

A Simple Static Headspace Method for Phase Equilibrium Measurement

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Abstract—In this paper, Henry's law constants (H) and infinite dilution activity coefficients (γ^∞) of 13 selected volatile organic compounds (VOCs) of environmental importance in silicon oil are presented. These were measured using an innovative simple headspace chromatographic technique developed in this study. In order to test the reliability of this method, the effect of liquid depth and shaking time on equilibrium establishment was tested. The effect of VOC concentration in terms of volume injected is also presented. The influence of temperature on the phase equilibrium was studied using the Van't Hoff relationship. Measurements were done at different temperatures to permit transport calculations for different seasons and also to allow temperature variation of the physical properties of the organic compounds to be evaluated. Great effort was taken to ensure best possible accuracy, trace and rectify possible sources of error. The results compare very well to those obtained from the dynamic gas liquid chromatographic technique by the same authors and those found in literature. This study provides a fast and cheap simple static headspace method for measuring phase equilibrium at infinite dilution. This is an innovative practical technique which can be applied in solving environmental engineering problems in particular the abatement of volatile organic compounds.

Keywords—Activity coefficient, environmental, Henry's law constant, Infinite dilution, static headspace, transport calculations

I. INTRODUCTION

THIS work is a continuation of our investigation of thermodynamic properties of volatile organic compounds in polymeric solvents. Volatile organic compounds (VOCs) are produced and released into the environment from several domestic and industrial processes. VOCs have high mobility and volatilities which make them significant contributors to air pollution problems. These properties allow them to be present in every media in the

environment including air, water and soil [1], [2]. Polymeric solvents such as silicon oil chemically known as polydimethyl siloxane (PDMS) can play a crucial role in key separation processes such as absorption of VOCs from contaminated air streams. Due to its unique properties such as stability at high temperatures, non flammability and negligible vapour pressure, silicon oil can be used in this separation process. For silicon oil to be used effectively as an absorbent it is essential to know how it interacts with different solutes. The important measure of this property is given by the activity coefficient at infinite dilution, (γ^∞), which describes the non-ideality of the chosen species in a mixture or Henry's law constant (H) representing air – solvent partitioning in dilute solution. The activity coefficient at infinite dilution is especially important because it describes the extreme case in which only solute – solvent interactions contribute to non ideality. Some of the most important properties controlling the partitioning between different environmental compartments encountered in literature are solubility, partition coefficient, Henry's law constant, [3] and infinite dilution activity coefficients [4], [5].

Infinite dilution studies are crucial in that environmental concern focus on the entirely dilute regions, parts per million. In most separation processes, this is the most difficult and expensive part of separation. Also the greatest deviation from ideal behaviour is exhibited here. Infinite dilution studies are also crucial in obtaining high purity products. Henry's law constant or coefficient (H) allowing for temperature dependence expresses the affinity of a solvent toward a VOC in terms of partial pressure P_i of the VOC with its mole fraction x_i in solvent. For environmental consideration at infinite dilution this expressed as

$$H = \lim_{x_i \rightarrow 0} \frac{P_i}{x_i} \quad (1)$$

Henry's law constant is an equilibrium partitioning coefficient reflecting the relative volatility of a particular compound indicating its behaviour and fate in the environment as well as the applicability of potential treatment methods such as absorption and stripping.

In literature Henry's law constant is expressed in many different units and the six commonly encountered definitions are related through (2) which is used to compare data from various sources.

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$$\begin{aligned}
 H_{cc} &= H_{yx} \left(\frac{\rho G}{MW_G} \right) \left(\frac{MW_L}{\rho_L} \right) = H_{px} \left(\frac{1}{RT} \right) \left(\frac{MW_L}{\rho_L} \right) = H'_{px} \left(\frac{1}{RT} \right) \left(\frac{MW_L}{\rho_L} \right) \\
 &= H_{pc} \left(\frac{1}{RT} \right) = H'_{pc} \left(\frac{1}{RT} \right)
 \end{aligned}
 \tag{2}$$

In this study the following dimensional form of H is used (3).

