Experimental Determination of the Octanol-Water Partition Coefficient for Acetophenone and Atrazine

OMATOYO K. DALRYMPLE

Department of Civil & Environmental Engineering
University of South Florida, Tampa, USA

Octanol-water partition coefficient (K_{ow}) values were determined for acetophenone and atrazine in the lab. Each compound was dissolved in water to a known concentration and placed in an octanol-water system and allowed to equilibrate. Concentration in the aqueous phase was then determined by use of a UV-visible spectrophotometer. Based on a simple mass balance, the concentration in the octanol phase was determined and the K_{ow} was calculated as the ratio of the concentration in the octanol phase to the concentration in the aqueous phase at neutral pH. The results are presented as both K_{ow} and $\log(K_{ow})$. In general, the values are in good agreement with those reported in the literature. The results are discussed in terms of further understanding of the possible behavior and fate of the chemicals in the environment.

KEYWORDS: Partition coefficient; log K_{ow}; acetophenone; atrazine.

INTRODUCTION

The octanol-water partition (K_{ow}) coefficient can be viewed as the hydrophilic-lipophilic balance of a substance. It is a measure of the tendency of the substance to prefer an organic or oily phase rather than an aqueous phase. The K_{ow} of a substance can be measured in a laboratory and provides an important indication of the chemical's ability to partition itself in the environment between an organic phase, such as fish and soil, and an aqueous phase. Partition coefficients are used extensively in chemical and environmental engineering to determine the behavior and fate of chemicals. The octanol-water partition coefficient is recognized by the US government and some international organizations as a physical property of organic pollutants equal in importance to vapor pressure, water solubility and toxicity. One of its most important applications is the determination of bioconcentration factors of pollutants for aquatic life, and as such, it is considered a required property in studies of new or problematic chemicals (US EPA, 2004).

In general, pollutants with low K_{ow} values (e.g., less than 10) may be considered relatively hydrophilic (especially if Henry's Law constant is also low); they tend to have high water solubility, small soil/sediment adsorption coefficients, and small bioconcentration factors for aquatic life. Conversely, chemicals with high K_{ow} values (e.g., greater than 10^4) are very hydrophobic and adsorb to soil/sediments and tend to bioaccumulate.

In this experiment, the K_{ow} for acetophenone and atrazine was determined. Acetophenone is the simplest aromatic ketone and is used as an intermediate for pharmaceuticals, agrochemicals and other organic compounds. It is also used as a solvent for plastics, resins, cellulose ethers, and esters. Atrazine is a herbicide used to kill weeds, primarily on farms, but has also been used on highway and railroad rights-of-way. The US EPA restricts the use and application of atrazine to trained personnel. It is difficult to degrade biologically and is commonly detected in groundwater and surface water contaminant in agricultural areas (Sawyer et al, 2003). Figure 1 shows the structure of these two compounds.
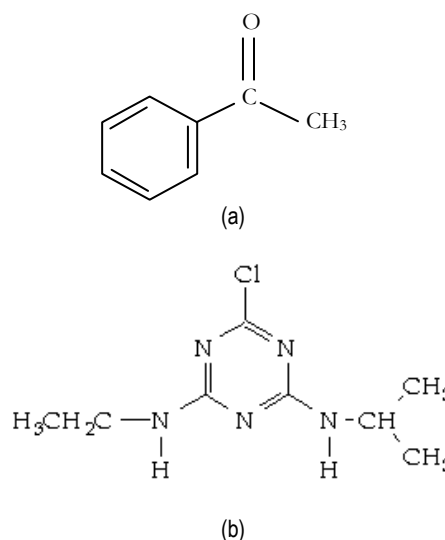

Figure 1. Structures of the compounds used in the experiment; (a) Acetophenone - C_8H_8O; (b) Atrazine – $C_8H_{10}ClN_5$

PURPOSE

The purpose of this experiment was to determine the octanol-water partition coefficient for acetophenone and atrazine at room temperature and then compare these values to those in the literature to determine the success of the method.

MATERIALS AND METHOD

Solutions of acetophenone and atrazine were prepared. Acetophenone was dissolved in deionized water to a concentration of 1000 mg/L. Atrazine was dissolved in deionized water with 1% ethanol to a concentration of 20 mg/L.

