

Phase Equilibrium of Volatile Organic Compounds in Silicon oil Using the UNIFAC Procedure: An Estimation

Edison Muzenda¹, Geoffrey Simate², Mohammed Belaid³, Freeman Ntuli⁴ and Mansoor Mollagee⁵

¹Research Coordinator, School of Mining, Metallurgy and Chemical Engineering, University of Johannesburg, P. O. 17011, 2028, Johannesburg, South Africa

Corresponding author email: emuzenda@uj.ac.za

²Graduate Student, School of Chemical and Metallurgical Engineering, University of the Witwatersrand, P/Bag 3, Wits 2050, Johannesburg, South Africa

^{3,4}Senior Lecturers, Faculty of Engineering and the Built Environment, University of Johannesburg, P. O. 17011, 2028, Johannesburg, South Africa

⁵Head of Department, Department of Chemical Engineering, Faculty of Engineering and the Built Environment, University of Johannesburg, P. O. 17011, 2028, Johannesburg, South Africa

ABSTRACT

This paper focuses on the phase equilibrium of volatile organic compounds in silicon oil chemically known as PDMS (polydimethylsiloxane) at infinite dilution. Measurements can be expensive and time consuming, hence the need for thermodynamic models which allow the calculation of the phase equilibrium behavior using a limited number of experimental data. The objective of this study was to predict infinite dilution activity coefficients of selected VOCs (volatile organic compounds) in PDMS using the Original UNIFAC model. The predicted results show that PDMS can be used to abate volatile organic compounds from contaminated air streams. The results obtained in this work are comparable to those obtained by the same authors through measurements such as the static headspace and the dynamic gas liquid chromatographic techniques as well as other literature. Although the UNIFAC group contribution method over estimate the infinite dilution activity coefficients, the results of this work may be applied in preliminary phases of process design, simulation and feasibility studies.

Keywords: Group contribution, Phase equilibrium, Simulation, Thermodynamic Models, Volatile organic

1.0 INTRODUCTION

Estimating the performance of absorbers or strippers in the abatement of volatile organic compounds requires reliable knowledge of the phase equilibrium concentrations in the air/gaseous and liquid streams. These can be made available in form of infinite dilution activity coefficients. The phase equilibrium of volatile organic compounds in water and other solvents is of great interest due to the emphasis on the pollutants' environmental fate and risk assessment. The growth in environmental legislations, the increasing influence of public opinion and the inception of the "permit to operate" principle are playing increasing pressure on industry to avoid and minimize gaseous emissions such VOCs. Scrubbing of the waste gases using selective high boiling solvents is a reversible technique, which allows both the cleaning of the waste gas and recovery of VOC. Infinite dilution studies are crucial in that environmental concern focus on the entirely dilute regions, parts per million.

Predictive methods especially those based on group contribution methods can replace measurements if they are giving precise and reliable estimations. The UNIFAC group – contribution method for estimating activity coefficients provides the process engineer with rapid and reliable method for predicting equilibrium conditions required in absorption and stripping column design. In this work the original

UNIFAC (Fredenslund et al 1975, 1977) was applied in the estimation of the required phase equilibrium data. The concept, theory, procedure and the idea behind group contribution methods is well presented in literature including the works of these authors Muzenda et al (2010a, 2010b) and Muzenda (2010).

For systems where limited or no experimental data is available it is advantageous to use predictive tools such as the group contribution methods such as ASOG (Wilson and Deal, 1962; the well-known UNIFAC model (Fredenslund et al., 1975, 1977) and the various modifications of the UNIFAC (Weidlich and Gmehling, 1987, Hooper et al, 1988). Several activity coefficient models have been tested in the literature for their accuracy and reliability in the prediction of infinite dilution activity coefficients in nonaqueous mixtures (Thomas and Eckert, 1984; Gmehling et al., 1983; Kontogeorgis et al., 1994; Voustras et al., 1985; Muzenda, 2010; Muzenda, 2010a; Muzenda et al., 2010b). In all cases the values of the infinite dilution activity coefficient are generally low, well below 100. This desirable situation does not arise with important industrial solvent water, which presents a unique behavior in solutions with organic compounds. Water exhibits great non ideality with organics with the resulting γ^∞ values very large in particular high molecular weight compounds for example n-decane in water in the order of 10^8 . It was the purpose of this work to test the applicability of the UNIFAC model in the prediction of infinite dilution activity coefficients of organic in PDMS.

