

## Henry's Constants Prediction Study of VOC in Several Types Solvents by UNIFAC-FV

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**Abstract.** Absorption of hydrophobic volatile organic compounds (VOC) such as toluene, was studied. In order to characterise the absorption capacity of toluene/oil solvent systems, the Henry's constant (H) was determined. Prediction of Henry's constants are also carried out using UNIFAC-FV model which is known to be suitable for hydrocarbon gases and high-boiling point hydrocarbon solvent.  $\text{kg/cm}^2$ ,  $220 \text{ kg/cm}^2$  dan  $260 \text{ kg/cm}^2$ .

**Kata kunci :** VOC, oil, Hendry's constant, UNIFAC-FC and toluene

### 1 Introduction

Nowadays, many industries generate malodorous and/or toxic volatile organic compounds (VOC's). Because the distance separating residential and industrial areas has been shortening, odour nuisance has grown. Thus authorities receive more and more complaints from communities. At present, several processes are available to remove odorous compounds at low concentration: chemical scrubbing, biological treatment and adsorption. Despite being one of the most commonly used process in gas recovering, adsorption can not be considered as a final treatment but only as a pollution relocation and/or concentration step. Therefore, it requires additional treatments such as thermal desorption and thermal oxidation. Concerning the chemical way, scrubbing is mainly processed with an aqueous solution (acidic, basic, oxidant) because the targeted compounds are more or less soluble in water. The gaseous compound is transferred into the liquid scrubbing solution, and then removed by chemical reactions. The mass transfer rate is enhanced by the chemical reaction taking place in the liquid phase. However, some VOC's are not very soluble in water (called hydrophobic VOC's) and their mass transfer from the gas phase to the aqueous phase is not easy to achieve, even with the help of chemical reactions. As a consequence, the removal efficiencies remain very low. Because of their hydrophobic character, the efficiency of biological treatment of such compounds is also limited. To the best of our knowledge, there is yet no process that can successfully remove hydrophobic VOC's at low concentration from exhausted industrial gas streams.

In our studies, VOC is represented using toluene. We presume that a type of oil will be a suitable solvent to scrub-out the of VOC. In this paper, we report our theoretical study to predict the absorption capacity of interesting solvents based on the solubility of gas in an infinite dilution. In this case, the absorption capacity is represented using Henry's constant which may be predicted using a thermodynamic method.

### 2. Thermodynamic Background

Solubility as a fundamental factor in the absorption capacity of oil for low boiling point tars has been studied extensively for various volatile organic matters<sup>[1, 2, 3, 4, 5, 6]</sup>. Solubility of gas in liquid may be expressed as follows:

$$y_i P = H_i w_i \quad (1)$$

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Since effect of the pressure on Henry's constant is negligible at low pressures of less than 2 atm. The dimensionless constant  $H$  defined by M.-D. Vuong, et.al.<sup>[1]</sup> with following equation:

$$C_{i,G} = H^* \cdot C_{i,L} \quad (2)$$

In both equations, Henry's constant can be calculated from the measurements on mol fraction of solute in the gas phase ( $y_i$ ), total pressure ( $P$ ), weight fraction of solute in liquid phase ( $w_i$ ), molar concentration of solute in gas and liquid phase ( $C_{i,G}$  and  $C_{i,L}$  respectively), all at the equilibrium conditions. Typical values of Henry's constant for toluene in several solvents are presented in Table 1. The higher  $1/H^*$  (dimensionless) or the lower  $H$  (weight-fraction Henry's constant, Equation 1) is the more soluble toluene in the respective solvents.

Table 1 Henry's constant of toluene in four solvents<sup>[1]</sup>

Solvent	$1/H^*$ (dimensionless)	$H$ (atm/weight frac.)
	Equation 2	Equation 1
di-(2-ethyl)hexyladipate (DEHA)	2821	0.0794
n-Heksadecane	990	0.1894
Oleyl alcohol (70%)	1637	0.1324
Water	4	60.8695