$$H_{pc} = \frac{y_i P_T}{C_L} \left[\frac{kPam^3}{mole} \right]
 \tag{3}$$

The activity coefficient at infinite dilution is a crucial parameter in the prediction of phase partitioning of a solute. It also one of the basic thermodynamic properties used to obtain the adjustable parameters in various activity coefficient models of multi – component systems. In most cases it is used for the characterization behaviour of a single solute molecule completely surrounded by solvent molecules, which represent the maximum non ideality of the solute behaviour in solution. This means that the activity coefficient (γ^∞) of a solute provides specific information about the molecular interactions between the solute and the solvent, eliminating solute – solute interactions. The infinite dilution is also an indicator of partitioning of dilute contaminants in the environment and it can also be used to predict properties related to the environmental fate for example Henry's law constant and solubility in different absorbents. Activity coefficients are correction factors which can be applied to Raoult and Henry's laws to account for deviations from ideal behaviour. In assessing the solubility of gases and vapours in solutions the crucial factor alongside the vapour pressure of the pure substance is the activity coefficient of the dissolved substance, there is an inverse of proportionality between the solubility and the activity coefficient of a chemical. In absorption operations low activity coefficients are highly desirable.

The activity coefficient at infinite dilution γ_i^∞ is calculated as (4)

$$\gamma_i^\infty = \frac{P_i}{x_i P_i^o}
 \tag{4}$$

Where p_i , p_i^o and x_i are the VOC partial pressure, vapour pressure at temperature of interest and liquid mole fraction respectively. The temperature dependence of H_i and γ_i^∞ can be expressed by an exponential function of reciprocal absolute temperature (van't Hoff relation).

$$\ln H_i = A + \frac{B}{T(K)}
 \tag{5a}$$

$$\ln \gamma_i^\infty = A + \frac{B}{T(K)}
 \tag{5b}$$

In this work we developed a simple headspace chromatographic technique for measuring Henry's law constants and infinite dilution activity coefficients for binary solute mixtures. The solute – solvent systems are binary mixtures of silicon oil and the following volatile organic compounds pentane, hexane, heptane, triethylamine, toluene, xylene, cyclohexane, butyl acetate, diethyl ether,

chloroform, acetone, ethyl methyl ketone and isobutyl methyl ketone. These binary mixtures represent several important functional groups covering a wide range of solubility and volatility characteristics typical in that found in industrial hazardous waste. The volatile organic compounds studied here are from the following families; alkanes, halogenated hydrocarbons, aromatics, ethers, amines and cyclic hydrocarbons. In selecting a suitable solvent for waste gas problems, the following criteria are considered: high absorption capacity for the separating component, selectivity with reference to other gases, low toxicity and low volatility [6]. The absorption capacity is influenced by the interactions between VOC and solvent molecules which can result in possible affinity or mutual repulsions. PDMS can be used as a scrubbing medium in waste air scrubbing. It is highly suitable for solvent vapours from waste air, especially in the absorption of alcohols, esters and chlorinated hydrocarbons, aromatics and ketones. Owing to its high boiling point and stability up to 150°C, it can be desorbed at standard temperature and pressure for solute recovery.

Comprehensive reviews of experimental methods used to determine Henry's law's constants and activity coefficients at infinite dilution were given [7] - [9] and these include; Equilibrium Partitioning in Closed Systems (EPICS) [10] – [17]; Sequential phase equilibrium [18]; pressure difference [19] – [21], differential static cell [22], [23], GLC [24] – [29], Headspace [9], [30] – [32], Direct [33] – [38] and purge [39], [40].

The simple headspace gas chromatography is an analytical technique used to measure the vapour phase composition of a volatile liquid or solid component in equilibrium with a solvent in a sealed vessel. The simple headspace method Evanson [32] was developed to determine the effect of sodium hypochlorite on the vapour liquid equilibrium of styrene monomer and water. In this work this method is improved to ascertain equilibrium establishment, study the effect of liquid depth, temperature control and use of shaker flasks for calibration as compared to the traditional air bags. This method makes use of the calibration curve for the calculation of headspace concentration of a volatile organic compound. When using the simple headspace method the following should be specified: experimental temperature, flask volume, volume of solvent, VOC injected into flask, volume of gas injected into GC, total pressure, molecular weight and density of VOC, universal gas constant, peak area after equilibrium and the gradient of the calibration curve. Volatile organic compounds can be abated using the following methods; absorption, adsorption, condensation, combustion, biological and membrane technology systems. This paper presents the essential equilibrium necessary for physical absorption and stripping processes.

