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Henry's Law Constant for Selected Volatile Organic Compounds in High-Boiling Oils

Tarun K. Poddar and Kamalesh K. Sirkar*

Department of Chemical Engineering, Chemistry and Environmental Science, New Jersey Institute of Technology, Newark, New Jersey 07102-1982

Henry's law constants of four different volatile organic compounds, namely, acetone, methanol, methylene chloride, and toluene between air and high-boiling oils were determined experimentally by the headspace-GC technique over a temperature range. The Henry's law constants were fitted as a function of temperature to an equation.

Introduction

Absorption systems are often used to remove and recover organic vapors from process air/gas streams. A high boiling and inert liquid like silicone oil is an excellent absorbent for volatile organic compounds in air (Armand et al., 1990). Silicone oil can also be used as an inert liquid phase to carry out exothermic reactions at high pressure and temperature (Lee and Foster, 1990). For analysis and/or design of any gas−liquid mass transfer process, one needs several properties. One of them is the equilibrium solubility (i.e. Henry's law constant) of the solute in the liquid phase. This work on determination of Henry's law constant was carried out during studies on removal of volatile organic compounds from air by membrane-based absorption and stripping (Poddar et al., 1996a).

Henry's law is applicable to dilute solutions and near atmospheric pressure. Carrol (1991) had discussed thermodynamic definitions and various limitations of applying Henry's law. Theoretically, one can estimate the Henry's law constant using vapor−liquid equilibrium data or by using computer models such as UNIFAC, UNIQUAC, etc. To utilize vapor−liquid equilibrium data or computer models, the physicochemical nature of the system should be well-known. Unfortunately, many liquid systems, especially environmental samples involved in the determination of partition coefficient, are not physicochemically well-defined. Moreover these techniques are quite elaborate. Hence, there is a great need for the estimation of the Henry's law constant from simple experiments without detailed thermodynamic information.

MacKay and Shiu (1981) reported three methods for the measurement of Henry's law constant. The first method uses vapor pressure and solubility data; the second method involves direct measurement of vapor phase and liquid phase concentrations, and the third method is batch air stripping. In the first method it is difficult to get reliable solubility data. In the second method there is difficulty in measuring the concentrations of the two phases accurately, especially at a low concentration. The third method, batch air stripping (MacKay et al., 1979; Hutter et al., 1994), may have a limitation of approaching equilibrium.

Simple methods based on headspace gas chromatography have been recently applied to Henry's law constant determination (Gossett, 1987; Robbins et al., 1993). Variable volume and multiple extraction are two different headspace techniques utilized for this purpose. In the present work Henry's law constants for acetone, methanol, methylene chloride, and toluene between air and two different high-boiling oils (silicone oil and Paratherm, a heat transfer oil) have been determined experimentally by the variable volume headspace technique.

Theoretical Considerations

Determination of the Henry's law constant by the static headspace technique is based on the principle of establishing thermal and chemical equilibrium within the enclosed sampling vessel when the solute is present at a low concentration. A simple material balance can be written for the equilibrium of a known volume of sample, V_o (cm^3), having an initial concentration of species i, c_{io} (mol/cm^3), as

$$V_o c_{io} = V_l c_{il} + V_g c_{ig} \qquad (1)$$

Here V_g and V_l are the headspace volume and liquid volume in the sample vial in cm^3. c_{il} (mol/cm^3) and c_{ig} (mol/cm^3) are equilibrium concentrations of organic solute in the liquid and vapor, respectively. It is assumed that there is no evaporation loss of liquid matrix during the establishment of equilibrium. Equilibrium concentrations of species i in the gas and liquid phases are related by an equilibrium constant, namely, Henry's law constant

$$H_i = c_{ig}/c_{il} \qquad (2)$$

Considering V_o is equal to V_l (completely nonvolatile matrix and evaporation of solute does not change the volume of the liquid matrix), substitution of eq 2 into eq 1 and rearrangement yield

$$\frac{1}{c_{ig}} = \frac{1}{H_i c_{io}} + \frac{1}{c_{io}}\left(\frac{V_g}{V_l}\right) \qquad (3)$$

The vapor concentration c_{ig} is directly proportional to the gas chromatograph (GC) peak area, A_p:

$$c_{ig} = R_f A_p \qquad (4)$$

where R_f is the response factor. Hence, eq 3 can be further written as

$$\frac{1}{A_p} = \frac{R_f}{H_i c_{io}} + \frac{R_f}{c_{io}}\left(\frac{V_g}{V_l}\right) \qquad (5)$$

Equation 5 suggests that a plot of $1/A_p$ versus (V_g/V_l) will give a straight line with a slope (R_f/c_{io}) and a y-intercept

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* To whom correspondence should be addressed.

