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Organics – PDMS Interactions: A Phase Equilibrium Study

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***Abstract*—T**he vapour – liquid equilibrium of 80 organics in Polydimethylsiloxane (PDMS) were predicted using the UNIFAC Lynby, Larsen et al., 1987 [1]. The organics were selected from 8 family functional groups namely cycloalkanes, aldehydes, alcohols, carboxylic acids, esters, ethers, thiols and amines. PDMS showed great absorption affinity for all organics in particular carboxylic acids and ethers.

***Keywords*—**Absorption, functional groups, organics, vapour-liquid equilibrium.

I. Introduction

VOLATILE organic compounds (VOCs) are released from industrial and chemical plants, domestic solvents, products stored at home and office [2]. VOCs are used in paint thinners, lacquer thinners, moth repellents, air fresheners, aerosol sprays, degreasers and dry cleaning fluids [2]. It is essential to limit and control the emissions of VOCs because of their adverse effects on climate change, the growth and decay of plants and the health of human beings and animals [3]. Carcinogenicity studies of certain classes of hydrocarbons indicated that some cancers appear to be caused by exposure to aromatic hydrocarbons found in soot and tars [3]. VOCs together with NOx in the presence of sunlight contribute to photochemical smog and increasing ozone pollution [3], [4]. VOCs are relatively are largely found in the atmosphere because of their relatively high vapour pressure. However VOCs have also been found to contaminate ground water, municipal drinking water and subsurface soil and hence have significant contribution to cumulative exposure to pollution for humans and the environment [5]. Governments worldwide have taken steps to reduce the release of VOCs into the atmosphere by passing legislation which enforces industrial air pollution reduction [6]-[8].

Phase equilibrium in the form of infinite dilution activity coefficients can be predicted using a number of physical property models such as group contribution and molecular simulation [9]. In this work, the modified UNIFAC group-contribution model of phase equilibria and heats of mixing, Lngby of Larsen et al (1987) [1] was used to compute the desired phase equilibrium.

II. The Modified UNIFAC Lyngby Model

The UNIFAC Lyngby model of Larsen et al. (1987) [1] was in this work to predict activity coefficients of 80 organics. The model differs from the original UNIFAC and UNIFAC Dortmund in that the combinatorial component and the temperature dependence parameters are presented by equations (1) and (3) respectively.

$$\ln \gamma_i^C = \ln \frac{\omega_i}{x_i} + 1 - \frac{\omega_i}{x_i} \qquad (1)$$

where

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \qquad (2)$$

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}(T - T_0) + c_{nm}\left(T \ln \frac{T_0}{T} + T - T_0 \right)}{T} \right) \qquad (3)$$

In (3) T0 is a reference temperature, usually 298.15K. Predictions were performed at 303.15K and VOC mole fraction was varied from 10-3 to 1. The group interaction parameters, group volumes and surface areas were obtained from UNIFSTAT (1.9.0.147). The temperature dependence parameters Ψnm were calculated using (4).

$$\Psi_{nm} = \exp\left(-\frac{a_{nm} + b_{nm}(T - T_0) + c_{nm}\left(T \ln \frac{T_0}{T} + T - T_0 \right)}{T} \right) \qquad (4)$$

The group interaction parameters were obtained from the UNIFAC Dortmund Data Base. The residual activity coefficients of group k in a reference solution containing only molecules of type i, Γk(i), were calculated using (5).

$$\ln \Gamma_k^{(i)} = Q_k \left[1 - \ln\left(\sum_m \Theta_m^{(i)} \Psi_{mk} \right) - \sum_m \frac{\Theta_m^{(i)} \Psi_{km}}{\sum_n \Theta_n^{(i)} \Psi_{nm}} \right] \qquad (5)$$

Where

$$\Theta_m^{(i)} = \frac{Q_m X_m^{(i)}}{\sum_n Q_n X_m^{(i)}} \tag{6}$$

$$X_m^{(i)} = \frac{\sum_j \nu_j^m x_j}{\sum_j \sum_n \nu_{n.j} x_j} \tag{7}$$

For a mixture, the residual activity coefficients of group k, Γk, were calculated using (8).

