World Academy of Science, Engineering and Technology
International Journal of Chemical and Molecular Engineering
Vol:5, No:2, 2011

Absorption of Volatile Organic Compounds into Polydimethylsiloxane: Phase Equilibrium Computation at Infinite Dilution

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Open Science Index, Chemical and Molecular Engineering Vol:5, No:2, 2011 publications.waset.org/14927/pdf

***Abstract*—**Group contribution methods such as the UNIFAC are very useful to researchers and engineers involved in synthesis, feasibility studies, design and optimization of separation processes. They can be applied successfully to predict phase equilibrium and excess properties in the development of chemical and separation processes. The main focus of this work was to investigate the possibility of absorbing selected volatile organic compounds (VOCs) into polydimethylsiloxane (PDMS) using three selected UNIFAC group contribution methods. Absorption followed by subsequent stripping is the predominant available abatement technology of VOCs from flue gases prior to their release into the atmosphere. The original, modified and effective UNIFAC models were used in this work. The thirteen selected VOCs that have been considered in this research are: pentane, hexane, heptanes, trimethylamine, toluene, xylene, cyclohexane, butyl acetate, diethyl acetate, chloroform, acetone, ethyl methyl ketone and isobutyl methyl ketone. The computation was done for solute VOC concentration of 8.55×10^{-8} which is well in the infinite dilution region. The results obtained in this study compare very well with those published in literature obtained through both measurements and predictions. The phase equilibrium obtained in this study show that PDMS is a good absorbent for the removal of VOCs from contaminated air streams through physical absorption.

***Keywords*—**Absorption, Computation, Feasibility studies, Infinite dilution, Volatile organic compounds

I. Introduction

IN this work we present activity coefficients at infinite dilution of selected volatile organic compound in silicon oil chemically known as polydimethylsiloxane (PDMS). Design of diffusional operations of phase contacting type such as absorption and distillation constitute a greater part of chemical engineering design. To design such processes, quantitative information on the phase equilibrium is required. 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. Reliable knowledge of phase equilibria is crucial in the design of absorption processes for the abatement of volatile organic compounds from contaminated air streams. It is also important for other separation processes such as distillation and design of multiphase reactors. 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 as volatile organic compounds. 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. For mixtures containing many components it is almost impossible to get a complete overview of properties at different compositions, temperature and pressure because of the enormous amount of measurements needed. Predictive methods especially those based on group contribution methods can replace measurements if they are giving precise and reliable estimations. The estimated properties will always not be precise compared to well - made measurements but this will suffice for purposes of process simulation, design, synthesis and development. Of importance is that predictive methods can be used to check the results of experimental work. The basic idea behind group contribution estimates is the addition of empirically – derived quantities, each characteristic of the chemical subunit of the compound in question. The underlying principle of any group contribution method is that: whereas they are thousands of chemical compounds of interest to science and technology, the number of structural and functional groups which constitute these compounds is much smaller. The most successful methods presently used for calculating activity coefficients in the liquid phase are the group contribution methods such as the UNIFAC (UNIQUAC Functional Group Activity Coefficients) Fredenslund et al. [1]. In this study, infinite dilution activity coefficients of VOCs were computed using three UNIFAC models namely the Original UNIFAC (Fredenslund et al., 1975, 1977) [1], [2], Modified UNIFAC (Bastos et al., 1988) [3] and Effective UNIFAC (Nagata and Koyabi., 1981) [4].

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II. The UNIFAC Models

The *Universal Functional Activity Coefficient* (UNIFAC) method is a semi-empirical system for the prediction of non-electrolyte activity estimation in non-ideal mixtures. UNIFAC uses the functional groups present on the molecules that make

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up the liquid mixture to calculate activity coefficients. By utilizing interactions for each of the functional groups present on the molecules, as well as some binary interaction coefficients, the activity of each of the solutions can be calculated. The UNIFAC model was first developed in 1975 by Fredenslund et al.

A. 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.

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^r \quad (1)$$

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

Combinatorial part; In the UNIFAC, the combinatorial part is calculated using the Staverman – Guggenheim function as used in the UNIQUAC model and this is given in equation 2 below.

