

Phase Equilibrium of Volatile Organic Compounds in Polymeric Solvents Using Group Contribution Methods

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Abstract—Group contribution methods such as the UNIFAC are of major interest to researchers and engineers involved synthesis, feasibility studies, design and optimization of separation processes as well as other applications of industrial use. Reliable knowledge of the phase equilibrium behavior is crucial for the prediction of the fate of the chemical in the environment and other applications. The objective of this study was to predict the solubility of selected volatile organic compounds (VOCs) in glycol polymers and biodiesel. Measurements can be expensive and time consuming, hence the need for thermodynamic models. The results obtained in this study for the infinite dilution activity coefficients compare very well those published in literature obtained through measurements. It is suggested that in preliminary design or feasibility studies of absorption systems for the abatement of volatile organic compounds, prediction procedures should be implemented while accurate fluid phase equilibrium data should be obtained from experiment.

Keywords—Volatile organic compounds, Prediction, Phase equilibrium, Environmental, Infinite dilution.

I. INTRODUCTION

THIS work is a continuation of my interest in the phase equilibrium of volatile organic compounds in aqueous and polymeric solvents. Reliable knowledge of the phase equilibrium behavior of pure compounds, their mixtures in the whole composition, wide temperature and pressure range is crucial for the prediction of the fate of the chemical in the environment and other applications. In this work, activity coefficients at infinite dilution of selected volatile organic compounds in glycol polymers and biodiesel are presented. The biodiesel used here is a methanol transesterified product of rape seed oil. 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]

II. THERMODYNAMIC FUNDAMENTALS

Traditionally, two different approaches have been used for vapour - liquid equilibrium (VLE) computations; equations of state and activity coefficient models. In both cases, the starting point is the equality of the fugacity of each component in the two phases (1).

$$f_i^v = f_i^L \quad (1)$$

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Where for N – component mixture f_i^v is the fugacity of component i in the vapour phase and f_i^L is the fugacity of component i in the liquid phase. In the equation of state approach the real behaviour of both phases is described by the fugacity coefficients ϕ_i , and (1) is rewritten as

$$y_i \phi_i^V = x_i \phi_i^L \quad (2)$$

The fugacity coefficients in (1) may be obtained from any equation of state using well –known relationship from classical thermodynamics. One of these equations is

$$\ln \phi_i = \frac{1}{RT} \int_V^{\infty} \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j=1} - \frac{RT}{V} \right] dV - \ln \frac{PV}{RT} \quad (3)$$

In order to calculate the required fugacity coefficients the PVT behaviour of the vapour and the liquid as a function of composition must be known for the whole pressure range. This behaviour can be described using equations of state for both vapour and liquid phases. In the activity coefficient model approach (1) can be written as

$$x_i \gamma_i P_i^S \phi_i^S P_{oy_i} = y_i \phi_i^V P \quad (4)$$

For low to moderate pressures and non-associating fluids, the fugacity coefficients in the saturation state (ϕ_i^S) and in the vapour above the mixture show nearly the same value and the Poynting factor (P_{oy_i}) is approximately equal to one. In this situation a simple relation can be used to calculate vapour – liquid equilibria (VLE) (1);

$$x_i \gamma_i P_i^S = y_i P \quad (5)$$

In process design, the required phase equilibrium information is commonly expressed by K factors

$$K_i = \frac{y_i}{x_i} \quad (6)$$

Where y_i is the mole fraction component in the vapour phase and x_i is the mole fraction of component i in the liquid phase.

III. GROUP CONTRIBUTION METHODS (ORIGINAL, MODIFIED AND EFFECTIVE)

Gmehling [2] reported that Scatchard and Hildebrand developed the first predictive model (regular solution theory) which could only be applied for non polar systems in 1931. In order to be able to handle all kinds of systems, Gmehling started the development of the group contribution method at the University of Dortmund. Reference [3] proposed a group contribution method called UNIFAC (UNIQUAC Functional Group Activity Coefficients). In concept the UNIFAC model

follows the analytical solution of groups model of [4], where the activity coefficients in mixtures are related to interactions between structural groups. The UNIFAC model combines the UNIQUAC model with the solution of groups. In the UNIFAC method, the activity coefficients are calculated from a combinatorial and a residual part. Whereas the combinatorial part takes into account the size and shape of the molecule, the residual part considers the enthalpic interactions. This method involves (a) a suitable reduction of experimentally determined activity coefficient data to obtain parameters characterizing interactions between pairs of structural groups in non electrolyte systems (b) the use of these parameters to predict activity coefficients for other systems which have not been studied experimentally but with same functional groups. The logarithm of the activity coefficient is the sum of two contributions as shown in (7).