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk} \right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}} \right] \tag{8}$$

Where

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{9}$$

$$X_m = \frac{\sum_j \nu_j^m x_j}{\sum_j \sum_n \nu_{n.j} x_j} \tag{10}$$

The residual activity coefficients are of component i were obtained from (11).

$$\ln \gamma_i^R = \sum \nu_k^{(i)} \left(\ln \Gamma_k - \ln \Gamma_k^{(i)} \right) \tag{17}$$

The combinatorial (entropic) contribution to the activity coefficient due to size and shape of the functional group is represented by (18).

$$\ln \gamma_i^C = \ln \frac{\omega_i}{x_i} + 1 - \frac{\omega_i}{x_i} \tag{18}$$

Where

$$\omega_i = \frac{x_i r_i^{2/3}}{\sum_j x_j r_j^{2/3}} \tag{19}$$

The activity coefficient was calculated from (20).

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{20}$$

III. RESULTS AND DISCUSSION

The solubility of 80 organics in PDMS selected from cycloalkanes, aldehydes, alcohols, carboxylic acids, esters, ethers, thiols and amines family groups in the form of infinite dilution activity coefficients is presented and discussed in this section. Solubility is influenced by temperature, pressure, concentration as well as the nature of solute and the solvent. The solubility of organics in PDMS was influenced by intermolecular forces such as dipole-dipole moments, hydrogen bonding and the London dispersion forces.

Fig. 1 shows the variation of activity coefficients with mole fraction of cycloalkanes in PDMS. PDMS has strong affinity for cycloalkanes as both are nonpolar plus the strong intermolecular forces that exist between them.

A. Cycloalkanes

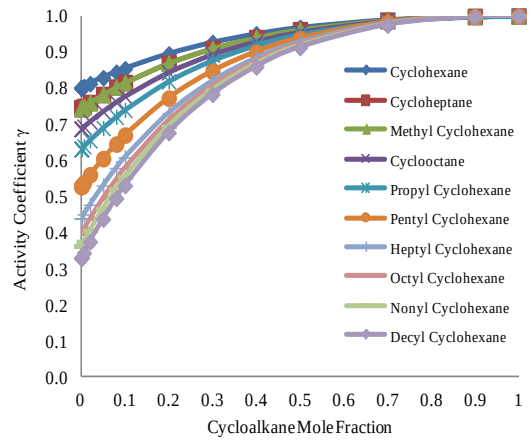

Fig. 1 Variation of activity coefficients with mole fraction for cycloalkanes in PDMS

London dispersion forces in PDMS and cycloalkane molecules induce dipole interactions, causing mutual attraction resulting in high solubility. The solubility as shown in Fig. 1 increases with an increase in cycloalkane size. This is because large cycloalkanes have large surface areas giving rise to greater London dispersion forces and their sizes approach that of PDMS.

B. Aldehydes

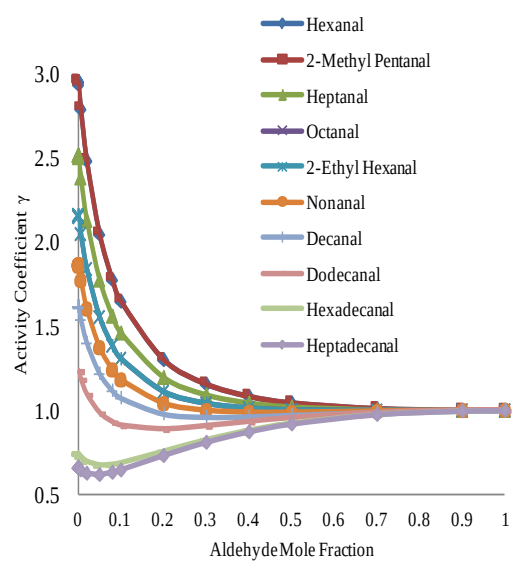

Fig. 2 Variation of activity coefficients with mole fraction for aldehydes in PDMS

The C=O bond in aldehydes molecules is polar due to the difference in electronegativity between the carbon and oxygen

atoms. In small aldehyde molecules (<C5) that polarity translates itself to the whole molecule because the non-polar C-C and C-H bonds do not significantly contribute to the van der Waals forces. As the hydrocarbon chain increases the aldehyde molecules increasingly become nonpolar. The resulting intermolecular forces between the large aldehydes molecules and the solvent (PDMS) is dipole-dipole attraction, and hence increased solubility, Fig 2.