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

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 from equation (4)

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

The parameter θ_m represents the surface area fraction of group *m* and is calculated from the equation (5)

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (5)$$

The summation covers all the groups and X_m is the mole fraction of group *m* in the mixture and is given by equation (6)

$$X_m = \frac{\sum v_m^{(j)} x_j}{\sum_n \sum_j v_n^j x_j} \quad (6)$$

Where: j = 1, 2, 3 ……. M (number of components)

n = 1, 2, 3 ……..N (number of groups)

The group interaction parameter ψ is calculated from equation (7)

$$\psi_{nm} = \exp\left(\frac{-a_{nm}}{T} \right) = \exp\left[\frac{-(U_{mn} - U_{nm})}{RT} \right] \quad (7)$$

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

B. Modified UNIFAC (Bastos et al., 1988)

This modified UNIFAC was developed especially suited for infinite dilution activity coefficient. The combinatorial part of the a original UNIFAC (Fredenslund et al., 1975, 1977) is modified as in (8)

$$\ln \gamma_i^c = \ln\left(\frac{\phi_i}{x_i} \right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} q_i \left(\ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right) \quad (8)$$

Where

$$\phi_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j} \quad (9)$$

The residual part of this model has the same form as in the original UNIFAC, where the interaction parameters were obtained by fitting infinite dilution coefficient data.

C. Effective UNIFAC (Nagata and Koyabi., 1981)

In their modifications Nagata and Koyabu (1981) modified the residual term and this is expressed in (10).

$$\ln \gamma_i^R = \sum_K v_k^{(i)} \left\{ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right\} - \left\{ \ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i} \right\} \quad (10)$$

The residual activity coefficients, Γ_k and $\Gamma_i^{(i)}$ are calculated by

$$\ln \Gamma_k = 1 - \left(\ln \sum_m X_m \psi_{mk} \right) - \sum_m \left(\frac{X_m \psi_{km}}{\sum_n X_n \psi_{nm}} \right) \quad (11)$$

The group interaction parameter is from(12)

$$\psi_{mn} = \frac{Q_m}{Q_n} \exp\left(-\frac{a_{mn}}{T} \right) \quad (12)$$

III. Methodology

A. Assumptions of the Group Contribution Methods

- The liquid solution is treated as a solution of groups which make up the components of the mixture. The groups are selected to be convenient structural groups such as CH_2, CH_3, C=C, ACH etc.

- The excess Gibbs free energy of the solution is considered to be the sum of two contributions. One accounts for the molecular difference in size and shape and is called the combinatorial part while the other one accounts for the energetic contribution and is known as the residual part. As a result of this assumption, the logarithm of the activity coefficient may be written as:

$$\ln \gamma_i^{\infty} = \ln \gamma_i^c + \ln \gamma_i^r$$

Where: $\ln \gamma_i^c$ is the combinatorial part & $\ln \gamma_i^r$ as the residual part.

- The residual part resulting from group interactions is assumed to be the difference between the sum of individual contribution in the pure component environment.
- The individual group contributions in any environment are treated as a function of group concentrations and temperature only. Group Contribution Methods are attractive in the sense that they are based on this assumption of group independence. A typical assumption is that the properties of a carbonyl group (CO) in a mono ketone are the same as those in a diketone and that the properties of this carbonyl group in a linear ketone like hexanone are the same as those in cyclic ketone like cyclohexane.

B. Procedure

The basic idea of the solution of groups model is to utilize existing phase equilibrium data to predict data for systems for which no experimental data is available. The UNIFAC model follows Analytical Solution of Groups (ASOG), Derr and Deal (1969) [5], where the activity coefficients in mixtures are related to interactions between structural groups. The model involves:

- A suitable reduction of experimentally obtained activity coefficients data to obtain parameters characterizing interactions between pairs of structural groups in non-electrolyte systems
- The use of these parameters is to predict activity coefficients for the systems which have not yet been studied experimentally but which contain the same functional groups