The solutions of both substances were then carefully diluted with deionized water using pipettes, test tubes and graduated cylinders to obtain a series of different, but known concentrations in order to create a calibration curve. The curve establishes a relationship between aqueous concentration and absorbance measured by the UV spectrophotometer. A sample of each dilution series was pipetted into a cuvette and placed in the UV spectrophotometer. The instrument was set to 246 nm and 228 nm for acetophenone and atrazine respectively. A cuvette with deionized water was used as a blank to zero the spectrophotometer before measurement of each group of samples. The series of dilutions for each substance is shown in tables 1 and 2.

Using aqueous solutions of acetophenone and atrazine at concentrations of 1000 mg/L and 20 mg/L respectively, stock solutions were prepared with varying volumes. Corresponding volumes of octanol were also prepared. These are indicated in tables 3 and 4. A ring stand was set up to hold a separatory funnel in which the stock solutions were poured followed by octanol. The funnel was then removed from the stand and gently shaken. The stem was pointed up and excess pressure was released by slowly opening the stopcock. This venting procedure was repeated until most of the pressure was released. The funnel was then vigorously shaken for about 30 seconds with intermediate venting. It was then left to rest in place on the ring stand to allow the substances to equilibrate in the two phases. The Henry's Law constant of both compounds were low enough to ignore loss of mass via volatilization.

Once distinct layers appeared after about 20 minutes, equilibrium was assumed to have been reached. Atrazine in the octanol-water system took a longer time to reach equilibrium and did not separate as well as acetophenone. However, samples of aqueous solutions of both substances were then extracted by draining the flask into a beaker and pipetting some into a cuvette. In the case

of atrazine, samples were taken from the bottom of the aqueous phase, where the separation was best. Absorbance measurements using the UV spectrophotometer were again made in similar steps as described above. The results are shown in tables 3 and 4.

DATA SUMMARY

The raw data from the experiment are presented in tables 1 to 4 below.

Table 1. Calibration data for acetophenone

Approximate concentration of stock solution: 1000 mg/L				
sample number	Volume of stock solution used (mL)	Diluted into total volume (mL)	Resultant concentration of sample (mg/L)	Measured Absorbance (dimensionless)
1	0.15	10.0	15.0	1.427
2	0.20	8.0	25.0	2.447
3	0.20	10.0	20.0	1.97
4	0.10	10.0	10.0	0.977
5	0.50	100.0	5.0	0.499
6*	0.10	10.0	1.0	0.085

*sample 6 was prepared by diluting 1 ml into 10 ml and then diluting 0.1 ml of the resultant solution into 10 ml.

Table 2. Calibration data for atrazine

Approximate concentration of stock solution: 20 mg/L				
sample number	Volume of stock solution used (mL)	Diluted into total volume (mL)	Resultant concentration of sample (mg/L)	Measured Absorbance (dimensionless)
1	0.500	10.0	1.00	0.181
2*	1.000	5.0	0.20	0.039
3	1.000	4.0	5.00	0.974
4	0.500	5.0	2.00	0.343
5	1.500	3.500	8.57	1.655
6	1.000	2.000	10.00	2.053
7	0.300	10.0	0.60	0.121
8	2.000	6.000	6.67	1.239
9	1.000	6.000	3.33	0.628

*sample 2 was prepared by taking 1 mL of sample 1, and diluting it into 5 mL.

Table 3. Extraction data for acetophenone

sample number	Volume of stock solution used (mL)	Volume of octanol used for extraction (mL)	Measured Absorbance (dimensionless)	Concentration of solution after extraction (mg/L)	Concentration in octanol after extraction (mg/L)
		Approximate concentration of stock solution: 1000 mg/L			
1	40.00	60.00	1.65	16.91	655.40
2	30.00	70.00	1.14	11.68	423.57
3	20.00	80.00	0.61	6.21	248.45
4	50.00	50.00	2.49	25.48	974.52

Table 4. Extraction data for atrazine

sample number	Volume of stock solution used (mL)	Volume of octanol used for extraction (mL)	Measured Absorbance (dimensionless)	Concentration of solution after extraction (mg/L)	Concentration in octanol after extraction (mg/L)
		Approximate concentration of stock solution: 20 mg/L			
1	95.00	5.00	0.46	2.34	335.45
2	88.70	10.00	0.22	1.13	167.36
3	85.00	15.00	0.15	0.76	109.03
4	75.00	25.00	0.06	0.28	59.16

DATA ANALYSIS

Calibration curves were prepared for each substance. The curves relate the measured absorbance by the UV spectrophotometer to the actual concentration of the compounds in aqueous solution. Acetophenone absorbs UV radiation at 246 nanometers (nm), while atrazine absorbs at 228 nm. The instrument measures the amount of radiation absorbed by the compounds in the solution. Absorbance (A) is the $\log_{10}$ of the fraction of radiant power leaving the sample to the incident radiant power. According to the Beer-Lambert Law $A = \varepsilon bc$, where ε is the molar absortivity with units $L.mol^{-1}.cm^{-1}$, b is the length of the sample (path length of the cuvette) and c is concentration in mol L^{-1}.

