The Air-Water Partition Constant: Using Headspace GC to Determine an Important Physicochemical Parameter

Background:
The transfer of organic contaminants between water and the atmosphere is one of the key processes affecting the transport and distribution of many organic compounds in the environment (1). For neutral compounds, at dilute solution concentrations in pure water, the air-water distribution ratio is often referred to as the Henry’s Law constant (\(K_H\)).

\[
X_{\text{aq}} \equiv X_{\text{g}}
\]

\(K_H\) is defined as the ratio of a compound’s abundance in the gas phase to that in the aqueous phase at equilibrium under conditions of infinite dilution.

\[
K_H \equiv \frac{C_{\text{air}}}{C_{\text{water}}} = \frac{P_i}{C_w}
\]

where \(C_{\text{air}}\) and \(C_{\text{water}}\) are the concentrations in air and water, respectively. Since the partial pressure of a gas can be used to express it’s concentration, \(K_H\) is often determined as \(P_i\) of the chemical in the gas phase and \(C_w\) is its molar concentration in water. Henry’s law constant can also be estimated from the vapour pressure of the pure liquid \((P^o)\) and the water solubility \((C_{w\text{sat}})\).

\[
K_H \equiv \frac{P^o}{C_{w\text{sat}}}
\]

There are several unit systems employed in reporting Henry’s law constants depending on how the gas phase concentrations are expressed (i.e., atm, Pa, torr etc). If the gas phase concentration is converted to the same units as the aqueous phase concentration, we define the unitless Henry’s Law sometimes denoted as \(K_H'\) or \(K_{aw}\).

\[
K_H' = K_{aw} = \frac{K_H}{RT}
\]

A compound with a relatively large value of \(K_H\) \((K_{aw})\) will have a tendency to partition from the aqueous phase and enter the atmosphere. Even molecules with very low vapour pressures such as the pesticide DDT \((P^o \approx 1.3 \times 10^{-5} \text{ Pa at } 25^\circ\text{C})\) can partition into the atmosphere from water due to their extremely low water solubility \((C_{w\text{sat}} \approx 1.4 \times 10^{-8} \text{ M at } 25^\circ\text{C})\). Since DDT is relatively unreactive, it can be atmospherically transported large distances accounting for it’s detection far from the sites where it was applied \((K_{aw} \approx 4 \times 10^{-4} \text{ at } 25^\circ\text{C})\).

### Table 1: Selected properties and \(K_{aw}\) values for some organic compounds (1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(P^o) (Pa)</th>
<th>(C_{w\text{sat}}) (mM)</th>
<th>(K_{aw}) (calc from (P^o/C_{w\text{sat}}))</th>
<th>(K_{aw}) (expt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>12,600</td>
<td>0.676</td>
<td>0.129</td>
<td>n/a</td>
</tr>
<tr>
<td>benzene</td>
<td>12,600</td>
<td>22.4</td>
<td>0.224</td>
<td>0.224</td>
</tr>
<tr>
<td>(\gamma)-hexachlorocyclohexane</td>
<td>7.08x10^{-3}</td>
<td>2.51x10^{-2}</td>
<td>1.15x10^{-4}</td>
<td>n/a</td>
</tr>
<tr>
<td>hexachlorobenzene</td>
<td>2.51x10^{-3}</td>
<td>2.82x10^{-3}</td>
<td>0.0363</td>
<td>0.0288</td>
</tr>
</tbody>
</table>
Traditionally, air-water partition constants are determined using static methods whereby an organic solute is left to equilibrate between an aqueous phase and the atmosphere in the headspace of a closed container (2-4). Other dynamic methods using open, flow through systems have also been employed (5). Both of these techniques require that the concentration of the compound be quantified by conventional analytical techniques. A convenient variation on the static method has been proposed by Lincoff (6). It does not require the determination of absolute chemical concentrations and is therefore less time consuming. This approach will be employed in this lab and is based on a mass balance of the organic compound between two phases in a closed system, Figure 1 (7). The total amount of organic compound in the bottle must be equal to the sum of the amounts in each phase. Hence, we can write

\[ \text{total #mol added} = C_w V_w + C_g V_g \]

where \(C_w\) and \(C_g\) are the molar concentrations in the aqueous and gas phases and \(V_w\) and \(V_g\) are the volumes of each phase. If the same mass of compound is introduced into two closed containers containing different volumes of pure water, a mass balance expression can be written for each system. Equating these two expressions and introducing Henry’s law to substitute for the aqueous phase concentrations yields an equation relating \(K_{aw}\) to the headspace concentrations and known volumes.

\[ K_{aw} = \frac{(C_{g1}/C_{g2})V_{w1} - V_{w2}}{V_{g2} - (C_{g1}/C_{g2})V_{g1}} \]

where \(C_{g1}\) and \(C_{g2}\) are the concentrations in the headspace of bottle one and two, respectively and \(V_{w1}\) and \(V_{w2}\) are the volumes of the aqueous phases in the two bottles. Thus, the only experimental information needed to determine \(K_{aw}\) is the ratio of the gas-phase concentrations \((C_{g1}/C_{g2})\) and the volumes. In this treatment, absolute concentrations are not necessary and any proportional measure of concentration (such as GC peak areas) will suffice (7).