2.0 The UNIFAC Model

2.1 Original UNIFAC (Fredenslund et al., 1975, 1977)

In the original UNIFAC model (Fredenslund et al., 1975, 1977) the activity coefficient is expressed as in Equation 1.

$$\ln \gamma_i = \ln \gamma_i^{comb} + \ln \gamma_i^{res} \quad (1)$$

The combinatorial part ($\ln(\gamma_i^{comb})$) accounts for the differences in size and shape of the molecules and the residual part ($\ln \gamma_i^{res}$) accounts for effects of energetic interactions between groups. For similar groups exhibiting almost a thermal behavior, the residual activity coefficients is expected to be very close to zero.

2.1.1 Combinatorial Part

The UNIFAC uses the same combinatorial expression as the UNIQUAC model (Abrahams and Prausnitz, 1975).

$$\ln \gamma_i^{comb} = \left\{ \ln \frac{\phi}{x_i} + \frac{\phi}{x_i} \right\} - \frac{zq_i}{2} \left\{ \ln \frac{\phi}{\theta_i} + 1 - \frac{\phi}{\theta_i} \right\} \quad (2)$$

2.1.2 Residual Part

The assumption in the solution of groups method, is that the contribution from group interactions is equal to the sum of the individual contributions of each solute in the solution minus the sum of the individual contributions in pure component can be expressed as in Equation 3

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (3)$$

The terms Γ_k and $\Gamma_k^{(i)}$ are functions of group concentrations and temperature only, both can be calculated using Equation 4.

$$\ln \Gamma_k = Q_k \left\{ 1 - \left(\ln \sum_m \theta_n \psi_{mk} \right) - \sum_m \left(\frac{\theta_n \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right) \right\} \quad (4)$$

The group interaction parameter ψ is calculated from Equation 5.

$$\psi_{nm} = \exp\left(\frac{-a_{nm}}{T}\right) = \exp\left[\frac{-(U_{mn} - U_{nm})}{RT}\right] \quad (5)$$

Where U_{mn} is the measure of interaction energy between groups m and n.

3. METHODOLOGY

In this study, the activity coefficient plays an important role in the design of absorption and stripping towers. Three UNIFAC models were used in the prediction of the desired phase equilibrium. The procedure involves (i) suitable reduction of experimentally activity data to obtain parameters characterizing interactions between pairs of structural groups (ii) use of these parameters to predict activities in other systems which have not been studied experimentally but which contain the same functional groups. Two general types of parameters are used; the reduced van der Waals parameters (reduced van der Waals Volume R_k and the reduced van der Waals surface area Q_k) and the group interaction parameters a_{mn} and a_{nm} ($a_{mn} \neq a_{nm}$). The calculations were performed on excel spreadsheets developed using the equations above.

