

# Volatile Organic Compounds –Polymeric Solvents Interactions – A Thermodynamic Computational Attempt

Edison Muzenda

**Abstract**—This work attempted to model the phase equilibrium involving 50 volatile organic compounds (VOCs) with furfural and normal methyl pyrrolidone (NMP). Polar furfural and dipolar aprotic NMP were tested in this work as potential solvents for the abatement of selected VOCs through physical absorption. Five (5) VOC family groups were studied namely alkanes, alkenes, alcohols, aldehydes and carboxylic groups. The modified UNIFAC Dortmund and Lyngby were used in the phase equilibrium computation. NMP showed better absorption affinity for alkenes, alcohols and carboxylic acids compared to furfural. The solubility decreased with increase in size of the VOCs for both solvents.

**Keywords**—Computation, phase equilibrium, solubility, volatile organic compounds.

## I. INTRODUCTION

**V**OLATILE organic compounds (VOCs) are carbon based compounds of varying chain length, usually bonded with other elements such as hydrogen, oxygen, fluorine, chlorine, bromine, sulphur and nitrogen. They have boiling points in the range of 50-100°C, corresponding to having saturated vapour pressures greater than 102kPa at room temperature to significantly vaporise into the atmosphere and participate in photochemical reactions. However carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbide are not VOCs. VOCs are categorized as methane (CH<sub>4</sub>) and non-methane (NMVOCs). Methane is an extremely harmful greenhouse gas which contributes to global warming. Among the NMVOCs, the aromatic compounds such as benzene, toluene and xylene are considered to be carcinogenic. VOCs have detrimental effects on human health as they contribute to respiratory illnesses, and some are mutagenic or toxic to reproduction and harmful to the unborn [1]. They also have harmful environmental effects (crop, vegetation and materials damage, reduced visibility) when they chemically interact with oxides of nitrogen and sunlight to form ground-level ozone a component of smog. For this reason, governments around the world have implemented

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legislation to guide industry to responsibly deal with the challenges caused by VOCs.

Sources of VOCs include transportation, fuel combustion and domestic solvent usage and as well as commercial and industrial processes. Group contribution methods such as UNIFAC (UNIversal Functional Group Activity Coefficient) are very useful in the synthesis, feasibility studies, design and optimization of separation processes. They can be successfully used in the prediction of phase equilibrium and excess properties in the development of chemical and separation processes [2]. The UNIFAC Lyngby modified UNIFAC of Larsen et al (1987) [3] has been previously discussed [4]. The Modified UNIFAC Dortmund of Weidlich and Gmehling (1987) [5] and its computational procedure were previously discussed [6, 7], [8] – [13].

## II. RESULTS AND DISCUSSION

### A. Alkanes

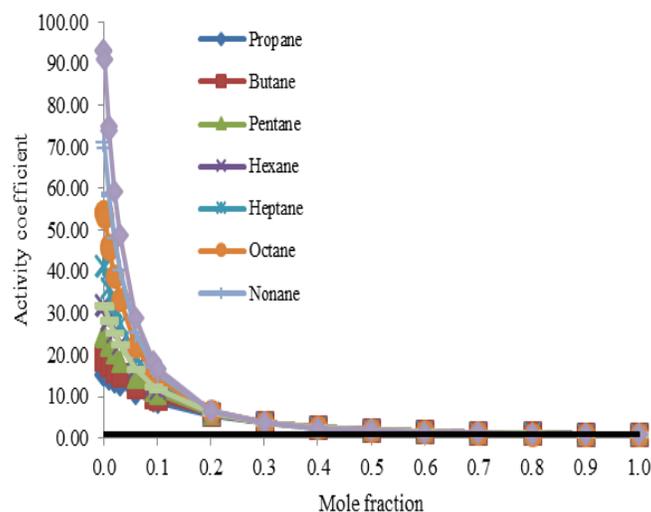


Fig. 1 Variations of activity coefficients with mole fraction of alkanes in Furfural (Modified UNIFAC Dortmund)