C. Carboxylic Acids

As shown in Fig. 3 carboxylic acids are very soluble in PDMS because the acid exists as a dimer in the nonpolar solvent [10], [11]. The hydrogen bonds of the dimeric structure are not disrupted when the acid dissolves in a nonpolar solvent. Carboxylic acids behave as nonpolar solutes and as the dimer is a large structure with huge van der Waals forces, this increases their solubility in PDMS.

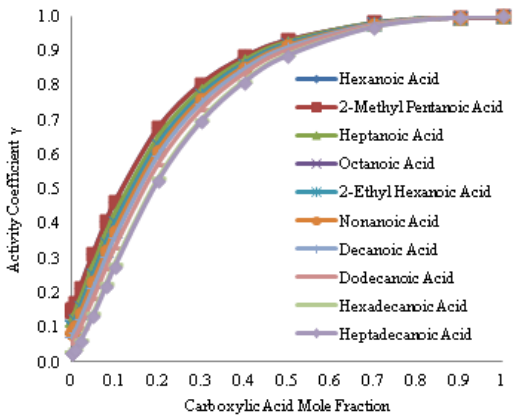

Fig. 3 Variation of activity coefficients with mole fraction for carboxylic acids in PDMS

D. Alcohols

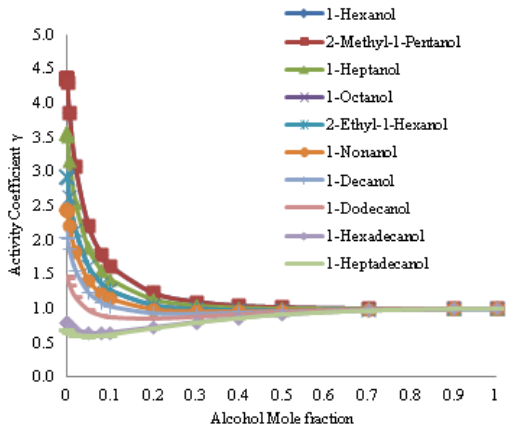

Fig. 4 Variation of activity coefficients with mole fraction for alcohols in PDMS

Alcohols are polar due to the O-H bond of the hydroxyl group. The oxygen is more electronegative than the hydrogen atom and this has an electron pulling effect [12]. The intermolecular forces between alcohol and PDMS depend on the number of C-C and C-H bonds in the alcohol. For smaller alcohols (<C4) the dipole force of the hydroxyl group is the dominant force leading to strong dipole-dipole interactions in addition to the hydrogen bonding among alcohol molecules. This slightly reduces the solubility of these smaller alcohols in the non-polar PDMS solvent. For larger alcohols (C4<), London dispersion forces become more dominant making the VOCs nonpolar, resulting in increased solubility. This trend is also enhanced by the size similarity, "like dissolves like", Fig 4.

E. Ethers

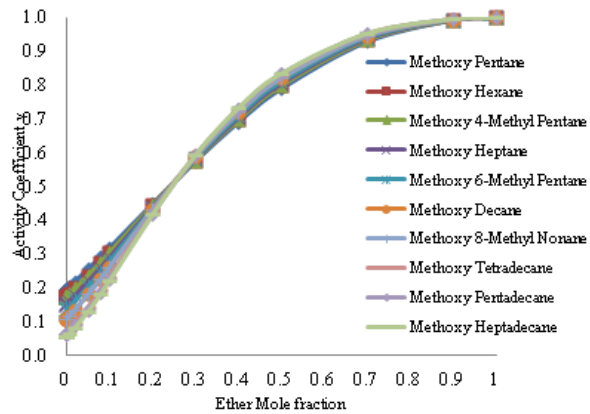

Fig. 5 Variation of activity coefficients with mole fraction for ethers in PDMS

Ethers are very soluble in PDMS as shown in Fig. 5. Ethers are compounds that have two alkyl or aryl groups attached to an oxygen atom and general formula is R-O-R'. The C-O dipoles of the ethers do not cancel out as the C-O-C linkage is bent at bond angles of 109o [13]. As a result ethers have small net dipole moment. The dipole moments are weakened as the size of ethers increase. The steric hindrance of large alkyl groups further weakens the net dipole moment of the C-O-C bond by increasing its bond angle. The induced non-polarity increases the solubility of larger ethers in PDMS.