4. RESULTS AND DISCUSSION

4.1 Infinite Dilution Activity Coefficients of VOCs in PDMS

The results obtained in this study presented in table 1 are comparable to those obtained in literature for similar systems through measurements and predictions as summarized Muzenda et al (2010a) 2. The solubility of substances is determined by balance of intermolecular forces between the solvent and the solute, and the entropy change that accompanies the solvation. Molecules with large dipole moments and dielectric constants are considered to be polar. Polarity is determined by the functional groups present. The polarity of molecules will depend on the following; the extent to which it can form hydrogen bonds, the number of electronegative atoms, polarizability of bonds or atoms and the net dipole moment of the molecules. Polar will dissolve polar, nonpolar will dissolve nonpolar. The differences in solubility of the volatile organic compounds in water and PDMS is mainly due to polarity variation. Organic compounds can be arranged in order of increase in polarity as alkanes, ethers, esters, amines, aldehydes, ketones, alcohols, carboxylic acids and amides. Aldehydes, ketones and esters have large dipole moments due to the electronegative oxygen that can bond with water accounting for high solubility of low molecular weight molecules such acetone in water. Alkanes such as pentane, hexane and heptane are not soluble in water due to the following factors. For molecules to dissolve in water they have to break the intermolecular forces within the substance in this case the Van der Waals dispersion forces. They have to break the intermolecular forces (hydrogen bonds) in the water so that the substances can fit between the water molecules. Breaking these attractions requires energy especially for hydrogen bonds. A substance

will dissolve if there is enough energy released when new bonds are formed with water to compensate for what is used in breaking the original attractions. The only new attractions between alkanes and water are the Van der Waals forces and these release less energy compared to what is used in breaking the hydrogen bonds. Therefore the differences in solubility is mainly due to polarity and the fact that “like dissolves like”. From the predicted results, PDMS are better absorbing solvents compared to the common solvent, water. Although water is readily available and cheap compared to PDMS, it quickly saturates and hence cannot effectively clean contaminated air streams. The next study on the possibility of using PDMS to scrub volatile organic compounds from contaminated air streams will focus on the mass transfer and flow characteristics in both packed and tray columns. Absorption and stripping towers will be used using the data predicted in this study.

Table 1: Mole - and - Weight fraction based infinite dilution activity coefficients of VOCs in PDMS at 303K

VOC Family	VOC	Infinite Dilution Activity Coefficients	
		Mole Fraction Based	Weight Fraction Based
Alkanes	Butane	1.421	24.449
	Pentane	1.408	19.518
	Hexane	1.356	15.74
	Heptane	1.279	12.768
	Octane	1.188	10.4
Ketones	Acetone	5.095	87.724
	Methyl ethyl ketone	1.328	18.414
	Methyl Isobutyl Ketone	3.963	39.572
	Cyclohexanone	1.001	10.199
Aldehydes	Acetylacetone	6.438	64.298
	Formaldehyde	0.669	22.271
	Acetaldehyde	4.919	111.643
	Propionaldehyde	1.358	23.366
	Butyraldehyde	1.325	18.372
Aromatics	Pentanal	1.251	14.519
	Cyclohexane	1.404	16.691
	Toluene	2.094	22.728
	Ethybenzene	1.071	10.089
	Xylene	2.315	21.811
Carboxylicacids	Trimethylbenzene	1.073	8.926
	Formic acid	1.154	25.062
	Acetic Acid	7.44	123.692
	Propionic acid	1.386	18.714
	Acrylic acid	2.502	34.724
	Oxalic acid	1.467	16.299

4.2 Variation of Activity Coefficients of Organics with Mole Fraction

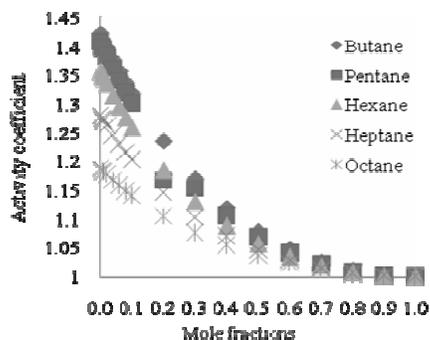


Figure 1: Activity coefficients variation with mole fraction (Alkanes)

Figure 2: Activity coefficients variation with mole fraction (Aldehydes)