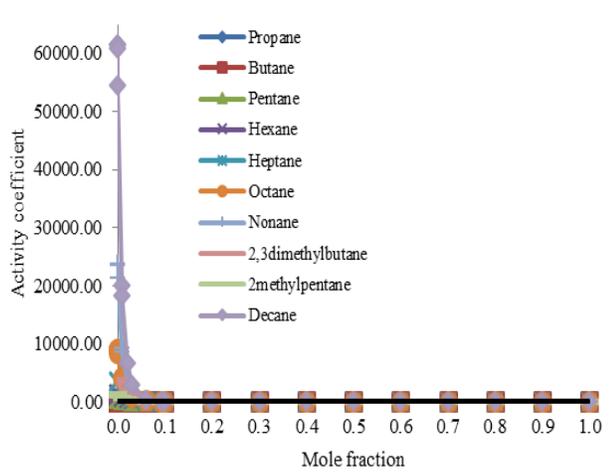


Fig. 2 Variation of activity coefficients with mole fractions of alkanes in furfural (modified UNIFAC Lyngby)

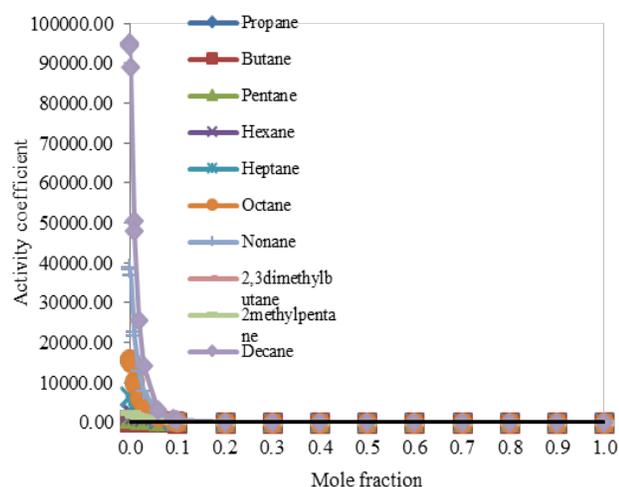


Fig. 3 Variation of activity coefficients with mole fraction of alkanes in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Dortmund)

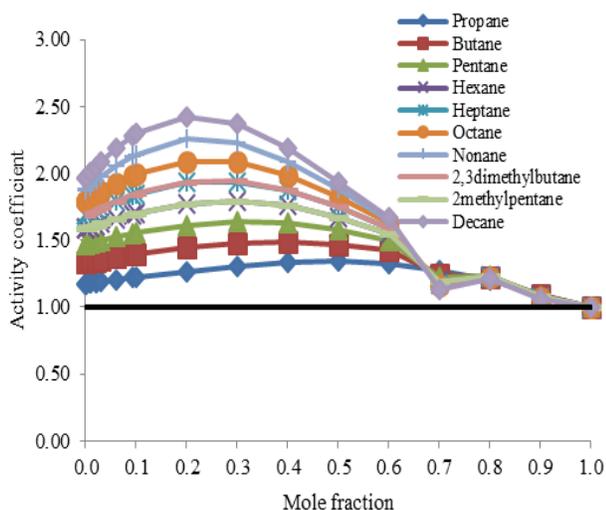


Fig. 4 Variation of activity coefficients with mole fraction of alkanes in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Lyngby)

Figs. 1 to 4 show the variation of activity coefficients with mole fraction of alkanes in furfural and NMP. The activity coefficients at infinite dilution of alkane VOCs increase with increasing molecular weight (chain length). Alkanes are nonpolar, intermolecular attraction among molecules are due to London dispersion (LD) forces from momentary dipoles due to fluctuating electron densities. The total effect of LD forces increase with increasing molecular size and hence the decrease in solubility with increase in VOC chain length.