$$\ln \gamma_i = \ln \gamma_i^c + \ln \gamma_i^R \quad (7)$$

A. Original UNIFAC

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 (8) below.

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

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 (9).

$$\ln \gamma_i^R = \sum_k v_k^{(i)} \left[\ln \Gamma_k - \ln \Gamma_k^{(i)} \right] \quad (9)$$

The terms Γ_k and $\Gamma_k^{(i)}$ are functions of group concentrations and temperature only, both can be calculated from (10).

$$\ln \Gamma_k = Q_k \left\{ 1 - \left(\ln \sum_m \theta_m \psi_{mk} \right) - \sum_m \left(\frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{nm}} \right) \right\} \quad (10)$$

The parameter θ_m represents the surface area fraction of group m and is calculated from (11).

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \quad (11)$$

The summation covers all the groups and X_m is the mole fraction of group m in the mixture and is given by (12)

$$X_m = \frac{\sum v_m^{(j)} x_j}{\sum_n \sum_j v_n^j x_j} \quad (12)$$

Where: $j = 1, 2, 3 \dots \dots \dots M$ (number of components)

$n = 1, 2, 3 \dots \dots \dots N$ (number of groups)

The group interaction parameter ψ is calculated from (13)

$$\psi_{nm} = \exp\left(\frac{-a_{nm}}{T}\right) = \exp\left[\frac{-(U_{nm} - U_{nm}^0)}{RT}\right] \quad (13)$$

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

B. Modified UNIFAC

A modified UNIFAC was developed by [5], [6]. The main differences compared to the original UNIFAC are (i) an empirically modified combinatorial part is introduced (ii) temperature – dependent group interaction parameters are used (iii) additional main groups such for cyclic alkanes, formic acid were added. The residual part remain unchanged. The combinatorial part is given by (14) below

$$\ln \gamma_i^c = \left\{ \ln \frac{\psi_i}{x_i} + 1 - \frac{\psi_i}{x_i} \right\} - \frac{zq_i}{2} \left\{ \ln \frac{\phi_i}{\theta_i} + 1 - \frac{\phi_i}{\theta_i} \right\} \quad (14)$$

C. Effective UNIFAC

In their modifications, [7] modified the residual term and this is expressed in (15).

$$\ln \gamma_i^R = \sum_K v_k^{(i)} \left\{ \ln \Gamma_k - \ln \Gamma_k^{(i)} \right\} - \left\{ \ln \frac{\theta_i}{x_i} + 1 - \frac{\theta_i}{x_i} \right\} \quad (15)$$

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

$$\ln \Gamma_k = 1 - \left(\ln \sum_m X_m \psi_{mk} \right) - \sum_m \left(\frac{X_m \psi_{km}}{\sum_n X_n \psi_{nm}} \right) \quad (16)$$

The group interaction parameter is from equation (17)

$$\psi_{nm} = \frac{Q_m}{Q_n} \exp\left(-\frac{a_{nm}}{T}\right) \quad (17)$$

IV. REVIEW ON THE SYSTEM OF INTEREST

Reference [8] measured thermodynamic properties based on weight fraction of organic compounds in three Polyethylene glycol (PEG) polymers using gas chromatographic technique (GLC). PEG-600, -1000, and -4000 were coated on the solid support, 60 – 80 mesh of Uniport B in the range of coverage

ratio of 0.1 – 0.3. The measurements were carried out in the range 329.65 – 350.3K. Helium was used a carrier gas and the flow rate was maintained at 20ml/min. The sample size was

varied below $0.1 \mu\text{l}$. The authors measured infinite dilution activity coefficients of ethanol, ethyl acetate, dichloromethane, benzene and hexane. The infinite dilution

activity coefficient $\gamma_1^\infty(w)$ based on the weight fraction was calculated using (18) below

$$\ln \gamma_1^\infty(w) = \ln \frac{273R}{M_1 p_1^o V_g} - \frac{B_{11} - v_1^0}{RT_c} p_1^o \quad (18)$$