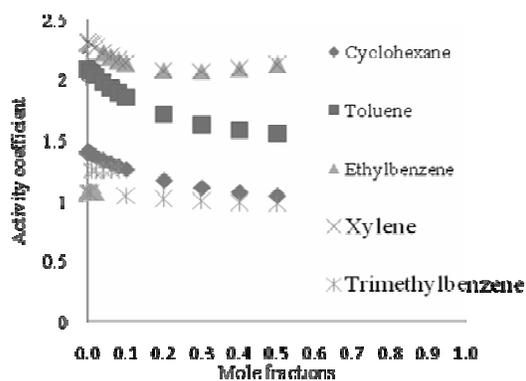


Figure 4: Activity coefficients variation with mole fraction (Carboxylic acids)

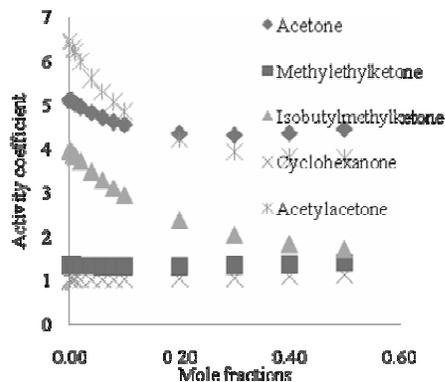


Figure 3: Activity coefficients variation with mole fraction (Ketones)

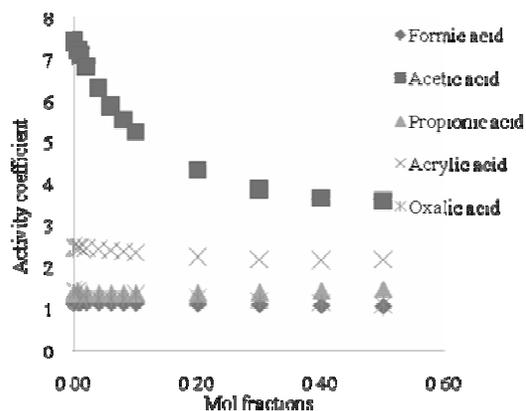
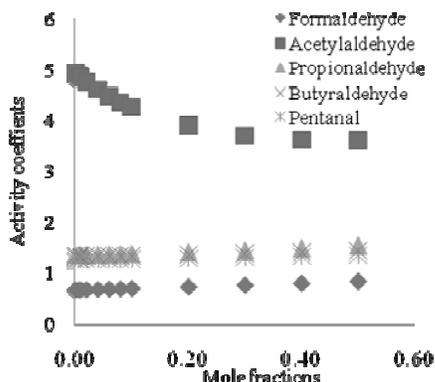


Figure 5: Activity coefficients variation with mole fraction (Aromatics)



Figures 1 to 5 show the variation of activity coefficients with mole fraction. The trends obtained in this study are in agreement with solution thermodynamics theory. The greatest deviation from ideal behavior is observed at infinite dilution. Infinite dilution in the diagrams is in the region where a molecule of the solute is completely surrounded by PDMS molecules, where the VOC mole fraction is nearly zero. Infinite dilution studies are crucial as they represent the most expensive and difficult part of the separation and the most accurate characterization of the system behavior. The studies are also of great significance as environmental concerns focus on very dilute regions, parts per million.

5. CONCLUSION

The important role played by infinite dilution activity coefficients in the qualitative and quantitative analysis of separation processes justifies the considerable efforts dedicated to the establishment of accurate correlation and predictive methods. In engineering design, prediction procedures in particular group contribution methods find much application in the preliminary design / feasibility studies. This is because it is easier to make a calculation than to perform an experiment. In addition to this, computations can be performed in a very short time, no financial input in the case of manual calculations or a one off expense in the case of computerized predictions. Performing an experiment takes a lot of time and in some cases significant financial input is required. Therefore it is suggested in this work that in preliminary design or feasibility studies of absorption systems for the abatement of volatile organic compounds, the Original UNIFAC model can be applied.

6. ACKNOWLEDGEMENT

The authors are indebted to the investigators whose work was reviewed in this study and their research project students Tshiwela L Selamulela, Motsumi J Diphare and Siyabonga B Madikane for the performing most of the calculations and simulations. The authors gratefully acknowledge the financial support of the department of Chemical Engineering at the University of Johannesburg.