F. Esters

Esters have a general formula RCOOR and are very polar because of the C=O bond. As the non-polar hydrocarbon is increased, esters become non-polar and hence their solubility in PDMS is influenced by their size, Fig 6.

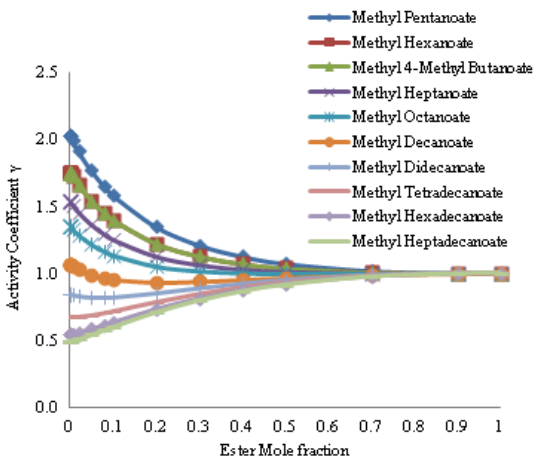

Fig. 6 Variation of activity coefficients with mole fraction for esters in PDMS

G.Thiols

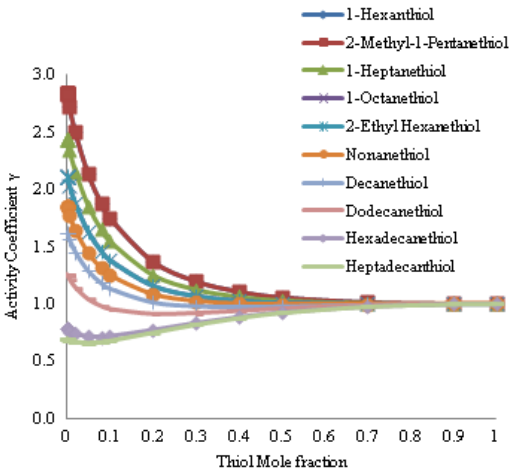

Fig. 7 Variation of activity coefficients with mole fraction of thiols in PDMS

Thiols contain a sulfhydryl group –SH and due to the small electronegativity difference between sulphur (2.5) and hydrogen (2.1), the S-H bond is essentially non-polar [14], [15]. Thus making thiols with a hydrocarbon alkyl group non-polar enhancing their solubility in PDMS.

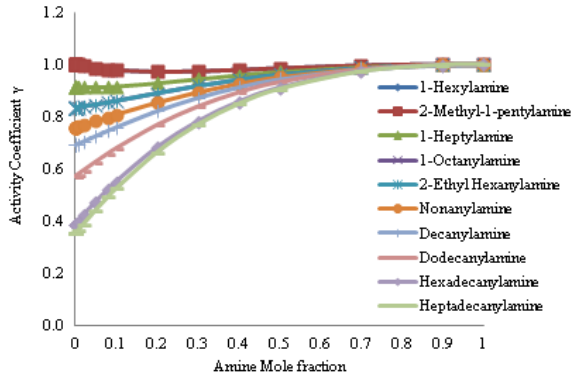

Fig. 8 Variation of activity coefficients with mole fraction for amines in PDMS

The difference in electronegativity of the nitrogen (3.0) and hydrogen (2.1) atoms make the N-H bonds in amines polar. This polarity is enhanced in amines with short hydrocarbon chains due to the huge influence of the polar N-H bonds. Fig. 8 shows that solubility increases with increasing amines molecular weight. The polarity of amines approaches zero as their chain length increases.