## 2.1 UNIFAC FV

A number of empirical approaches to the estimation of  $H$  at low pressure are available using group/bond contribution or structural parameters. Promising methods for correlation at ambient condition are those making use of the above relationships for activity or fugacity coefficients for dilute aqueous dilution. Limiting activity coefficients are popular in engineering applications (Sandler, 1996) and lead directly to  $H$  after a combination with vapor pressure. The weight-fraction Henry's constant,  $H_1$ , can be given thermodynamically by

$$H_1 = \gamma_1^\infty \frac{M_2}{M_1} f_1^{oL} \quad (2)$$

where  $\gamma_1^\infty$  is the activity coefficient at infinite dilution,  $M_1$  and  $M_2$  are the molecular weights, and  $f_1^{oL}$  is the fugacity of pure solute in the liquid state. The activity coefficient at infinite dilution can be estimated based on the UNIFAC-FV model (Oishi and Prausnitz, 1978) and presented in the following expression of the weight-fraction Henry's constant<sup>[3]</sup>:

$$\begin{aligned} \ln H_1 = & \ln f_1^{oL} + \ln \frac{r_1'}{r_2'} + \frac{z}{2} M_1 q_1' \ln \frac{r_2' q_1'}{r_1' q_2'} - \frac{z}{2} M_1 q_1' \ln \frac{r_1' q_2'}{r_2' q_1'} + \dots \\ & 3C_1 \ln \left[ \left( \frac{-\frac{2}{v_1^3} - 1}{v_1^3 - 1} \right) / \left( \frac{-\frac{2}{v_1^3} - 1}{v_1^3 - 1} \right) \right] - c \left( \frac{v_1}{v_2} - 1 \right) \left( 1 - \frac{1}{v_1^3} \right)^{-1} + \dots \\ & \sum_k v_k^{(i)} * (\ln \Gamma_k^{(m)} - \ln \Gamma_k^{(i)}) \end{aligned} \quad (3)$$

Parameters  $r_i'$  and  $q_i'$  are relative molecular volume and surface area respectively. They can be calculated using the following equation from the sum of molar group volume and group surface area parameters ( $R_k$  and  $Q_k$  in Table 2).

$$r_i' = \frac{1}{M_i} \sum_k v_k^{(i)} R_k \quad (4)$$

$$q_i' = \frac{1}{M_i} \sum_k v_k^{(i)} Q_k \quad (5)$$

Parameter  $v_k^{(i)}$  is the number of groups of type  $k$  in molecule  $i$ .

Table 2 Group volume and surfaces area parameters <sup>[11]</sup>

Main grup	Subgrup	$k$	$R_k$	$Q_k$
1 CH <sub>2</sub>	CH <sub>3</sub>	1	0,9011	0,848
	CH <sub>2</sub>	2	0,6744	0,540
	CH	3	0,4469	0,288
	C	4	0,2195	0,000
2 C=C	CH=CH	6	1,1167	0,867
3 ACH	ACH	10	0,5313	0,400
4 ACCH <sub>2</sub>	ACCH <sub>3</sub>	12	1,2663	0,968
5 OH	OH	15	1,0000	1,200
9 CH <sub>2</sub> CO	CH <sub>2</sub> CO	20	1,4457	1,180
13 CH <sub>2</sub> O	CH <sub>2</sub> O	26	0,9183	0,780
	CH-O	27	0,6908	0,468

The last term in equation (1) is the residual activity coefficient due to interaction among groups. The group residual activity coefficient,  $\Gamma_m^i$  is calculated using the following equations.

$$\ln \Gamma_k = M_k Q_k' \left[ 1 - \ln \left( \sum_m \theta_m' \Psi_{mk} \right) - \sum_m \left( \frac{\theta_m' \Psi_{km}}{\theta_m' \Psi_{mm}} \right) \right] \quad (6)$$

where

$$\theta_m' = \frac{Q_m' W_m}{\sum_n Q_n' W_n} \quad (7)$$

$$Q_k' = \frac{Q_k}{M_k} \quad (8)$$

and

$$\Psi_{jk} = \exp \left( - \frac{a_{jk}}{T} \right) \quad (9)$$

The group area parameter per gram  $Q_k$  is defined by  $Q_k/M_k$  is the weight fraction of group  $m$ . The group-interaction parameters  $a_{mn}$  and  $a_{mm}$  (having units of degrees Kelvin) are factors for temperature dependency of interaction (see Table 3). While the group residual activity coefficient of group  $k$   $\Gamma_k^{(i)}$  in equation (6) is a solution containing only molecules of type  $i$ .