II. METHODS

A. Materials

All the thirteen volatile organic compounds listed in table 1) were obtained from Merck Ltd with a stated purity greater than 99% and were used without further purification. Silicon oil of 10cs viscosity with a corresponding average molecular weight of 1000 was obtained from Dow Corning USA.

TABLE I
 SOLUTE DESCRIPTION AND CODE

Code no.	Compound	Code no.	Compound
1	n - pentane	8	butyl acetate
2	n - hexane	9	diethyl ether
3	n - heptane	10	chloroform
4	triethylamine	11	acetone
5	toluene	12	ethylmethylketone
6	xylene	13	isobutylmethylketone
7	cyclohexane		

B. Procedure

The equipment consisted of an enclosed system of 594 ml conical flask with a glass side arm. The flask was closed on top with a rubber stopper and with a subseal on the side arm. At start up a fixed volume of silicon oil (200 ml) was added into the flask and the desired volume of the volatile organic compound was injected through the subseal. The flask was then subjected to manual shaking for a minute. Afterwards, the flask was placed in a water bath shaker for an hour to ensure good mixing and maintain the required temperature. Five flasks were used for each VOC concentration and two injections were made from each flask after 1 hr shaking time. An air tight syringe was used to take a sample from the flask. A gas sample volume of 0.5 ml was injected into the GC.

C. Calibration Curves

The simple headspace method relies on the availability of accurate and reproducible calibration equations in order to determine the concentration in both the gas and liquid phases. The shaker flasks were thoroughly cleaned and then oven dried. Known volumes of VOC corresponding to the required parts per million were injected into the flasks. The VOCs were allowed to vaporize in the water bath shaker at 303K. Gas samples were withdrawn using a gas tight syringe and injected into the GC. This procedure was repeated for all the concentrations of interest. Calibration curves were obtained by plotting concentration (kg/m³) against peak area in units.

D. Chromatographic Conditions

A Perkin Elmer 8500 Gas Chromatograph equipped with a flame ionization detector was used for gas sample analysis. Conditions were as follows: Carrier gas was helium at a flow rate of 35 ml/min, Injector and detector temperature at 250°C and Column diameter of 1/8 inch of stainless steel packed with 30% Carbowax P60 – 80 mesh.

III. RESULTS AND DISCUSSION

The activity coefficients at infinite dilution of the thirteen volatile organic compounds were measured with high reproducibility and precision. The results obtained in this work agree very well with those obtained by the same authors through the dynamic gas liquid chromatographic technique (GLC) [28], [29], [41], those reported [42] using GLC and [44] employing the GCLF – EOS and UNIFAC – FV. The good agreement found between static headspace with experimental and predictive methods indicate that it can be successfully used to simplify experimental procedures and reducing costs. When full attention is paid to the experimental set up and procedures, the simple

headspace method can be of value in phase equilibrium studies. In order to obtain each value of the activity coefficient five flasks were used and two injections made from each flask. Therefore the peak area used in the calculation is an average of ten (10) measurements. The low activity coefficients and Henry's law constants indicate that silicon oil is good absorbent for the selected volatile organic compounds. Compared to water and other polymeric solvents in literature, the thermodynamics of VOCs in silicon oils dictates an easy absorption process while stripping will be difficult. It was the objective of this work to find the minimum time period required to achieve equilibrium. This was tested by varying shaking times in the water bath from 0.5 to 24 hours. From the results shown in Fig. 1, it was found that half an hour was enough for equilibrium establishment. Using various volumes of silicon oil from 200 to 500 ml tested the effect of liquid depth on the phase equilibrium. The results shown in Fig. 2 shows that varying amount of solvent within the experimental range did not affect the result; therefore 200 ml was used in this work for economic reasons.

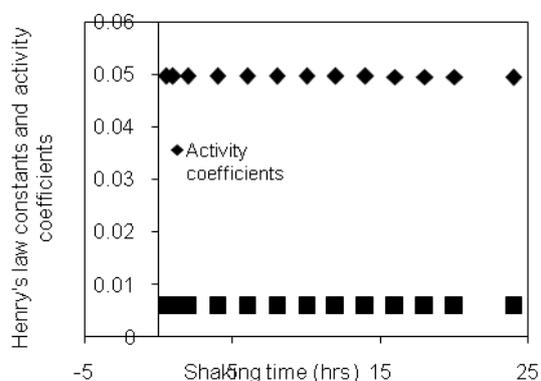


Fig. 1. Effect of shaking time on Henry's law constants and activity coefficients.