Figure 2 shows the calibration curve for acetophenone. The linear relationship between absorbance and concentration is very strong. For acetophenone at 246 nm, the aqueous concentration is related to absorbance by the following relationship:

$$C_{AC}^{water} = 10.25 \text{ x } A \qquad (1)$$

where A = absorbance

In the case of atrazine, figure 3 shows the calibration curve and the aqueous concentration is related to absorbance by:

$$C_{AT}^{water} = 5.10 \text{ x } A \qquad (2)$$

This is also a very strong relationship at 228 nm for atrazine.

These relationships were used to calculate the concentration of both substances in aqueous solution after mixing in the octanol-water system.

Concentration of the compounds in the octanol phase was calculated based on a mass balance of each in the two phases.

$$V^{aq}C_e^{aq} + V^{oct}C^{oct} = V^{aq}C^{initial} \qquad (3)$$

where V is the volume of the respective phases; C_e^{aq} is the aqueous concentration at equilibrium; $C^{initial}$ is the initial aqueous concentration and C^{oct} is the octanol phase concentration. Therefore, the octanol phase concentration was determined from the following relationship:

$$C^{oct} = V^{aq}(C^{initial} - C_e^{aq})/V^{oct} \qquad (4)$$

A second method was used to validate the results by substituting $C_e^{aq} = K_{ow}C^{oct}$ in the mass balance equation above. The following relationship was derived:

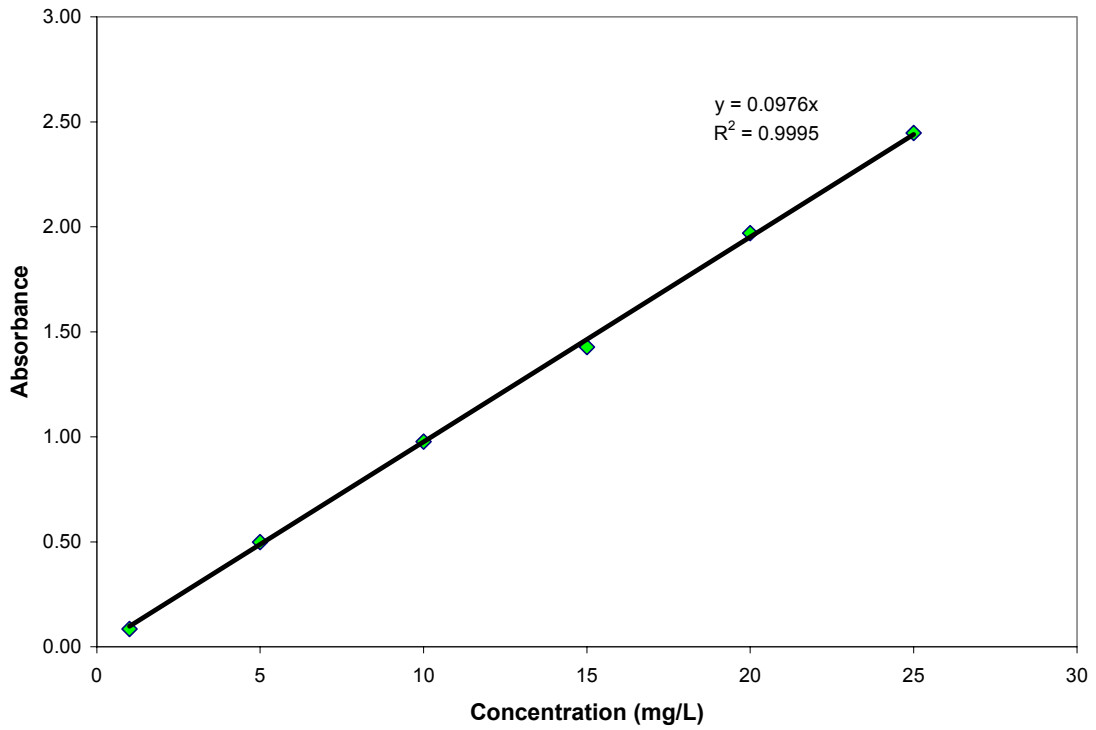$$C^{initial}/C_e^{aq} = (V^{oct}/V^{aq})K_{ow} + 1 \qquad (5)$$