Infinite dilution activity coefficients and Henry coefficients based on weight fraction at 340.5K are shown in Table 1 below:

TABLE I
INFINITE DILUTION ACTIVITY COEFFICIENTS AND HENRY'S LAW COEFFICIENTS BASE ON WEIGHT FRACTION

Solute	$\gamma_1^\infty(w)$			$H_1(w)/\text{kg atm mol}^{-1}$		
	PEG-600	PEG-1000	PEG-4000	PEG-600	PEG-1000	PEG-4000
Ethanol	6.39	7.48	8.16	4.09	4.79	5.21
Ethyl acetate	5.53	5.41	5.2	3.99	3.9	3.76
Dichloromethane	1.46	1.33	1.23	3.56	3.23	3.01
Benzene	5.08	4.54	4.24	3.34	2.99	2.79
Hexane	40.1	35.3	32.7	38.4	33.8	31.3

Reference [9] measured activity coefficients at infinite dilution of hydrocarbon solute systems in 1,4 – dicyanobutane using medium pressure gas-liquid chromatography. The hydrocarbon solutes were n-pentane, n-hexane, n-heptane, n-octane, n-decane, cyclopentane, cyclohexane, cycloheptane, 1-hexene, 1-heptene, 1-octene, 1-hexyne, 1-heptyne, 1-octyne and benzene. Measurements were performed at 293.15, 298.15 and 303.15K. The solid support was celite (Chromosorb W HP 80/100 mesh) loaded with 25 – 30 per cent by mass of solvent. They varied their flow rate from $0.70\text{cm}^3\text{s}^{-1}$ to $0.8\text{cm}^3\text{s}^{-1}$. Infinite dilution activity coefficients for toluene in aqueous solution of protein stabilizers glycerol, ethylene glycol, glucose, sucrose and trehalose were measured using the inert gas stripping method (IGS) [10]. The IGS method consisted of measuring the rate of elution of a volatile solute as an entering gas is passed through a highly dilute solution. The solute content was periodically analyzed by gas chromatography (GC). The infinite dilution activity coefficients of toluene in water – ethylene glycol system were 8789, 8345, 7856, 7338, 6617 and 6014 at 273.15, 283.15, 293.15, 303.15, 313.15 and 323.15K respectively.

Reference [11] determined infinite dilution activity coefficients of hydrocarbons in triethylene glycol and tetraethylene glycol using gas chromatography at 323.15 – 403.15K. The following hydrocarbons were studied n-heptane, n-octane, n-nonane, n-decane, benzene and toluene. The solid support was 80-100 mesh chromosorb W acid-washed and silanized. Hydrogen was used as a carrier gas and

its flow rate was 60ml/min. Their results for organic compounds of interest to this work at 373.15K; for toluene in triethylene glycol and tetraethylene glycol were 4.624 and 4.499 respectively, *n* – heptane in triethylene glycol and tetraethylene glycol were 93.256 and 50.197 respectively.

Reference [12] determined infinite dilution activity coefficients of volatile organic compounds in biodiesel by headspace chromatography and through calculations using different UNIFAC methods. Measurements were carried out for varying mole fractions of volatile organic compounds in biodiesel at 30, 35 and 40°C. A head space auto-sampler HS-40 Perkin Elmer automatic headspace sampler attached to a GC (Perkin Elmer) was used for this investigation. The three UNIFAC methods used by the authors were the original UNIFAC, DMD – UNIFAC and the LBY-UNI. The results of this work are shown in table 2. Generally all the results are in agreement with the exception of LBY-UNI which yielded higher values with large deviations from experimental results.