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(R_f/H_ic_{io}). A value of H_i can be directly obtained by dividing the slope by the y-intercept:

$$H_i = \text{slope}/y\text{-intercept} \qquad (6)$$

This technique is known as the variable volume headspace technique.

Experimental Section

Dimensionless Henry's law constants for acetone, methanol, methylene chloride, and toluene were determined independently in two different high-boiling oils, namely, silicone oil (200 fluid, Dow Corning, Midland, MI) of 5 × 10^{-5} $cm^2 \cdot s^{-1}$ kinematic viscosity and approximate molecular weight 300 and Paratherm heat transfer fluid (NF, Paratherm Corp., Conshohocken, PA) of 0.30 $g \cdot cm^{-1} \cdot s^{-1}$ viscosity and approximate molecular weight 350. All four organic solutes obtained from Fisher Scientific, Springfield, NJ, were of HPLC grade and had purities of 99.9%+.

Sample Preparation. A fixed volume of matrix liquid was first chilled in a refrigerator to about 4 °C. A particular liquid volatile organic solute was also chilled in a similar way and then a known quantity of it was added to the oil to make a solution of known concentration in the oil. This solution was kept stirred for about 10 min. The solution thus prepared in a tightly closed conical flask was stored in the refrigerator as a stock solution. The concentrations of the solutions were in the range of 30 to 130 mg/L; thus the solutions were quite dilute. However, as discussed before, there is no need to know the concentration of the solution to determine the H_i values. All solutions and samples were prepared, handled, and stored at a low temperature (around 4 °C) to minimize error from solute losses through volatilization.

Measurement of Henry's Law Constant. Sample vials of 22 mL volume (Tekmar, Cincinnati, OH) were used for all experiments. The exact volume of any vial was measured by obtaining the difference in the mass of an empty vial and that of the same vial filled with water and then dividing the mass difference by the density of water. The volumes of the sample vials were found to be essentially constant, 22 mL ± 0.2 mL. A sample vial was prepared in the following way. The stock solution bottle was taken out of the refrigerator and kept inside an open container filled with dry ice. An empty sample vial was also kept in an open container filled with dry ice in such a way that most of the surface area of the vial was in contact with dry ice. A small volume of the stock solution of known concentration was next transferred quickly from the stock solution bottle to the chilled sample vial. The vial was then tightly sealed immediately with a Teflon-coated silicone rubber septum and crimp cap. The Teflon-coated septum prevents the escape of volatile organic solute by permeation. The exact volume of the sample transferred was measured by taking the difference in mass of the empty vial and that of the vial along with the sample and then dividing the mass difference by the density of the sample at the temperature of equilibration.

In order to find out the equilibrium time for two different sample matrices (silicone oil and Paratherm) sample vials having the same amount of sample were exposed to different heating times at the same temperature. Figure 1 shows typical time vs area count plots for different organic solutes in silicone oil and in Paratherm. After 30 to 40 min, the headspace concentration became independent of heating time. These figures not only give information about equilibration time but also show the reproducibilities of the measurements.