6. REFERENCES

- Fredenslund, A., Jones, R. L., Prausnitz, J. M., (1975), *Group Contribution estimation of activity coefficients in non-ideal liquid mixtures*, Journal of American Institute of Chemical Engineers, Vol. 21, no. 116, 1086-1099.
- Fredenslund, A., Gmehling, J., Michelsen, M. L., Rasmussen, P., and Prausnitz, J. M., (1977), *Computerized Design of Multicomponent Distillation Column Using the UNIFAC Group Contribution Method for the Calculation of Activity Coefficients*, Industrial Engineering Chemistry Process Development, 16, 4, 450-462.
- Gmehling, J., Li, J. and Schiller, M., (1983), *A Modified UNIFAC Model. 2. Present Parameter Matrix and Results for Different Thermodynamic Properties*, Industrial Engineering Chemistry Research, 32, 178-193.
- Hooper, H. H., Michel, S., Prausnitz, J. M., (1998), *Correlation of liquid – liquid equilibria for some water- organic systems in the region 20-250⁰C*, Industrial and Engineering Chemistry Research, 27, 2182-2187.
- Kontogeorgis, G. M., Coutsikos, P. H., Tassios, D. and Fredenslund, A., (1994), *Improved Models for the Prediction of Activity Coefficients in Nearly Athermal Mixtures*, Fluid Phase Equilibrium, 92, 35 – 66.
- Kikic, I., Alessi, P., Rasmussen, P. and Fredenslund, A., (1980), *On the combinatorial Part of the UNIFAC and UNIQUAC Models*, Canadian Journal of Chemical Engineering, Vol. 58, 253 – 258.
- Nagata, I. and Koyabu, K., (1981), *Phase equilibrium by Effective UNIFAC group contribution method*, Thermochemica Acta, 48, 187-194.

- Muzenda, E., (2010), *Phase equilibrium of Volatile Organic Compounds in Polymeric Solvents Using Group Contribution Methods*, In Proceeding of the World Academy of Science, Engineering and Technology, 70,765 – 771.
- Muzenda, E., Belaid, M. and Ntuli, F., (2010), *Measurement of Infinite Dilution Activity Coefficients of Selected Environmentally Important Volatile Organic Compounds in Polydimethylsiloxane using Gas – Liquid Chromatography*” The Korean Journal of Chemical Engineering, 27, 5, 1509 – 1512.
- Muzenda, E., Belaid, M., Mollagee, M., F Ntuli, F., Jalama, K. and Kabuba, J., (2010), *Phase equilibrium of volatile organic compounds in very dilute aqueous and polymeric systems using the UNIFAC Model*” In Proceedings of the 3rd Technology and Innovation for Sustainable Development International Conference.
- Muzenda, E., Belaid, M., Mollagee, M., Ntuli, F. and Jalama, K., (2010), *Computerized feasibility studies and design of absorption systems using the UNIFAC group contribution method for activity coefficients calculation*, In Proceedings of the 3rd Technology and Innovation for Sustainable Development International Conference.
- Thomas, E. R. and Eckert, C.H. (1984), *Prediction of Limiting Activity Coefficients by a Modified Separation of Cohesive Energy Density Model and UNIFAC*, Industrial Engineering Chemistry Process Design and Development, 23, 194 – 209
- Vouostas, E. C., Kalospiros, N. S. and Tassios, D. P. (1985), *A Combinatorial Activity Coefficient Model for Symmetric and Asymmetric Mixtures*, Fluid Phase Equilibrium, 109.
- Weidlich, U. and Gmehling J., (1987), *A modified UNIFAC model: Prediction of VLE, h^E , and γ^∞* , Industrial Engineering Chemistry Research, 32, 178-193.
- Willson, G. M., Deal, C. H., (1962), *Activity coefficients and molecular structure*, Industrial Engineering Chemistry Fundamentals, 1, 20-23