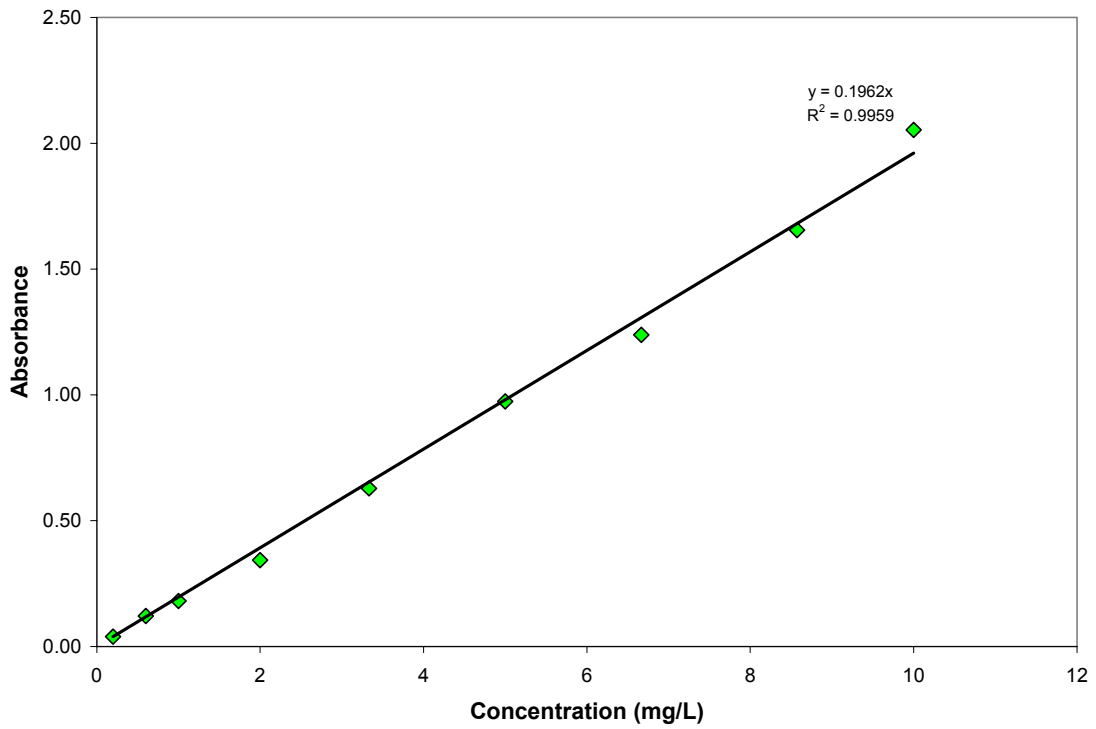**Figure 2.** Calibration curve for acetophenone