Figure 1: Sample bottle with aqueous solution and headspace.
EXPERIMENTAL

Objectives:

- Obtain Henry’s law constants $K_{aw}$ ($K_H$) values for a series of volatile and semi-volatile organic compounds from the peak areas using headspace GC-FID.

- Measure the temperature dependence of $K_{aw}$ ($K_H$) for *trans*-1,2-dichloroethene.

- Discuss structural features that relate to trends in observed Henry’s law constants.

Procedures:

Solution Preparations

Saturated aqueous stock solutions have been prepared by adding excess organic compound to 250 mL of deionized water and stirring at 25 °C for 10 days. Each of each of the following compounds will be supplied as saturated aqueous solutions in water; *trans*-1,2-dichloroethene, $n$-hexane, $n$-heptane, methylcyclohexane, $n$-octane, tetrachloromethane, trichloromethane, 1,1,1-trichloroethane and 1,3,5-trimethylbenzene.

Each group will be responsible for carrying out the $K_H$ determination on three compounds. Two of these will be done only at room temperature. Each compound will require four equilibrated solutions prepared at least 24 hours in advance of the headspace analysis. A third compound will be carried out at three temperatures. This will require a total of six equilibrated solutions prepared at least 24 hours in advance of the headspace analysis.

Compound #1: Obtain four clean dry 250 mL amber glass bottles with Teflon backed sealed septa caps. Choose one relatively insoluble compound from the list ($C_w^{sat} < 5$ mM) and prepare four aqueous solutions as follows. Pipet 20 mL of deionized water into a 250 mL bottle followed by 20 mL of the saturated aqueous stock solution. (Be careful NOT to pipet from the bottom of the saturated aqueous stock solution bottles). Prepare a second bottle, this time pipetting 200 mL of deionized water into a 250 mL bottle followed by 20 mL of the same aqueous stock solution. This set of samples form a pair and can be used to generate a value for $C_{g1}/C_{g2}$ from the relative peak areas. Prepare a duplicate set of samples in the same manner as above for a total of four samples. Cap all solutions immediately, shake well and label each bottle. Stir the sealed containers at constant temperature for at least 24 hrs before analyzing the headspace. ALL TRANSFER VOLUMES SHOULD BE ACCURATELY AND PRECISELY MEASURED AS WELL AS THE TOTAL INTERNAL VOLUME OF THE BOTTLES.

Compound #2: Obtain four clean dry 250 mL amber glass bottles with Teflon backed sealed septa caps. Choose one relatively soluble compound from the list ($C_w^{sat} > 5$ mM) and prepare four aqueous solutions as follows. Pipet 20 mL of deionized water into a 250 mL bottle followed by 2 mL of the saturated aqueous stock solution. (Be careful NOT to pipet from the bottom of the saturated aqueous stock solution bottles). Prepare a second bottle, this time pipetting 200 mL of deionized water into a 250 mL bottle followed by 2 mL of the same aqueous stock solution. This set of samples form a pair and can be used to generate a value for $C_{g1}/C_{g2}$ from the relative peak areas. Prepare a duplicate set of samples in the same manner as above for a total of four samples. Cap all solutions immediately, shake well and label each bottle. Stir the sealed containers at constant temperature for at least 24 hrs before analyzing the
headspace. ALL TRANSFER VOLUMES SHOULD BE ACCURATELY AND PRECISELY MEASURED AS WELL AS THE TOTAL INTERNAL VOLUME OF THE BOTTLES.

Compound #3: trans-1,2-dichloroethene
Obtain six clean dry 250 mL amber glass bottles with Teflon backed sealed septa caps. Pipet 20 mL of deionized water to three of these and 200 mL of deionized water to the remaining three. Pipet 1 mL of a saturated aqueous solution of trans-1,2-dichloroethene. Cap all solutions immediately and label each bottle. You will now have three pairs of solutions. Each pair will be equilibrated at a different temperature between 20 and 45 °C. Stir the sealed containers at constant temperature for at least 24 hrs before analyzing the headspace.