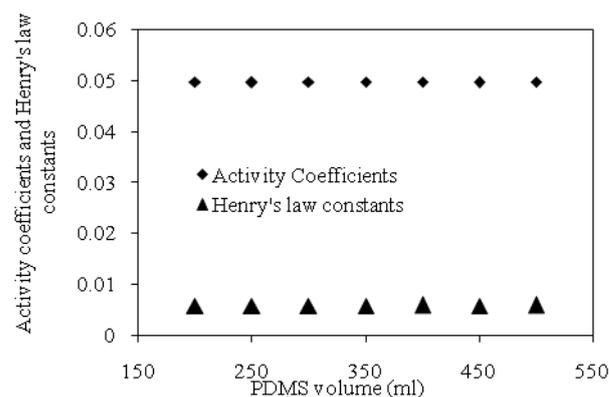
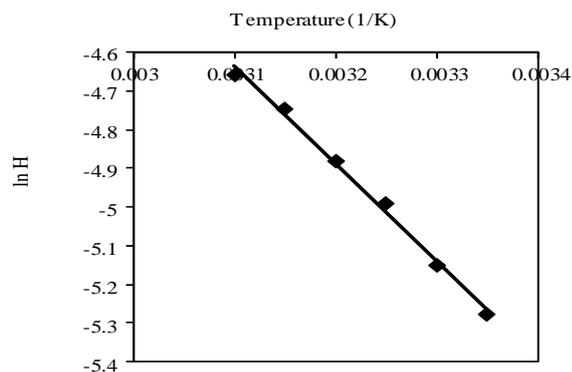
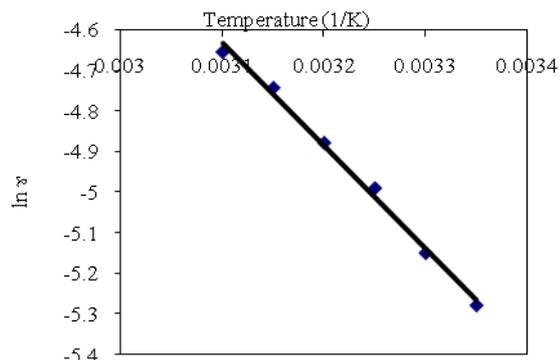


Fig. 2. Effect of PDMS volume on Henry's law constants and activity coefficients.

The choice of optimum temperature for an absorption process requires knowledge of temperature dependence of the activity coefficients. Typical Van't Hoff plots for acetone are shown in Figs. 3a and 3b.



(a)

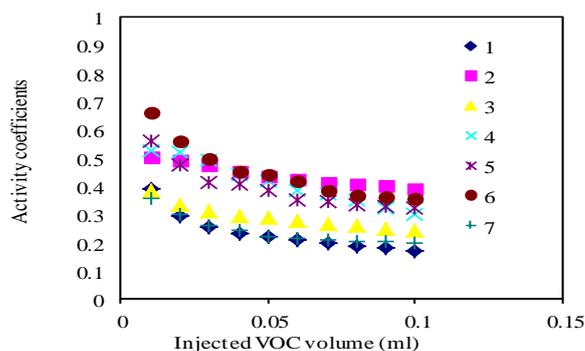


(b)

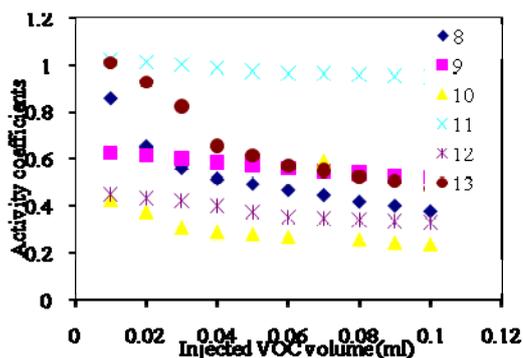
Fig. 3. Typical van't Hoff Plots (acetone) (a) Henry's law constant (b) Activity coefficient

The behaviour of H and γ with temperature variation in this study is similar to the observation of [44] – [47]. The results indicated that the higher the temperature, the higher the activity coefficients. This behavior is very good for desorption processes since the higher values at higher temperatures would ease the regeneration. It appears that the activity coefficients and Henry's law constants increase with increase in temperature. The temperature dependence means that regeneration and recovery of absorbent and VOCs can be achieved by increase in temperature during the desorption process.