Figure 3. Calibration curve for atrazine

Concentration of each compound in the octanol phase was plotted against the corresponding equilibrium aqueous concentration for the first relationship. The ratio of initial concentration to equilibrium concentration was plotted against volume ratios for the two phases for the second relationship. The slope of the line indicates the octanol-water partition coefficient (K_{ow}). The partition coefficient charts are shown in figures 4 to 7.
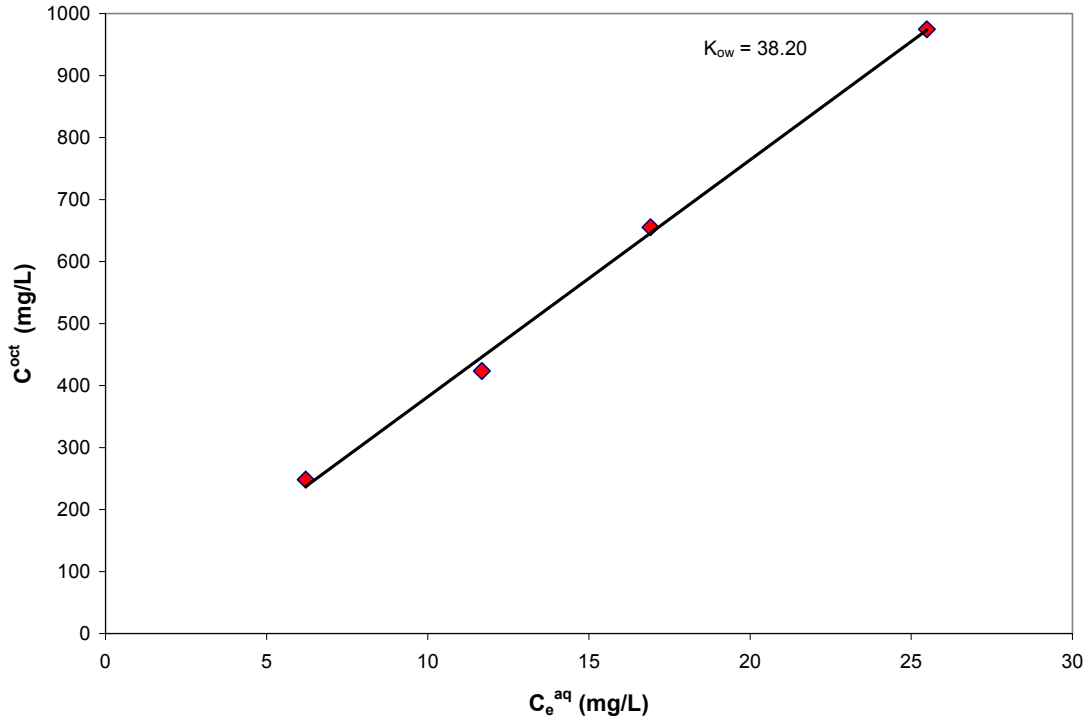

Figure 4. . Octanol-water partition coefficient curve for acetophenone (based on equation 4)
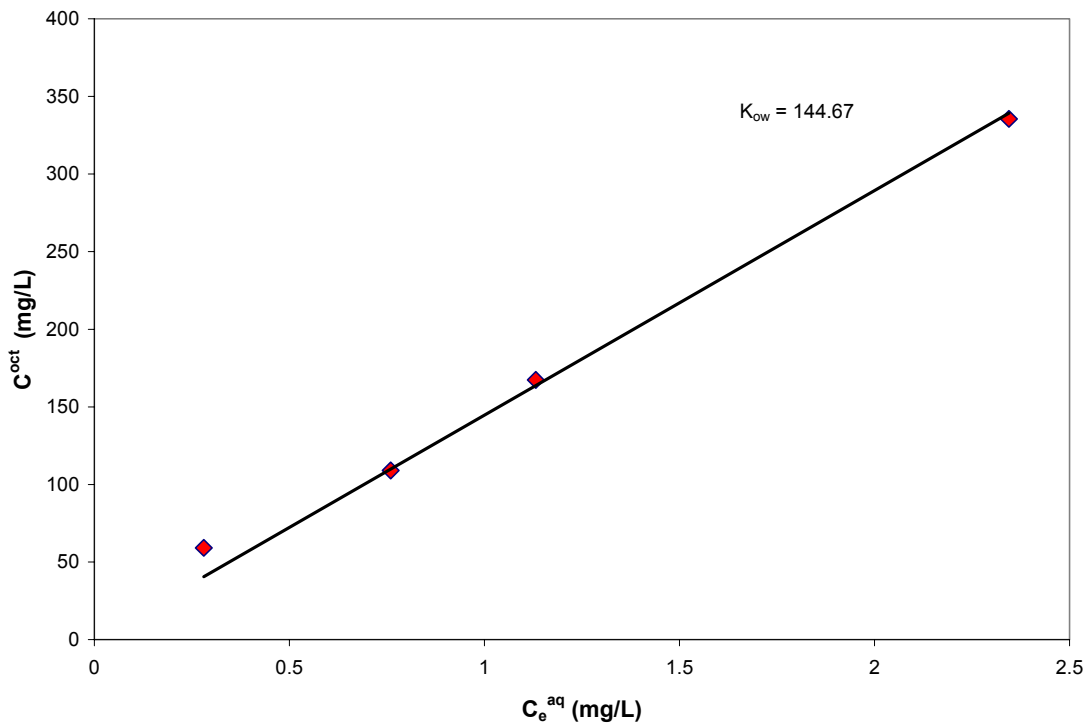