TABLE II
ACTIVITY COEFFICIENTS AT INFINITE DILUTION USING VARIOUS METHODS

	T (°C)	UNIFAC	DMD-UNI	LBY-UNI	Head space	GLC
1,2 - DCE	30	0.74	1.117	1.252	0.647	0.615
	35	0.735	1.094	1.228	0.668	
	40	0.732	1.073	1.203	0.699	0.647
Benzene	30	0.58	0.611	0.855	0.628	0.625
	35	0.579	0.612	0.85	0.636	
	40	0.579	0.613	0.846	0.647	0.647
Toluene	30	0.649	0.643	0.838	0.651	0.645
	35	0.651	0.646	0.835	0.672	
	40	0.652	0.649	0.833	0.718	0.671

V. METHODOLOGY

In this work, the activity coefficient plays an important role in the choice of a suitable solvent amongst water, ethylene glycol, propylene glycol and butylene glycol in the abatement of volatile organic compounds. The three versions of the UNIFAC can be used to predict the infinite dilution activity coefficients. The original and effective UNIFAC versions were used in this work. 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 be 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} ($a_{mn} \neq a_{nm}$).

VI. RESULTS AND DISCUSSION

Of the six solvents considered in this study biodiesel offers the most favourable phase equilibrium. As for the glycol polymers, solubility increases with the increase in molecular

weight of the solvent. Thus polyethylene glycol yielded the lowest infinite dilution activity coefficients of the volatile organic compounds in the four glycol solvents considered here. Butylene glycol yielded the lowest activity coefficients thus better solubility of the volatile organic compounds. This trend is the same for results obtained through the original and effective UNIFAC. The results of the prediction for toluene in this study compare very well to those obtained by [12]. In this work we obtained the infinite dilution activity coefficient of 0.641 for toluene and this very comparable to the values shown in table at 30°C. Biodiesel is a good absorption medium for aromatics and chlorinated hydrocarbons, because of their low activity coefficients i.e., good solubility in the solvent. Biodiesel (methyl oleate) has a very low vapour pressure and this a desirable property as it prevents secondary emissions. The effect of temperature on the activity coefficients of volatile organic compounds in propylene glycol is shown in fig 1. 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. Factors such as temperature and pressure will alter this balance. 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.

TABLE III
SUMMARY OF ORIGINAL UNIFAC RESULTS

VOC	EG	PRG	BG	PEG400	BD
Pentane	67.785	47.338	36.301		0.685
Hexane	38.919	19.576	11.96	38.42	0.778
Heptane	64.096	29.847	17.32		
Triethylamine	12.516	6.463	4.077	12.54	0.478
Toluene	19.745	11.535	7.824	8.14	0.624
Xylene	26.231	14.196	9.155	11.85	0.624
Cyclohexane	29.314	15.357	9.626		0.699
Butylacetate	23.845	13.04	8.572		0.902
Diethylether	6.98	4.45	3.222		0.544
Chloroform	2.856	2.184	1.799	3.01	0.429
Acetone	6.669	6.134	5.822	7.12	1.268
Ethylmethylketone	4.592	3.213	2.508	4.57	0.874
Isobutylmethylketone	11.853	6.953	4.822		1.171
Acetaldehyde				2.89	
Propionaldehyde				1.11	
Butyraldehyde				0.81	
Hexanal				0.56	
Heptanal				0.49	

EG – Ethylene Glycol, PRG – Propylene Glycol, BG – Butylene Glycol, PEG – Polyethylene Glycol, BD – Biodiesel (methyl oleate)

TABLE IV
SUMMARY OF EFFECTIVE UNIFAC RESULTS

VOC	Ethylene Glycol	Propylene Glycol	Butylene Glycol
Pentane	29.718	25.956	23.288
Hexane	19.833	13.112	9.443
Heptane	10.744	6.91	4.878
Triethylamine	10.478	6.751	4.797
Toluene	16.491	11.179	8.26
Xylene	29.495	16.698	10.712
Cyclohexane	10.044	7.089	5.388
Butylacetate	25.755	15.728	10.701
Diethylether	5.182	5.182	5.182
Chloroform	3.937	1.89	1
Acetone	2.94	2.38	2.171
Ethylmethylketone	4.739	3.356	2.564
Isobutylmethylketone	10.971	7.117	5.089