The reduced volume in equation (10) are given by

$$\bar{v}_1 = \frac{v_1}{15,17br_1'} \quad (10)$$

$$\bar{v}_2 = \frac{v_2}{15,17br_2'} \quad (11)$$

where  $v_1$  and  $v_2$  are, the volume per gram of tar model and that of solvent when equilibrium condition. In the equations (10) and (11), the characteristic parameters are usually:  $b = 1.32$  for alkanes and 1.18 for water as solvents (Antunes and Tassios, 1983). The value of  $b$  is 1.4 for various organic compounds as solvent (Nocon et al., (1983)) and  $z = 10$  [2].

Table 3 The group-interaction parameters  $a_{mn}$  and  $a_{nm}$  (K)

m\n	1	2	3	4	5	6	7	9
1	0	-200	61,13	76,5	986,5	697,2	1318	476,4
2	2520	0	340,7	4102	693,9	1509	634,2	524,5
3	-11,2	-94,78	0	167	636,1	637,3	903,8	25,77
4	-69,7	-269,7	-146,8	0	803,2	603,2	5695	-52,1
5	156,4	8694	89,6	25,82	0	-137,1	353,3	84
6	16,51	-52,39	-50	-44,5	249,1	0	-181	23,39
7	300	692,7	362,3	377,6	-229,1	289,6	0	-195,4
9	26,76	-82,92	140,1	365,8	164,5	108,7	472,5	0

## 2.2 Pseudo-Component

Vegetable oils are essentially mixtures of saturated and unsaturated triacylglycerides (TAGs). It is difficult to know the exact distribution of the fatty acid chains in vegetable oils. One possible solution to the problem is representing the oil as a mixture of simple TAGs (tripalmitin, triolein, etc.) in accordance with the fatty acid composition of the natural oil. In this this work, we used another alternative by means of representing the oil by a single pseudo-component having the same molecular weight and degree of unsaturation to the original oil.

In this work, the natural oil is represented by a single pseudo-triacylglyceride with the following molecular structure [7]:



The term in the square brackets represents the triglyceride functional group. The values of  $m$  and  $n$  reproduce molecular weight and degree of un-saturation of the natural oil, and are calculated from the fatty acid composition of the oil, as shown in Table 4.

Table 4. Typical fatty acid composition

Fatty acid	$x_i$		$n_i$	$m_i$
	sunflower oil [7]	palm oil [12]		
Palmitic	0.0670	0.4806	42	0
Stearic	0.0334	0.0430	48	0
Oleic	0.2583	0.3781	42	3
Linoleic	0.6391	0.0983	36	6
Linolenic	0.0022	0	30	9

The values of  $n$  and  $m$  in the pseudo-triacylglyceride, which represents the natural sunflower oil and palm oil, are calculated as follows:

$$n = \sum_{i=1}^N n_i x_i \tag{12}$$

$$m = \sum_{i=1}^N m_i x_i \tag{13}$$

where  $N$  is the number of fatty acids present in the natural oil and  $i$  is the fatty acid molecule.

### 2.3 Calculation

When the UNIFAC-FV model is applied to natural fatty oils, it is necessary to calculate the group composition of the oil from information on its fatty acid composition. In summary, the calculation to estimate Henry's constant are follows equation (10) until equation (11).

### 3 Result and Discussion

Based on experimental data, the values of the Henry's constant for each couple toluene/solvent are reported in Table 6. The lower weight-fraction Henry's constant is, the more important the tar model solubility in the solvent.

Table 5 Saturation concentrations  $C_L$  for different concentrations in air

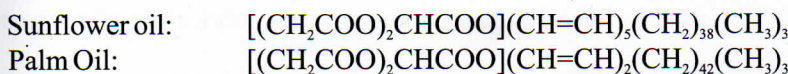
(1)	System (2)	303 K		333 K	
		$C_{G,out}$ (mg m <sup>-3</sup> )	$C_L$ (g L <sup>-1</sup> )	$C_{G,out}$ (mg m <sup>-3</sup> )	$C_L$ (g L <sup>-1</sup> )
Toluene	Sunflower Oil	6786	1.0454	6023	0.951
	Palm Oil	6713	1.2570	6580	1.1032
	Lubrication Oil	6709	1.3899	6342	1.2731
	water	2830	0.0056	6225	0.0448