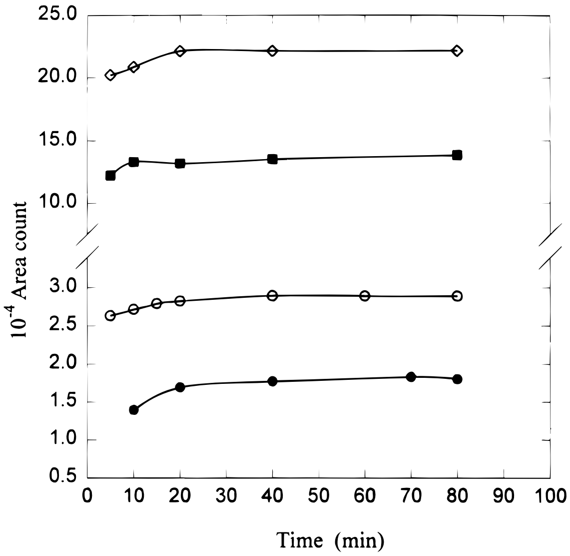

Figure 1. Time vs headspace concentrations (in terms of area count) for different volatile organic solutes: (○) acetone—silicone oil; (●) acetone—Paratherm; (◇) methanol—silicone oil; (■) methylene chloride—Paratherm. Temperature: 32 °C.

To carry out experiments according to the variable volume headspace technique, different sample vials were prepared by adding different known volumes of samples having a constant concentration of a particular volatile organic solute into each vial. A particular sample vial was then loaded into the headspace autosampler (model 7000, Tekmar, Cincinnati, OH) and allowed to equilibrate at a constant temperature. The headspace autosampler was interfaced with a GC (3400-STAR, Varian, Sugarland, TX) by means of an interfacing cable. The operating conditions of the autosampler are as follows: platen equilibrium time, 0.5 min; sample equilibrium time, 35—40 min; mixing time, 0.1 min; mixing power, 1; stabilization time, 0.5 min; vial pressure, 125.5 kPa; pressurization time, 0.15 min; pressure equilibrium time, 0.15 min; loop fill time, 0.12 min; loop equilibration time, 0.15 min; and injection time, 3—6 min. The built-in GC integrator provided output in terms of area count proportional to the vapor phase concentration in the headspace of the sample vial. Other sample vials for the same solute—oil combination were loaded into the autosampler one at a time and headspace concentrations were measured at the same temperature of equilibration. The analyses for all four organic solutes were accomplished using a 6 ft. × $^1/_8$ in. packed column (Varian Analytical Instruments, Sunnyvale, CA) having 0.3% Carbowax 20 M on Carbopack support. Flame ionization detector (FID) was used for composition measurement. Operating conditions used for analysis were 150 °C column temperature, 220 °C injector temperature, and 250 °C detector temperature. The experiments were repeated for various sample liquid volumes at the same temperature.

Once a set of data for area count versus gas to liquid volume ratio were obtained at a constant temperature, dimensionless Henry's law constants were calculated from eq 6 by making a plot according to eq 5. Experiments were also conducted to determine the Henry's law constant at different temperatures for a particular solute—oil system. The density, ρ_l ($g \cdot cm^{-3}$), of the liquid matrix is expressed as a function of temperature, t (°C), by the following equations. For silicone oil

$$\rho_l = 0.980 - 8.35 \times 10^{-4} t \qquad (7)$$

For Paratherm oil

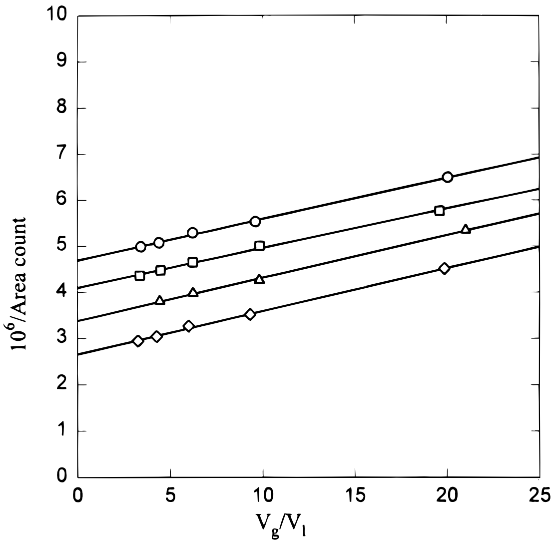

Figure 2. Plots of reciprocal of peak area vs ratio of headspace volume to liquid sample volume for determination of the Henry's law constant of acetone in silicone oil at different temperatures: (○) 25.6 °C; (□) 31.8 °C; (△) 37.8 °C; (◇) 45.9 °C.