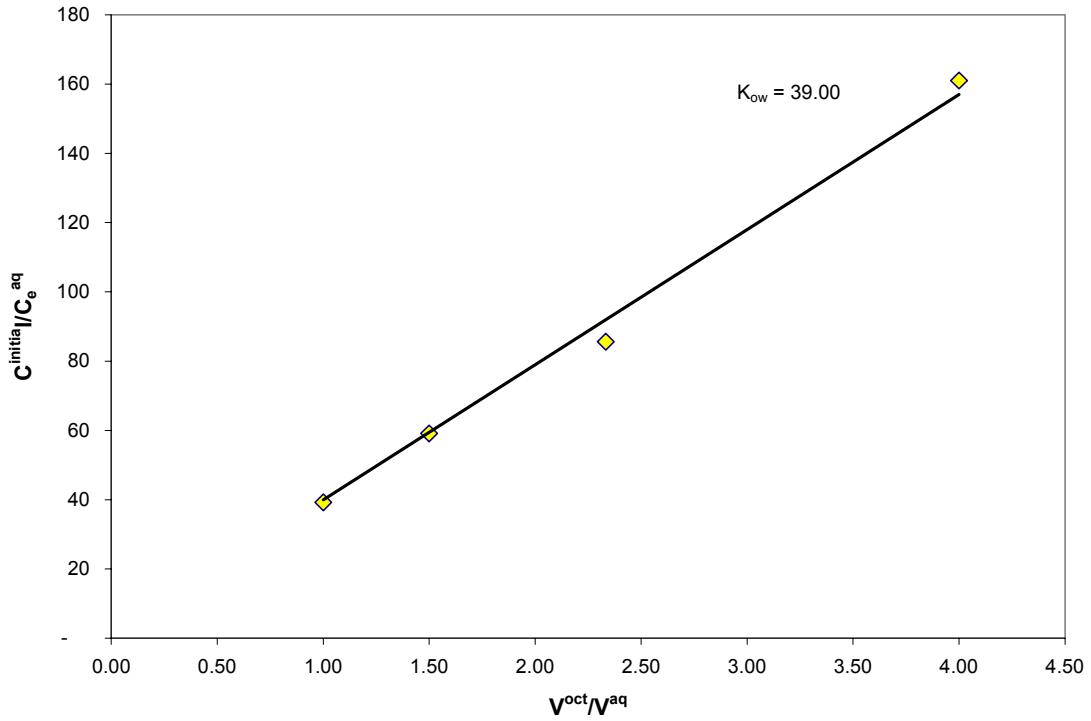**Figure 5.** Octanol-water partition coefficient curve for atrazine (based on equation 4)

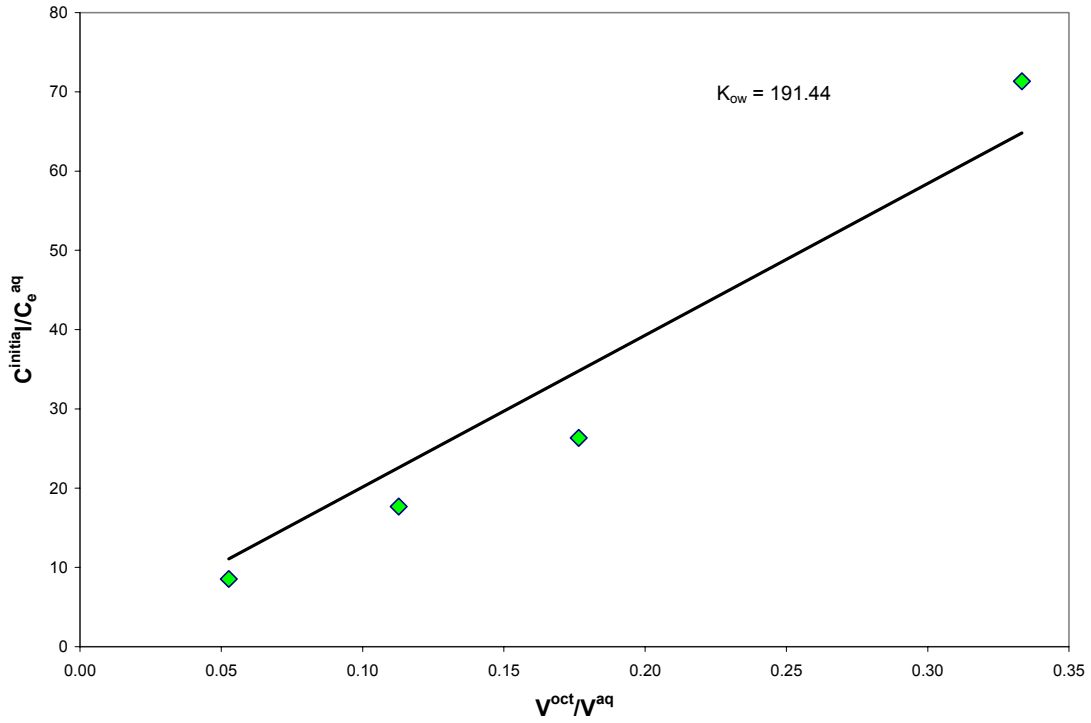**Figure 6.** Octanol-water partition coefficient curve for acetophenone (based on equation 5)