Typical activity coefficients or Henry's law constants versus mole fraction (added volume) plots are shown in Figs. 4a, 4b, 5a and 5b. In all cases the activity coefficients or Henry's law constants increase with the increase in dilution, this permits the design of separation processes at these conditions of environmental concern.

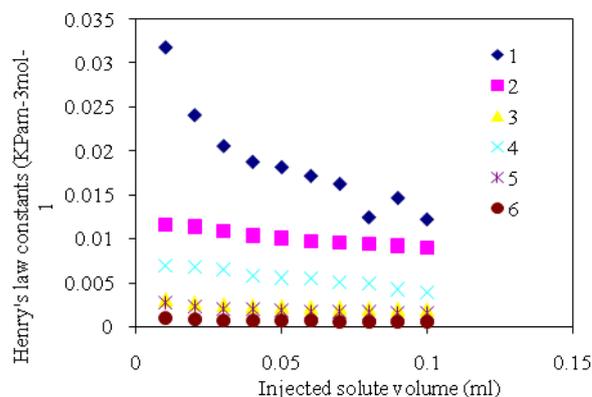


(a)

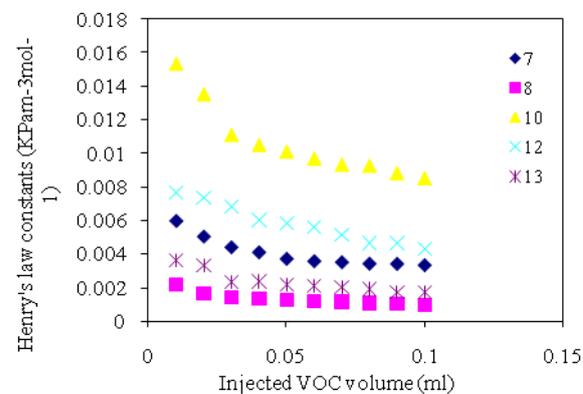


(b)

Fig. 4 (a) and (b) Concentration dependence of activity coefficients in 10cs PDMS



(a)



(b)

Fig. 5 (a) and (b) Concentration dependence of Henry's law constants in 10cs PDMS

TABLE II
ACTIVITY COEFFICIENTS AT INFINITE DILUTION (MOLE AND WEIGHT FRACTION BASED) AND HENRY'S LAW CONSTANTS IN PDMS (MW =10000)

OC	Static headspace (this work)			GLC (Prev)		Literature (Values & Methods)
	Mol frac	Wfrac	H (KPa mol)	Mol frac	Wfrac	
1	0.388	5.384	0.0318	0.384	5.323	6.066 (static)
2	0.503	5.833	0.0116	0.458	5.317	6.003 (static)
3	0.539	7.34	0.00429	0.539	5.382	6.109 (static)
4	0.525	5.187	0.00689	0.392	3.878	
5	0.56	6.08	0.00274	0.585	6.354	5.363 (static)
6	0.805	7.587	0.00113	0.617	5.808	
7	0.397	4.72	0.00674	0.399	4.378	5.378 (GLC)
8	0.86	7.401	0.00213	0.748	4.35	
9	0.624	8.413	0.633	0.359	4.489	
10	0.425	3.557	0.0153	0.374	3.133	3.366 (GLC)
11	1.026	17.669	0.474	0.865	14.895	
12	0.532	7.381	0.00909	0.739	10.245	
13	1.096	10.942	0.00377	0.841	8.396	

IV. CONCLUSION

Henry's law constants and activity coefficients at infinite dilution of 13 environmentally important organic compounds were measured by the simple static headspace method. This technique provides a reliable, accurate, cheap and rapid method for providing thermodynamic data of VOCs in polymeric solvents. In order to support our conclusions, improve efficiency and reliability of the simple headspace method some future investigations are required. These include continued vapour – liquid equilibrium of the same VOCs and additional representative binary systems in silicon oil, other polymeric solvents (such as biodiesel) and water. These are then compared with literature values obtained using various experimental and predictive methods. Further investigations on the temperature and concentration dependence studies involving the 13 and additional volatile organic compounds of the same families are recommended.

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