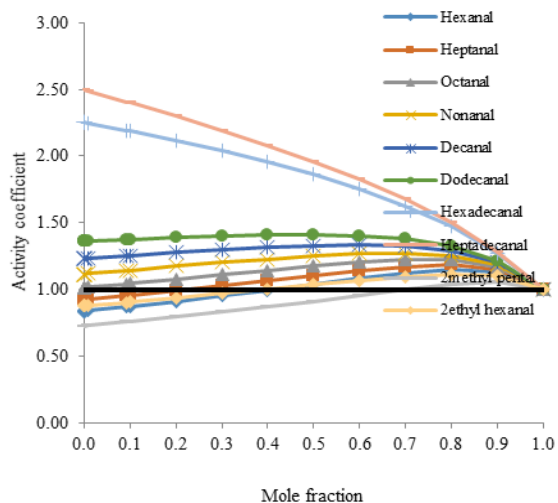


Fig. 8 Variations of activity coefficients with mole fractions of Aldehydes in DINP using Dortmund model

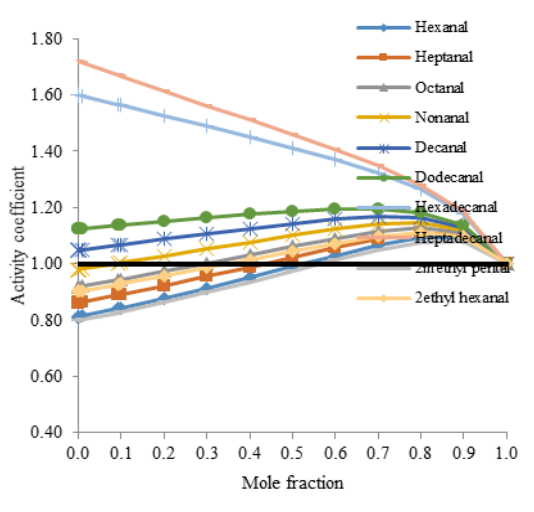


Fig. 10 Variations of activity coefficients with mole fractions of Aldehydes in DINP using Lyngby model

The aldehydes molecules are polar, C=O, due the electronegativity difference between carbonyl and oxygen atoms. Polarity of aldehydes decreases with increasing chain length of the aldehydes, thereby becoming non-polar due the additions of hydrocarbons. As the chain length is increased surface area increases and it requires a non-polar group to strongly interact with an aldehyde. Larger aldehydes structures, unlike short chained (<C5), interact strongly with alkanes molecules due to similar non polarity. Longer chained aldehydes develops a non-polar end far away from the polar head (C=O) which contributes to the aldehydes being slightly non-polar, and being soluble in DINP solvent (or have low activity coefficients) at infinite dilution. The results are affected by the lack of temperature-dependent interaction parameters between CH₃CO-ACCOO molecules from the

VII. SOLUBILITY OF KETONES IN DINP

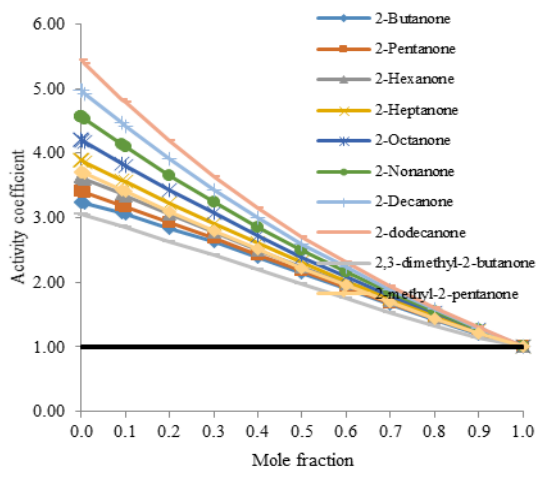


Fig. 9 Variations of activity coefficients with mole fractions of Ketones in DINP using Dortmund model

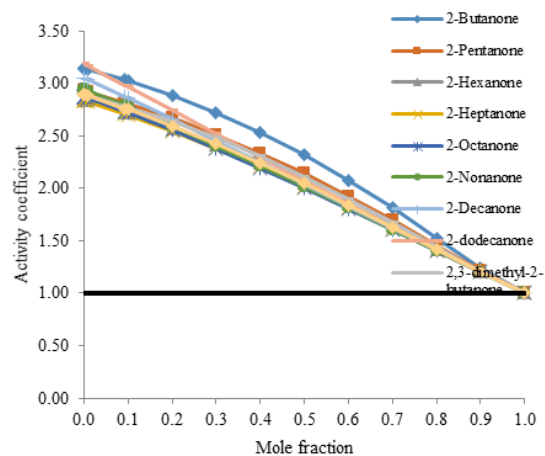


Fig. 10 Variations of activity coefficients with mole fractions of Ketones in DINP using Lyngby model

Ketones have permanent dipole moments due to the carbonyl group which is highly polarized. Ketones are slightly soluble in non-polar solvents. As the molecular weight (or chain length) increases the non-polar end is expected to dominate the polarity and the longer or heavier ketones become soluble in non-polar solvents (DINP for instances). The temperature dependent interaction parameters between ketone (CH₃CO) and aromatic-ester (AC-COO) are not available in the DDB.