IV. Results And Discussion

TABLE I
SUMMARY OF INFINITE DILUTION ACTIVITY COEFFICIENTS USING THE THREE UNFICAC VERSIONS

Code	VOC	Original	Modified	Effective
1	Pentane	1.4083	1.4419	1.9602
2	Hexane	1.3564	1.4462	2.1962
3	Heptane	1.2795	1.4413	2.4582
4	Triethylamine	1.2027	1.3355	2.2237
5	Toulene	2.094	2.1544	2.4701
6	Xylene	2.3156	2.4981	2.49
7	Cyclohexane	1.1925	1.2351	1.1842
8	Butylacetate	1.1876	1.2985	2.2033
9	Diethylacetate	1.1828	1.212	1.8283
10	Chloroform	0.724	0.7291	0.0001
11	Acetone	1.2243	1.136	2.2395
12	Ethylmethylketone	4.0291	4.0851	7.0951
13	Isobutylmethylketone	3.9664	3.735	0.1478

The infinite dilution activity coefficients shown in table 1 were obtained using the Original UNIFAC (Fredenslund et al., 1975, 1977), Modified UNIFAC (Bastos et al., 1988) and Effective UNIFAC (Nagata and Koyabi., 1981). As can observed from table 1, there are close agreements and disagreements among the UNIFAC versions applied in this work. In certain instances, the results obtained in this study are compare very well to those obtained through measurements by the same authors [6], [7]. These were obtained through the dynamic GLC technique and the improved and modified simple headspace method. As was the purpose of this work, this show that the UNIFAC model can be used to provide useful preliminary phase equilibrium data for the design and optimization of separation techniques.

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TABLE II

STATIC AND GLC SOLUTE MOLE AND WEIGHT – FRACTION BASED ACITVITY COEFFICIENTS AT INFINITE DILUTION

Compound	Static headspace		GLC Technique	
	Mole	Weight	Mole	Weight
Pentane	0.388	5.384	0.384	5.323
Hexane	0.503	5.833	0.458	5.317
Heptane	0.539	7.34	0.539	5.382
Triethyl amine	0.525	5.187	0.392	3.878
Toluene	0.56	6.08	0.585	6.354
Xylene	0.805	7.587	0.617	5.808
Cyclohexane	0.397	4.72	0.399	4.378
Butylacetate	0.86	7.401	0.748	4.35
Diethyl ether	0.624	8.413	0.359	4.489
Chloroform	0.425	3.557	0.374	3.133
Acetone	1.026	17.669	0.865	14.895
methyl ketone	0.532	7.381	0.739	10.245
yl methyl ketone	1.096	10.941	0.841	8.396

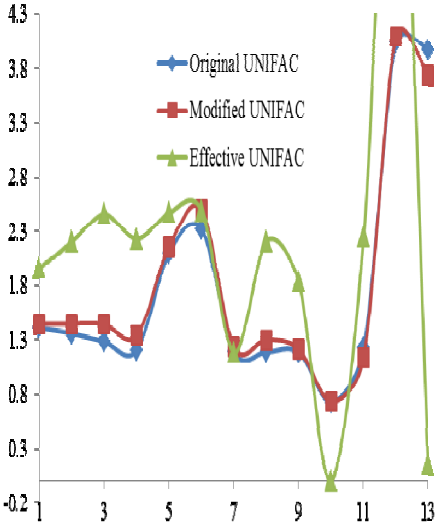


Fig. 1 Variation of predicted γ_i^{∞} using the three UNIFAC models

The variation of the predictions using the three UNIFAC group contribution methods is shown in fig 1. The original and modified UNIFAC procedures used in this work gave close agreement of the predictions. The effective UNIFAC [4] was found to overestimate the phase equilibrium in most cases with the exception for chloroform and isobutyl methyl ketone.

V. CONCLUSION

This paper presents infinite dilution activity coefficients if 13 environmentally important volatile organic compounds. The phase equilibrium results indicate that silicon oil (polydimethysiloxane) can be used to scrub VOCs from contaminated air streams. It is recommended to carry out a detailed vapour – liquid investigation at different temperatures. In their future studies, the authors will test other tools such artificial neural networks and commercial simulators like ASPEN Plus in phase equilibrium prediction.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of their universities and their research colleagues for fruitful discussions in the preparation of this article.

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