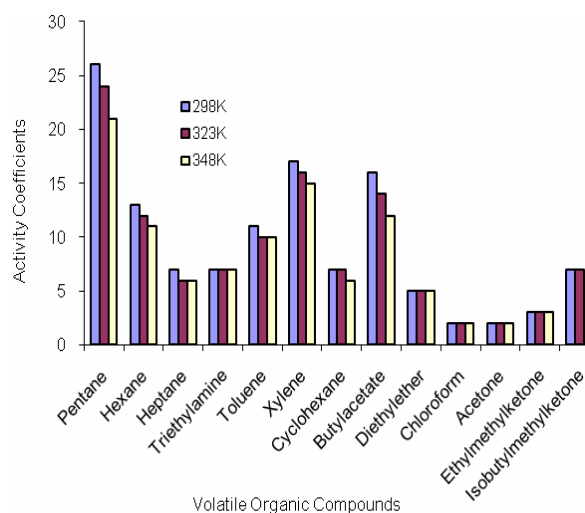


Fig. 1 Effective temperature (K) dependence in propylene glycol

The differences in solubility of the volatile organic compounds in glycols and biodiesel is mainly due to polarity variation. Organic compounds can be arranged in order of increasing polarity as alkanes, ethers, esters, amines, aldehydes, ketones, alcohols, carboxylic acids and amides. Glycols are polar with two hydroxyl ends which promote high solubility of compounds with large dipole moments such as butylacetate, diethylether, chloroform, acetone, ethylmethylketone and isobutylmethylketone. The high solubility of triethylamine in glycols is mainly due to hydrogen bonding. Therefore the differences in solubility is mainly due to polarity and the fact that "like dissolves like". In spite of its many successful applications, the UNIFAC model does have its limitations. Some of its major limitations [13] are: The activity coefficient approach limits the original UNIFAC to applications below 15 atm in pressure. The temperature range of UNIFAC's applicability is between 275 to 475K. Poor results are often obtained when UNIFAC is used for the prediction of activity coefficients at infinite

dilution (γ^∞), excess enthalpy (H^E) or for systems with components that are different in size. It has been found that UNIFAC with parameters based on vapour – liquid equilibrium data does not yield quantitative predictions of liquid – liquid equilibria. Owing to the solution of groups assumption, UNIFAC does not distinguish between isomers. Proximity effects cause large deviations between experimental and predicted phase behaviour. Proximity effects occur when two or more strongly polar groups are situated on the same or adjacent carbon atoms, for example, the –OH group in a glycol. Non-condensing gases are not included in the UNIFAC. Electrolytes and polymers are not included in the UNIFAC.

In order to improve the UNIFAC model, a large amount of experimental data for infinite dilution activity coefficients at various temperatures is needed to obtain the group interaction parameters. Also the molecules of ethylene, propylene, butylene glycol and polyethylene glycol may also be treated as special groups and their interaction parameters with other groups can be obtained from experimental data. To improve the UNIFAC predictions for systems with components that differ in size, the authors suggest the use of different modifications of UNIFAC's combinatorial part such as [5], [6], [14], [15]. The authors also recommend the use of temperature dependent interaction parameters in the residual part.

VII. CONCLUSION

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, prediction procedures should be implemented while accurate fluid phase equilibrium data should be obtained from experiment.

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NOMENCLATURE

a_{mn} = UNIFAC group interaction parameter between groups n and m

B_{11} = second virial coefficient of solute in the gas state

g^E = molar Gibbs excess energy

P = total pressure

P_i^o vapour pressure of pure solute i

Q_i = relative van der Waals surface of component i

Q_k = relative van der Waals surface of component k

R = gas constant

r_i = relative van der Waals volume of component i

R_k = relative van der Waals volume of structural group k

T = temperature, K

v_i^o - solute molar volume

x_i = mole fraction component i in the liquid phase

X_m = group mole fraction of group m in the mixture

y_i = mole fraction of component i in the vapour phase

Greek Symbols

Γ_k = group activity coefficient of group k in the mixture

$\Gamma_k^{(i)}$ = group activity coefficient of group k in the pure substance

θ = molecular surface area fraction

ϕ = molecular volume fraction

γ_i = activity coefficient of component i

v_k^i = number of structural groups of type k in molecule i

Ψ_{nm} = UNIFAC group interaction parameters between groups n and m

Indexes

c = column

C = combinatorial

E = excess quantity

i = component i

R = residual part

∞ = at infinite dilution

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