VIII. SOLUBILITY OF CARBOXYLIC ACIDS IN DINP

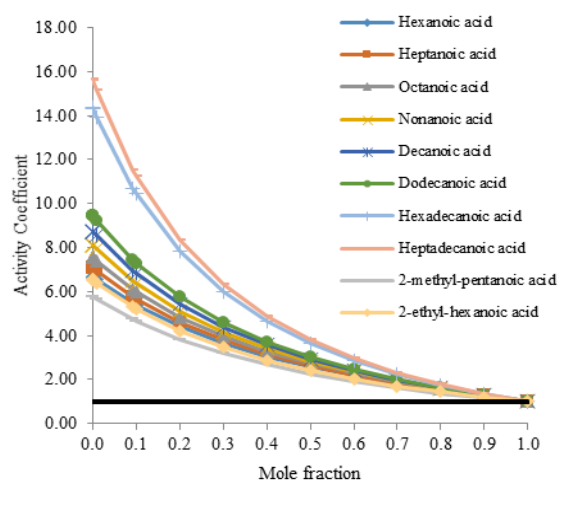


Fig. 11 Variations of activity coefficients with mole fractions of Carboxylic acids in DINP using Dortmund model

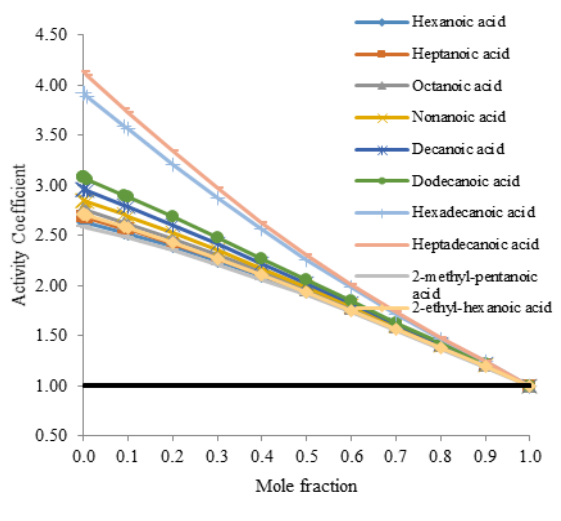


Fig. 12 Variations of activity coefficients with mole fractions of Carboxylic acids in DINP using Lyngby model

The Lyngby model gave slightly lower activity coefficients for VOCs in DINP at infinite dilution as compared to UNIFAC Dortmund procedure. Carboxylic acids are polar, O-H, and repel against the non-polar ends on the DINP, resulting in weak interactions between the molecules. Polar part of DINP is locked, or weakened, by the long hydrocarbon chains on the ester components, hence high infinite dilution activity coefficients. Generally, carboxylic acids are large molecules, hence weaker interactions with DINP due to increased bond energy of the carboxylic acids as a result of their heavier structures, higher van der Waals forces. For carboxylic acids, solubility decreases with increasing chain length. The acidic part of the group does not isolate itself with its polarity but rather shield the entire structure when in solution with DINP. The huge van der Waals forces of the carboxylic acids in DINP make them slightly soluble in DINP.

IX. SOLUBILITY OF CYCLOALKANES IN DINP

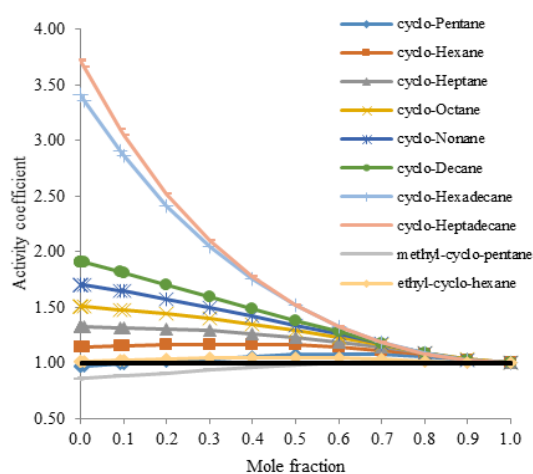


Fig. 13 Variations of activity coefficients with mole fractions of cyclo-Alkanes in DINP using Dortmund model

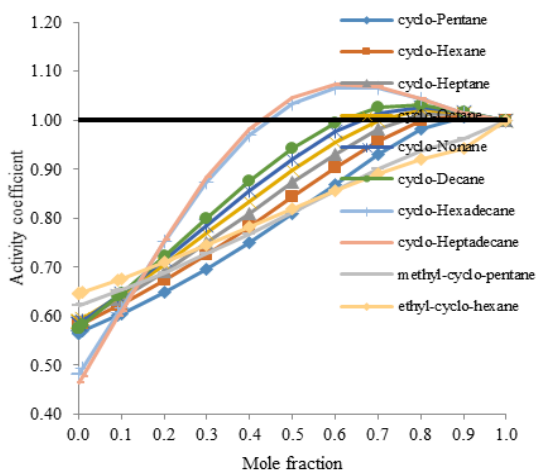


Fig. 14 Variations of activity coefficients with mole fractions of cyclo-Alkanes in DINP using Lyngby model

Cyclo-alkanes are non-polar due to the C-C and C-H bonds, thus relatively lower activity coefficients as the intermolecular forces are stronger between cyclo-alkanes and DINP. DINP has non-polar ends which are expected to dissolve the non-polar cyclo-alkanes. As the carbon length increases the solubility decreases as a result of increased surface area requiring more energy to break the bonds.

X. CONCLUSION

The Modified UNIFAC Dortmund model is more consistent and reliable than the Lyngby. Diisononyl phthalate has high affinity for low molecular weight and non-polar organics. Measurements are required to improve the quality of

modified UNIFAC Lyngby model and broaden its parameter database.

ACKNOWLEDGMENT

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