Gas Chromatography
Flush a gas-tight GC syringe ~ five times with the headspace being careful not to draw up any aqueous solution (see Figure 2). Inject 100. µL of the headspace of each sample into the GC injection port (Figure 3) and record the gas chromatogram of the headspace for all temperature equilibrated sample bottles. It is important that all injections volumes for a given compound are identical. Run multiple injections of the headspace of each sample through the GC in order to estimate the sample-to-sample variance in injection volume (compounds elute in 1-5 mins and multiple injections can be made on the same chromatogram). Record the peak areas and use them to calculate the $K_{aw}$ according to the expression given in the background section.

Record GC conditions and injection volumes.

Table 2: Selected properties of organic compounds in order of decreasing water solubility (1)

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS#</th>
<th>MW (g mol⁻¹)</th>
<th>$\rho$ (g mL⁻¹)</th>
<th>$C_w^{sat}$ (mM)</th>
<th>$P^o$ (Pa)</th>
<th>$K_H$ (Pa m³ mol⁻¹)</th>
<th>$K_{aw}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>trichloromethane</td>
<td>67-66-3</td>
<td>119.4</td>
<td>1.48</td>
<td>71.2</td>
<td>25100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E-1,2-dichloroethene</td>
<td>156-60-5</td>
<td>96.95</td>
<td>1.27</td>
<td>64.6</td>
<td>40700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1-trichloroethane</td>
<td>71-55-6</td>
<td>133.4</td>
<td>1.34</td>
<td>9.75</td>
<td>16600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>tetrachloromethane</td>
<td>56-23-5</td>
<td>153.8</td>
<td>1.59</td>
<td>5.38</td>
<td>14500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bromobenzene</td>
<td>108-86-1</td>
<td>157.0</td>
<td>1.50</td>
<td>2.83</td>
<td>557</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,3,5-trimethylbenzene</td>
<td>108-67-8</td>
<td>120.2</td>
<td>0.88</td>
<td>0.416</td>
<td>331</td>
<td></td>
<td></td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>108-87-2</td>
<td>98.19</td>
<td>0.77</td>
<td>0.163</td>
<td>6170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-hexane</td>
<td>110-54-3</td>
<td>86.18</td>
<td>0.66</td>
<td>0.151</td>
<td>19900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-heptane</td>
<td>142-82-5</td>
<td>100.2</td>
<td>0.68</td>
<td>0.0299</td>
<td>6170</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-octane</td>
<td>111-65-9</td>
<td>114.2</td>
<td>0.70</td>
<td>0.00876</td>
<td>1820</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note about units;
There are a number of units used to report these partitioning values, which can get confusing. For the purpose of this course, it will be useful to be familiar with the dimensionless $K_{aw}$ values. Other units may also be convenient, particularly when comparing data from different sources. For this purpose, it will be useful to have $K_H$ values in SI units of Pascals per mole per cubic meter (Pa m³/mol) or Pascals per mole per liter (Pa L/mol).

$$K_H = RT K_{aw}$$

making sure that the appropriate units are used for R – the universal gas constant.
Figure 2: Withdrawing headspace from sample bottle with gas-tight syringe.

![Diagram of sample bottle with septum cap and syringe](image)

**Note:** when using the GC-FID, the needle must not go all the way into the injector port! If it does, the tip of the needle will hit and crack the tip of the GC column, located inside the expansion chamber of the injector port.

Figure 3: Injecting sample into GC – injection port

![Diagram of injection port with syringe and GC column](image)
Calculations:
For each of the two compounds studied only at room temperature, you should have a total of four GC runs and corresponding peak areas. This will give you four pairs of peaks to generate a total of four independent K_{aw} determinations. Report the mean and standard deviation for compound #1 and #2. Share your results with others.

For trans-1,2-dichloroethene, you will have one pair of GCs at each of three temperatures. Calculate the K_{aw} at each temperature and share your results with others to obtain mean values and standard deviations.

Convert all values to K_{H} in units of Pa m^{3} mol^{-1} for comparison to literature values.

Plot ln K_{H} versus 1/T for trans-1,2-dichloroethene and obtain the slope.

Questions:
Derive the expression for K_{aw} used in this lab.

Compare your experimentally determined K_{H} values to i) accepted literature values, ii) values calculated from P^{o} and C_{w}^{sat} and iii) those estimated by the bond fragment contribution method (8) as outlined in Table 6.4 of Schwarzenbach (1).

How can the K_{H} values of the different compounds investigated be understood in terms of their chemical structure and the inter-molecular forces present (1).

Interpret the slope of the ln K_{H} versus 1/T plot (7, 9-10).

References:
(10) Hwang, I.C.; Kwak, H.Y.; Park, S.J., Determination and prediction of K(ow) and dimensionless Henry's constant (H) for 6 ether compounds at several temperatures, J. Ind. Eng. Chem., 2010, 16(4), 629-633.