IV. Conclusion

This study has shown that PDMS is thermodynamically suitable for the absorption of VOCs from contaminated air streams. The modified UNIFAC Lyngby of Larsen et al. (1987) [1] was found to be suitable in computing phase equilibrium of VOCs–PDMS systems as a function of temperature and composition. In all the groups studied solubility increased with increasing VOC size (chain length).

Acknowledgment

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Modeling the Virial Equation of Gas through Artificial Neutral Network

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***Abstract*—**Real gases do not obey ideal gas behavior due to intermolecular interaction and ideal gas equation of state (EOS) does not hold true. Virial EOS accounts for the intermolecular interactions in real gasses that do not obey ideal gas EOS at relatively high pressure. It consists of infinitive terms and coefficients and it works for high pressure (up to ~ 10 bars). Higher terms are needed for very high pressures. But in real world, and in laboratory theoretical and experimental data is not readily available for virial coefficients higher than the second one, therefore the equation is often used in truncated form. It is shown that the second VEOS coefficients can be experimentally measured along the isotherm, an important parameter called B(T). Researchers were interested in study about this coefficient and many scientific attempts were established so far. Statistical thermodynamics provides expressions for "B" only in terms of intermolecular potential energy, but here in this paper we want to imply a powerful instrument to have it in different temperatures. Consequently, the black box identification here is based on "soft computing" approach by means of artificial neural network (ANN). The main aim of this paper is to establish a reliable "interface" such as a predictor, in thermodynamics field. The use of this predictor should reflect the true behavior of B(T) with respect to T. The results show a good agreement with the experimental data.

***Keywords*—** soft computing, the second VEOS coefficient, predictor

I. Introduction

SOFT computing (SC) is not a new term; we have gotten used to reading and hearing about it daily. Nowadays, the term is used often in computer science and information technology. It is possible to define SC in different ways. Nonetheless, SC is a consortium of methodologies which works synergistically and provides, in one form or another, flexible information processing capability for handling real life ambiguous situations. Its aim is to exploit the tolerance for imprecision, uncertainty, approximate reasoning and partial truth in order to achieve tractability, robustness and low-cost solutions. SC includes fuzzy logic (FL), neural networks (NNs), and genetic algorithm (GA) methodologies. SC combines these methodologies as FL and NN (FL– NN), NN and GA (NN–GA) and FL and GA (FL–GA). Here we deal with neural networks. A neural network is a system of programs and data structures that approximates the operation of the human brain. A neural network usually involves a large number of processors operating in parallel, each with its own small sphere of knowledge and access to data in its local memory. Typically, a neural network is initially "trained" or fed large amounts of data and rules about data relationships (for example, "A grandfather is older than a person's father"). A program can then tell the network how to behave in response to an external stimulus. The paper describes use of soft computing methods (neural network techniques) in the development of network scheme for modeling the Virial equation of state (VEOS). We choose the Virial equation coefficients as case study because they play an important role in predicting the P – V – T manner of gas. The Virial equation is important because it can be derived directly from statistical mechanics. This equation is also called the Kamerlingh Onnes equation:

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \frac{D}{V_m^3} + \cdots \quad (1)$$

$$B = -V_c \quad (2)$$

$$C = \frac{V_c^{-2}}{3} \quad (3)$$

Where B, C and D are second, third and firth virial equation coefficient. If appropriate assumptions are made about the mathematical form of intermolecular forces, theoretical expressions can be developed for each of the coefficients. In this case B corresponds to interactions between pairs of molecules, C to triplets, and so on. Accuracy can be increased indefinitely by considering higher order terms. The coefficients B, C, D, etc. are functions of temperature only. Among the infinitive terms of VEOS, the second coefficients are of special importance that we select them. On basis of above facts, we attempt to linearize empirical data of B(T), for six alkanes, C1 to C6, by means of MATLAB which is known as a powerful toolbox for designing neural networks. Data of critical temperature and pressure, molecular weight and acentric factor are also implied as subsidiary data for a better estimation.

II. Modeling Methods and Materials

Modeling is an essential precursor in the parameter estimation process. Identification strategies of various kinds by means of input–output measurements are commonly used in many situations in which it is not necessary to achieve a

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