Figure 7. Octanol-water partition coefficient curve for atrazine (based on equation 5)

RESULTS

The experimental values for K_{ow} for both compounds and the corresponding log K_{ow} are shown in table 5.

Table 5. Experimental K_{ow} values for acetophenone and atrazine

Compound	K_{ow}		Log K_{ow}	
	Method 1	Method 2	Method 1	Method 2
Acetophenone	38.20	39.00	1.58	1.59
Atrazine	144.67	191.44	2.16	2.28

DISCUSSION

The table below shows recorded log K_{ow} values for acetophenone and atrazine from selected literature.

Table 6. Recorded values for log K_{ow}

Log K_{ow} (Acetophenone)	Reference
1.63	Schwarzenbach, R. P, Gschwench, P.M, Imboden, D.M (2003)
1.67	Texas Risk Reduction Program, 30 TAC 350.1-3501.5, March 2003
1.58	Hansch,C et al. (1995)
Log K_{ow} (Atrazine)	**Reference**
2.65	Schwarzenbach, R. P, Gschwench, P.M, Imboden, D.M (2003)
2.82	Texas Risk Reduction Program, 30 TAC 350.1-3501.5, March 2003
2.69	Sawyer, C. N., P. C. McCarty, G. F Parkin (2003)

Comparison with literature values for acetophenone shows the experimental value to be in good agreement. The log K_{ow} for atrazine is slightly lower than the literature values. This may be a result of experimental limitations such as limited time available to observe complete interphase transfer. Atrazine did not equilibrate as quickly as originally anticipated and may have affected the complete separation of the two solvents. The K_{ow} value is therefore off by about a factor of 3, even though the log K_{ow} seems slightly lower than the literature values.

The two experimental K_{ow} values for each compound differ only by about a factor of 4 with atrazine having the higher partition coefficient. These values indicate relatively low hydrophobicity for acetophenone and moderate hydrophobicity for atrazine.

Acetophenone has a hydrophilic section where the oxygen is located and this makes it more "comfortable" in water. Given that the value of atrazine is off by about a factor of 3, it is probably way more hydrophobic than indicated by the experiment. With a K_{ow} of 145-191 (or 445 from the literature), atrazine will probably partition itself with significant concentrations in the sediment and soil phases in a natural environment. On the other hand, acetophenone will partition strongly in the water phase.

Generally, atrazine seemed a more difficult compound to work with that acetophenone, which is very water soluble. Further, equation 5 seems to give values closer to the literature for both compounds probably because the need to calculate octanol-phase concentration was not necessary. This must have reduced the propagation of experimental errors in the calculations. However, it is recommended that any repeat of the experiment allot more time to observe the complete mass transfer of atrazine between the two phases.

REFERENCES

1. Hansch C, Leo, A. and Hoekman, D. (1995). Exploring QSAR: Hydrophobic, electronic, and steric constants. Am Chem Soc, Washington.

2. Sawyer, C. N., McCarty, P. C., and Parkin, G. F., (2003). Chemistry for Environmental Engineering, McGraw Hill, New York.

3. Schwarzenbach, R. P, Gschwench, P.M, and Imboden, D.M (2003). Environmental Organic Chemistry, 2nd Edition, John Wiley & Sons.

4. Texas Risk Reduction Program (2003), 30 TAC 350.1-3501.5, March 2003.

5. US EPA (2004), New Protocol on Persistent Organic Pollutants Negotiated under the UN Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution, retrieved from http://www.epa.gov/oppfead1/international/lrtap2pg.htm on December 1, 2005.