*B. Alkenes*

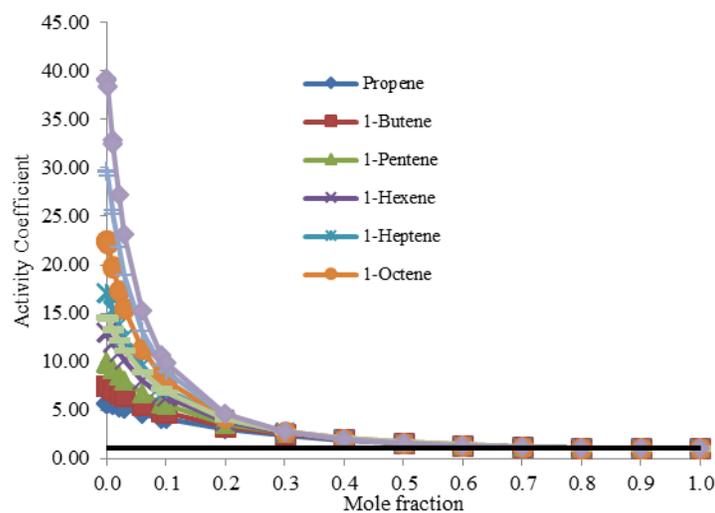


Fig. 5 Variation of activity coefficients with mole fraction of alkenes in furfural (Modified UNIFAC Dortmund)

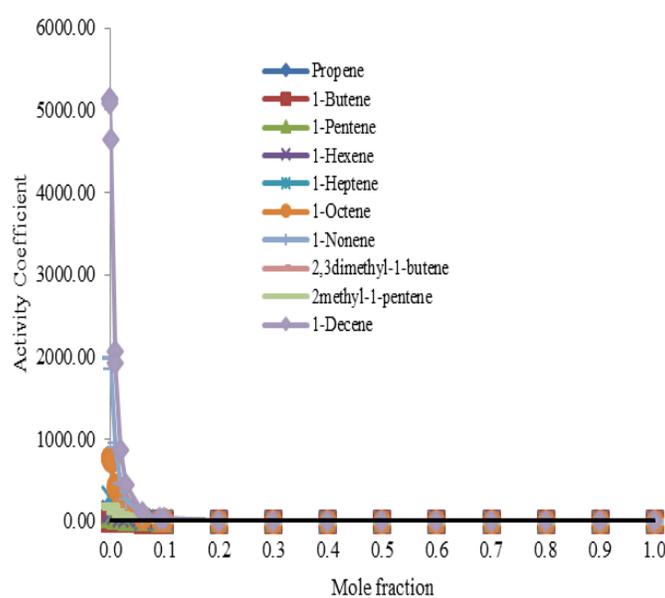


Fig. 6 Variations of activity coefficients with mole fraction of alkenes in furfural (Modified UNIFAC Lyngby)

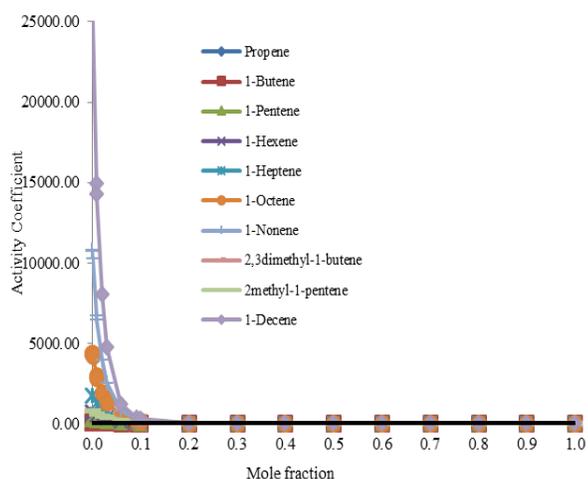


Fig. 7 Variation of activity coefficients with mole fraction of alkenes in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Dortmund)