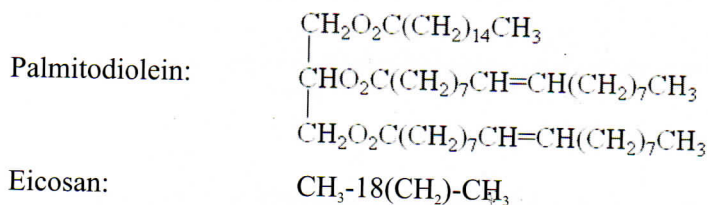
Table 6 Weight-fraction Henry's constant from experimental and literature

(1)	System (2)	$H$ exp. (atm/ weight frac.)		$H$ literature (atm/weight frac.)
		303 K	333 K	298 K
Toluene	Sunflower Oil	1.468	1.525	-
	Palm Oil	1.277	1.353	-
	Lubrication Oil	1.086	1.122	-
	water	19.650	35.560	60.869 <sup>[1]</sup>
	heksadecane	-	-	0.189 <sup>[1]</sup>
	oley alcohol (70%)	-	-	0.132 <sup>[1]</sup>

A recapitulative of experimental and literature given on Table 6, lubrication oil appears clearly to be better absorbent than others as it has high capacity of toluene absorption. System of toluene-water of experimental result compared with literature data, there are great deviation.

Predicted Henry's constant generally the VLE for the oil solution systems at infinite dilution is very difficult. The weight-fraction Henry's constant of systems were predicted by fixing  $C_1 = 1$  (equation (9)) and  $b=1.18, 1.32$  and  $1.4$  for water (equations (17) and (18)), alkanes and different organic compounds as solvent<sup>[3]</sup>, respectively. Molecule structure of sunflower oil and palm oil represented by a single pseudo-triacylglyceride with the following molecule structure:





For molecule structure of palm oil can be represented by palmitodiolein and lubrication oil by eicosan<sup>[10]</sup>.

Table 7 Weight-fraction Henry's constant from prediction with C1 =1; b=1.18 , 1.32 and 1.4 for water, alkanes and different organic compounds as solvent, respectively

(1)	System (2)	H UNIFAC-FV (atm/weight frac.)		
		298 K	303 K	333 K
	Sunflower Oil (pseudo- triacylglyceride)	-	0.095	0.379
Toluene	Palm Oil (pseudo- triacylglyceride)	-	0.130	0.444
	Palm Oil (palmitodiolein)	-	0.145	0.484
	Lubrication Oil (eicosan)	-	16	79
	water	59.2	-	-
	heksadecane	0.102	-	-
	oley alcohol (100%)	0.326	-	-

The results of prediction by UNIFAC-FV were tabled on Table 7, compared with experimental values (Table 6) has great deviation. To obtain better results, it requires the parameters of UNIFAC-FV model in order to correlate with the experimental data. Therefore, to determine the new parameters C1 of equation (9) and b of equations (11) and (12) was carried out by minimizing the sum of squares between experimental data of Henry's constant and those calculated by the UNIFAC-FV model. The new parameters were given in Table 8.

Table 8 External degree of freedom (C1) and b parameter of systems toluene(1)-solvent(2)

(1)	System (2)	C <sub>1</sub>			b		
		298 K	303 K	333 K	298 K	303 K	333 K
	Sunflower Oil (pseudo- triacylglyceride)	-	2.003	2.016	-	1.929	1.956
Toluene	Palm Oil (pseudo- triacylglyceride)	-	1.006	1.029	-	1.968	2.060
	Palm Oil (palmitodiolein)	-	1.014	1.040	-	1.974	2.071
	Lubrication Oil (eicosan)	-	1.298	1.311	-	1.315	1.408
	water	1.001	-	-	1.184	-	-
	heksadecane	1.134	-	-	1.631	-	-
	oley alcohol (100%)	1.002	-	-	1.259	-	-

#### 4 Conclusion

This paper aimed to review VOC model absorption knowledge to determine a absorption capacity several types of oil as absorbent. From experimental data, lubrication oil as the most attractive-

absorbent. To obtain better result of prediction by UNIFAC-FV, the parameter C1 and b for oil systems could be adjusted by minimizing the sum of squares between experimental data and those calculated by UNIFAC-FV. .

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