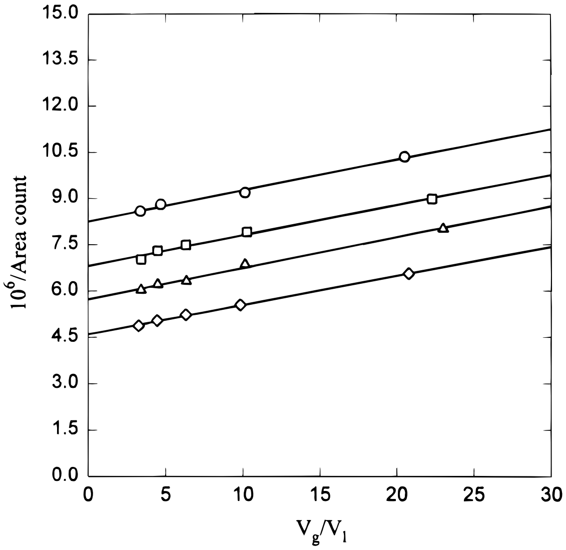

Figure 3. Plots of reciprocal of peak area vs ratio of headspace volume to liquid sample volume for determination of the Henry's law constant of methylene chloride in silicone oil at different temperatures: (○) 25.6 °C; (□) 31.8 °C; (△) 37.9 °C; (◇) 45.9 °C.

$$\rho_l = 0.879 - 4.21 \times 10^{-4}t \quad (8)$$

Results and Discussion

In the variable volume technique, the dimensionless Henry's law constant is determined by dividing the slope by the y-intercept of the linear regression of V_g/V_l and the reciprocal of the headspace peak area data. Representative plots of such linear regressions at various temperatures are shown in Figures 2 and 3. Experimental results fit the linear regression very well. Regression coefficients vary from 0.99 to 0.999. The initial concentration of a species (c_{io}) is inversely proportional to the slope of the straight line of eq 5. Almost identical values of slopes of different plots for a particular solute at various temperatures ensure constant initial concentration of the stock solution.

Henry's law constant is a strong function of temperature. At a constant pressure, the temperature dependence of Henry's law constant can be expressed by (Robbins et al., 1993; Hutter et al., 1994)

$$H_i = \exp\left(\frac{B_{H_i}}{T} - A_{H_i}\right) \quad (9)$$

where T is the absolute temperature (K) and A_{H_i} and B_{H_i} are constants which depend on the solvent−solute combination and need to be obtained from the experimental data. The constants A_{H_i} and B_{H_i} for each solute−absorbent combination were determined by linear regression of $1/T$ and $\ln(H_i)$ data. The plots of $1/T$ vs $\ln(H_i)$ for all four solutes with silicone oil and Paratherm are shown in Figures 4 and 5, respectively. The values of A_{H_i} and B_{H_i} obtained from such regression are provided in Table 1. Experimentally determined H_i values of all four solutes for both oils at different temperatures are given in Table 2. Equation 9 fits the experimental data within a maximum error of 9% and an average error of 2.5%.

The Henry's law constants for methanol in Paratherm are almost identical at different temperatures (Figure 5).

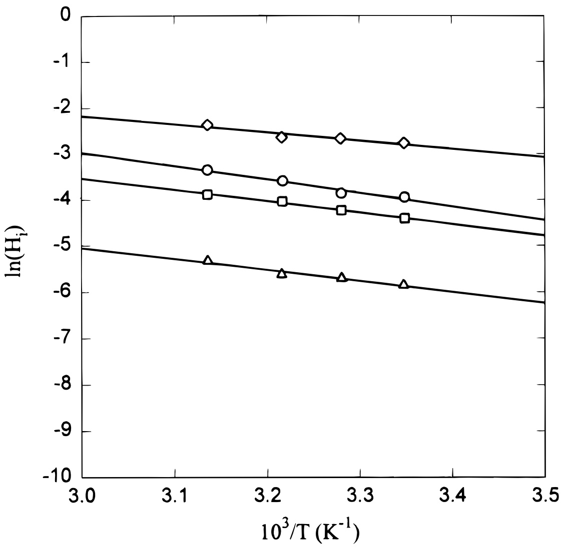

Figure 4. Variation of the natural logarithm of the Henry's law constant with the reciprocal of absolute temperature for different volatile organic compounds in silicone oil: (○) acetone; (◇) methanol; (□) methylene chloride; (△) toluene.