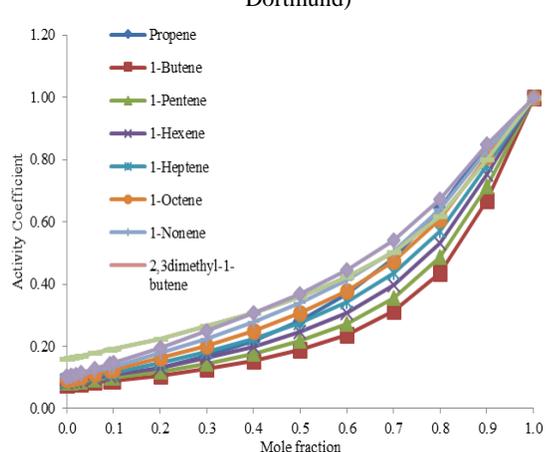


Fig. 8 Variation of activity coefficients with mole fraction of alkenes in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Lyngby)

Figs. 5 to 8 show the variation of activity coefficients with mole fraction of alkenes in furfural and NMP. The Lyngby predicts greater solubility for alkanes in Pyrrolidone, Fig 8. This requires further investigation.

### C. Alcohols

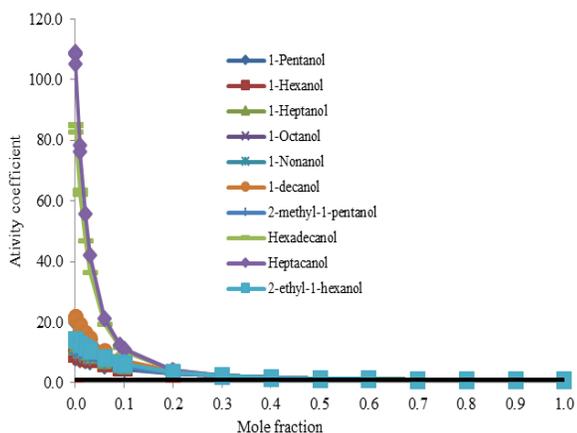


Fig. 9 Variation of activity coefficients with mole fraction of alcohols in furfural (Modified UNIFAC Dortmund)

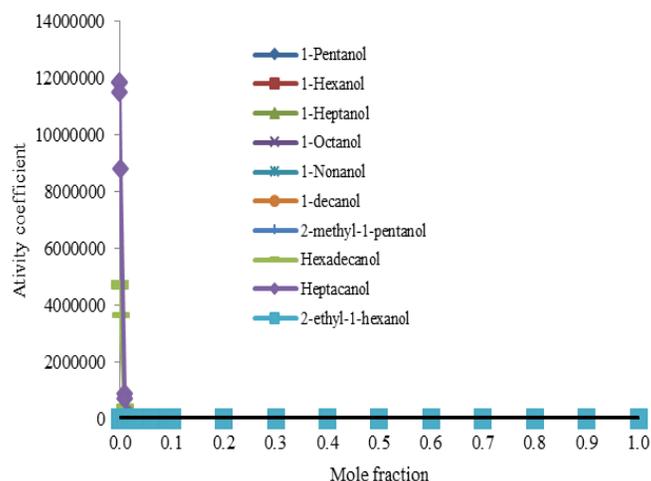


Fig. 10. Variation of activity coefficients with mole fraction of alcohols in furfural (Modified UNIFAC Lyngby)

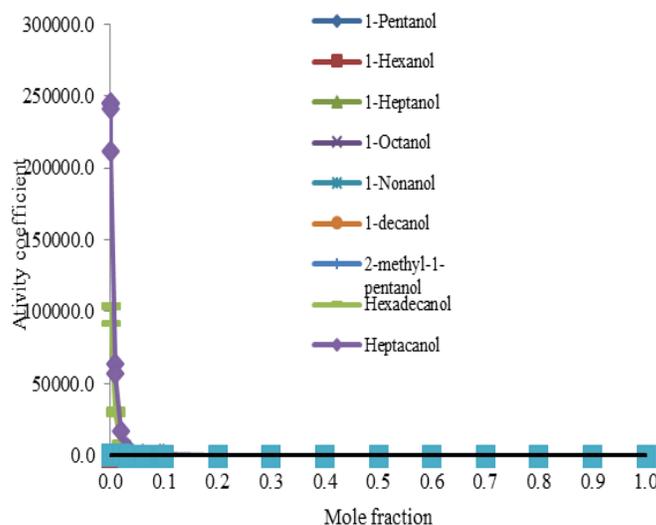


Fig. 11 Variation of activity coefficients with mole fraction of alcohols in N-Methyl Pyrrolidone (NMP) (Modified Dortmund model)

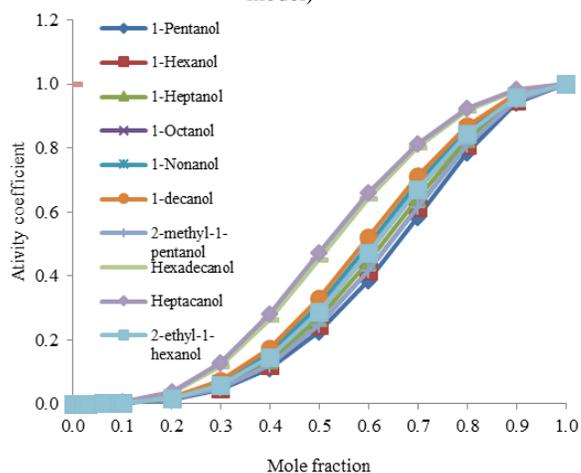


Fig. 12 Variation of activity coefficients with mole fraction of alcohols in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Lyngby model)

The interactions between alcohols with Furfural and NMP are shown in Figs 9 to 12. The Modified UNIFAC Lyngby and Dortmund tend to over predict the activity coefficients of alcohols in furfural and pyrrolidone. With the exception of the prediction in NMP using Modified UNIFAC Lyngby, all VOC gave almost similar phase equilibrium behaviour.

#### D. Aldehydes

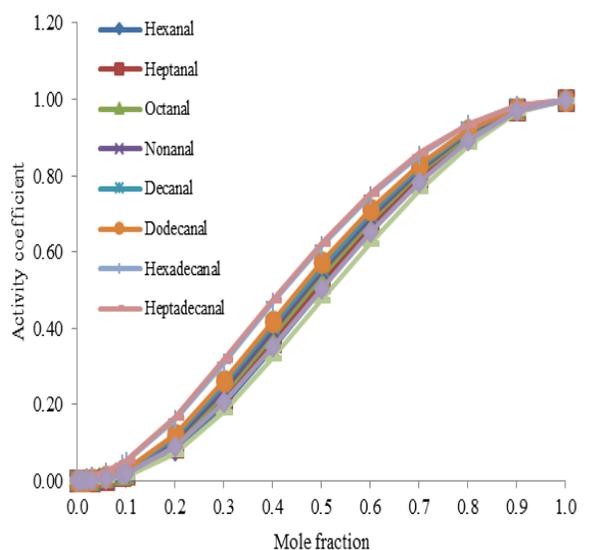


Fig. 13 Variation of activity coefficients with mole fraction of aldehydes in furfural (Modified UNIFAC Dortmund model)

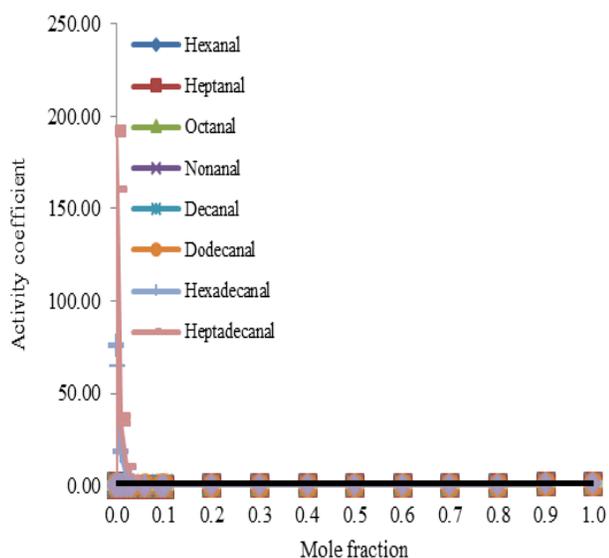


Fig. 14. Variation of activity coefficients with mole fraction of aldehydes in furfural (Modified UNIFAC Lyngby model)