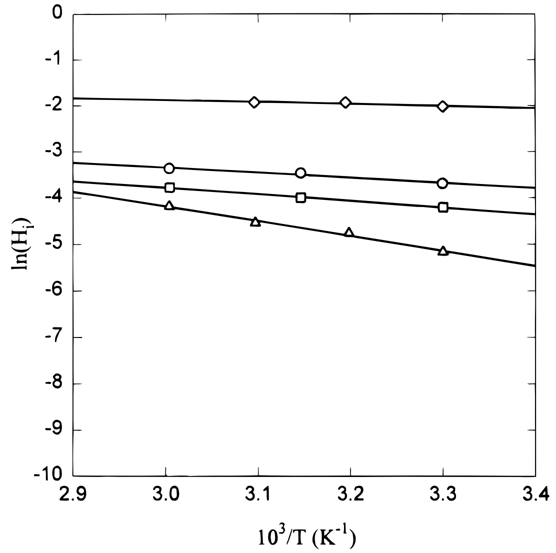

Figure 5. Variation of the natural logarithm of the Henry's law constant with the reciprocal of absolute temperature for different volatile organic compounds in Paratherm: (○) acetone; (◇) methanol; (□) methylene chloride; (△) toluene.

Table 1. Values of A_{H_i} and B_{H_i} of Eq 9

volatile organic compound	silicone oil		Paratherm oil	
	A_{H_i}	B_{H_i}	A_{H_i}	B_{H_i}
acetone	−5.878	−2948.8	−0.016	−1119.4
methanol	−3.240	−1802.3	0.525	−449.7
methylene chloride	−3.982	−2504.4	−0.551	−1444.6
toluene	−2.080	−2375.0	−5.42	−3203.4

Table 2. Henry's Law Constants for Different Solute−Absorbent Systems

volatile organic compound	silicone oil		Paratherm	
	temp (°C)	H_i	temp (°C)	H_i
acetone	25.6	1.92×10^{-2}	30.0	2.48×10^{-2}
	31.8	2.09×10^{-2}	44.8	3.11×10^{-2}
	37.8	2.74×10^{-2}	59.9	3.45×10^{-2}
	45.9	3.49×10^{-2}		
methanol	25.6	6.27×10^{-2}	30.0	1.32×10^{-1}
	31.9	6.91×10^{-2}	40.0	1.44×10^{-1}
	37.9	7.11×10^{-2}	49.8	1.45×10^{-1}
	45.9	9.40×10^{-2}		
methylene chloride	25.6	1.21×10^{-2}	30.0	1.48×10^{-2}
	31.8	1.44×10^{-2}	44.8	1.82×10^{-2}
	37.9	1.75×10^{-2}	59.8	2.28×10^{-2}
	45.9	2.05×10^{-2}		
toluene	25.6	2.85×10^{-3}	30.0	5.67×10^{-3}
	31.8	3.33×10^{-3}	40.0	8.54×10^{-3}
	37.9	3.60×10^{-3}	49.8	1.06×10^{-2}
	45.8	4.82×10^{-3}	59.9	1.52×10^{-2}

The values of Henry's constant reflect the relative absorption performances of the different volatile organic solutes with respect to the specific absorbent. In a particular absorbent, methanol has the highest Henry's constant value followed by acetone, methylene chloride, and toluene; for a particular solute, Paratherm exhibits higher H_i than silicone oil. These provide a qualitative indication about the likely absorption and stripping performance of a solute in an absorbent in a given device under given flow conditions (Poddar et al., 1996b).

Conclusions

The variable volume headspace-GC technique is a simple and efficient technique to determine partition coefficients of volatile organic solutes dissolved in any nonvolatile liquid matrix. The present work of partition coefficient determination for different organics of interest in silicone oil and Paratherm provides a guideline for their relative absorption performances with respect to a particular absorbent in any absorption equipment. The temperature dependence of Henry's law constants for different solute−oil systems are correlated with an equation similar to the Van't Hoff or Clausius−Clapeyron equation.

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