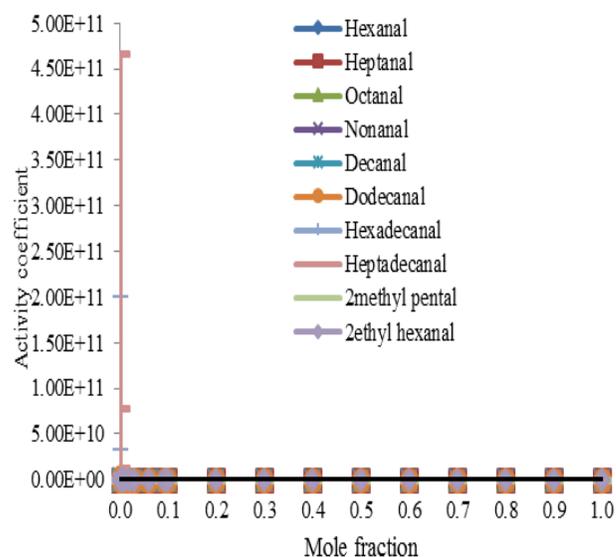


Fig. 15 Variation of activity coefficients with mole fraction of aldehydes in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Dortmund model)

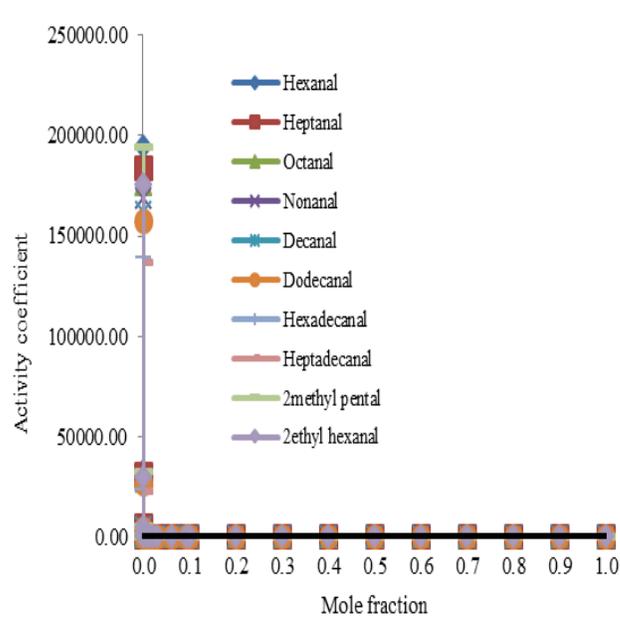


Fig. 16 Variation of activity coefficients with mole fraction of aldehydes in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Lyngby model)

The interactions of aldehydes with furfural and NMP are shown in Figs 13 to 16. Aldehydes are polar and the polarity decreases with increase in VOC chain length. This is due to the addition of the nonpolar alkyl groups. As furfural is an aromatic aldehyde, it is expected to have a high affinity for aldehyde VOC as 'like dissolves like', Fig 13.

## E. Carboxylic Acids

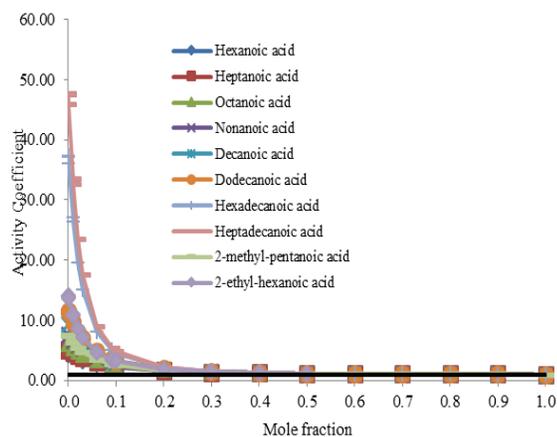


Fig. 17 Variation of activity coefficients with mole fraction of carboxylic acids in furfural (Modified UNIFAC Dortmund)

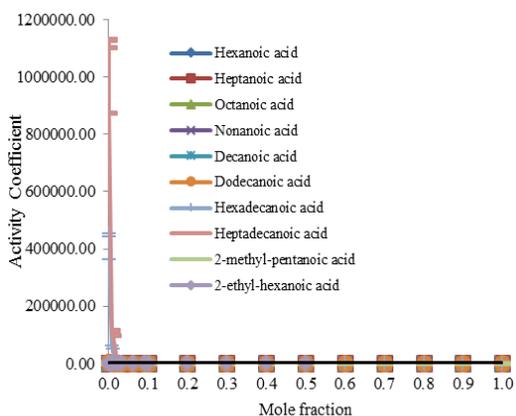


Fig. 18 Variation of activity coefficients with mole fraction of Carboxylic acids in furfura (Modified UNIFAC Lyngby)

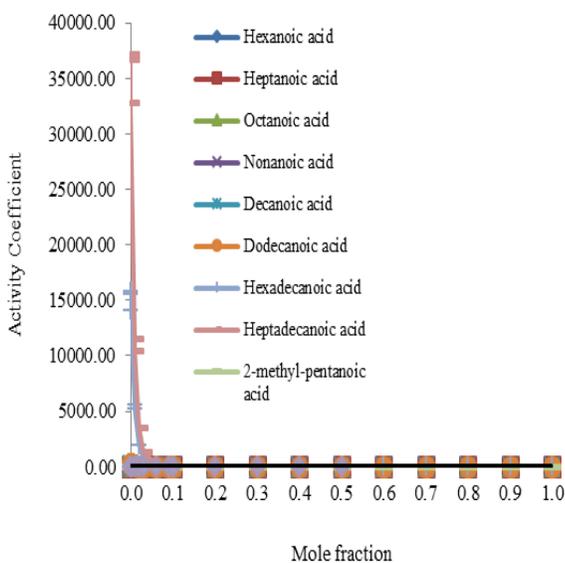


Fig. 19 Variation of activity coefficients with mole fraction of carboxylic acids in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Dortmund)

Figs. 17 to 20 show the variation of activity coefficient with mole fraction of carboxylic acids in furfural and NMP. Activity coefficients slightly increases with increase VOC chain length due to the increase in van der Waals forces of attraction, thus more energy is required to break the bonds between molecules

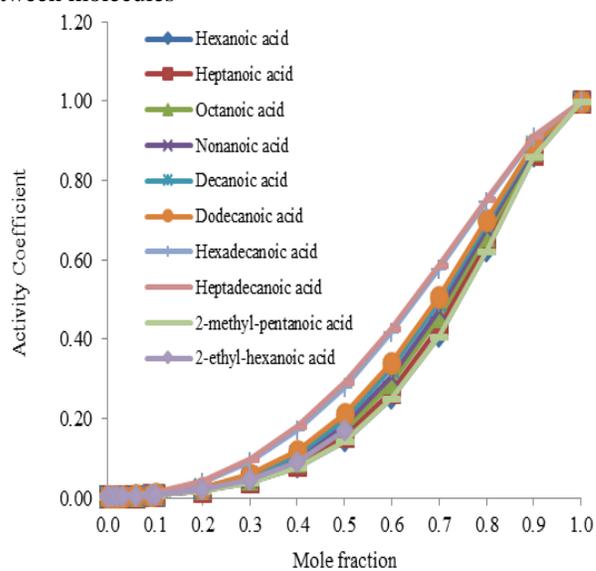


Fig. 20 Variations of activity coefficients with mole fraction of carboxylic acids in N-Methyl Pyrrolidone (NMP) (Modified UNIFAC Lyngby)

## III. CONCLUSION

This paper was an attempt to model the phase equilibrium involving volatile organic compounds and high molecular weight hydrocarbons. The models gave widely varying results. As reported some of the results do not sufficiently explain the expected interactions. No model produced consistent results. Thus, further work is required to test the suitability of these two models and also suggest improvements. We expect to report on improved computational results in my next communication.

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