

AIR–WATER PARTITIONING COEFFICIENTS OF ORGANICS IN DILUTE AQUEOUS SOLUTIONS

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Summary

Henry's Law constants were measured for 45 chemicals spanning a wide range of chemical structures and volatilities. A static headspace method, Equilibrium Partitioning in Closed Systems (EPICS), was used to measure Henry's Law constant, and the batch air stripping method was used as a check. Measurements were conducted over a temperature range of 10–30°C, and the data were correlated with a temperature regression equation. An average precision of 10% was obtained for the EPICS runs, and the Henry's constants agreed well with the batch air stripping results and other reported values.

Introduction

Soil and groundwater at many Air Force bases are contaminated with fuels, cleaning solvents, and degreasers because of past disposal practices, accidental spills, and leaking storage tanks. We are studying the fate and transport of contaminants in subsurface systems and conducting research aimed at developing treatment strategies for groundwater cleanup. Many of the contaminants are volatile, and a knowledge of their air–water distribution is required for the design of treatment processes and for providing insight into their behavior in the environment. Because the contaminants are usually present in subsurface systems at very low concentrations, Henry's Law for ideal dilute solutions is often appropriate for vapor–liquid equilibrium (VLE) calculations. Although many of the processes occurring in the environment may not reach equilibrium, an understanding of equilibrium conditions is essential in determining rate and direction of chemical movement.

The objective of this study was to experimentally determine the Henry's Law constant for contaminants of Air Force interest and general public concern over a range of temperatures expected in the environment. Two experi-

mental techniques were used to directly measure Henry's Law constant for the compounds in this study. One was a technique known as Equilibrium Partitioning in Closed Systems (EPICS) which was originally proposed by Lincoff and Gossett [1]. The other was a batch air stripping technique developed by Mackay et al. [2]. In Lincoff and Gossett's [1] original work, the EPICS procedure was developed and tested on five chlorinated organics over a small range of Henry's constants (2×10^{-3} – 1.3×10^{-2} atm m³/mol). In subsequent studies, Gossett [3] expanded the number of study compounds (14) and range of Henry's constants (2.2×10^{-3} – 2.9×10^{-2} atm m³/mol), again with short-chain chlorinated organics. A major goal of this project was to determine Henry's Law constants over a wide range (1.3×10^{-3} – 1.8×10^{-1} atm m³/mol) for compounds of differing structure and type. We hoped to test the general applicability of the EPICS procedure and compare the Henry's Law constants from this study with other reported values.

Experimental

EPICS Measurements

The EPICS procedure was that of Lincoff and Gossett [1] with minor modifications. Two replicate closed-system pairs per observation were used to obtain four estimates of Henry's Law constant, with a second complete set analyzed on a separate day to determine day-to-day precision. Therefore, a total of eight Henry's Law constant estimates were obtained for each component. An arithmetic average of these estimates is taken to be the true Henry's constant, with the coefficient of variation (COV) for the individual values reported.

Saturated stock solutions for each component were prepared by addition of organic solute slightly in excess of the solubility limit to a volume of water. All stock solutions were prepared in 1-l amber bottles and allowed to equilibrate for at least one week before use. For compounds denser than water, solutions were withdrawn directly from the amber bottles for preparation of the EPICS samples. For compounds less dense than water, the stock solutions were transferred to a 500-ml separatory funnel the day before using. Solutions were then withdrawn from the bottom of the separatory funnel for preparation of the EPICS sample bottles. Two pairs of 250-ml amber glass bottles were filled with 20 ml and 200 ml of distilled/deionized water, respectively. The same volume of saturated stock solution was then added to each of the four septum bottles producing a liquid concentration of approximately 10 mg/l in the 20 ml system. This ensured that the studies were conducted in the region where Henry's Law is obeyed (i.e., dilute solutions). The bottles were sealed with a silicone rubber septum cap with a Teflon[®] liner facing toward the bottle headspace. The loaded bottles were shaken vigorously by hand and then placed in a constant temperature water bath for a minimum of 16 h before analysis. After equilibration,

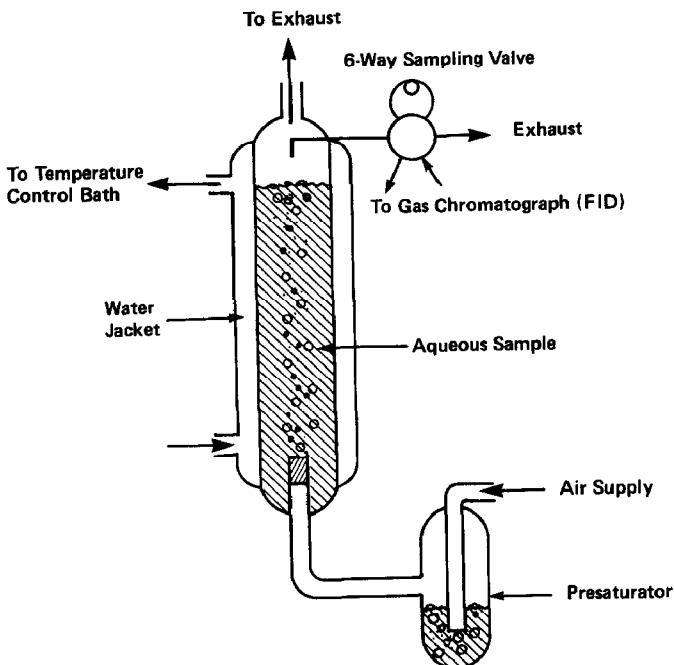


Fig. 1. Schematic of batch air stripping column.

headspace samples were withdrawn from the bottles via gas-tight syringe and injected into a Varian 3700 gas chromatograph equipped with a flame ionization detector (FID). The GC column consisted of a 5.5-cm by 0.05-cm O.D. stainless steel tube packed with 80/100 mesh Porasil[®] B. Retention times were typically less than one minute.

Batch air stripping measurements

A batch air stripping column was assembled from glass, water-jacketed columns, each 61-cm long with a 2.54-cm inside diameter. Experimental details were similar to those described by MacKay et al. [2]. Figure 1 shows a schematic of the bubble column system.

The exit gas was analyzed with a gas chromatograph equipped with a flame ionization detector. The column effluent was passed through a sample loop attached to a six-port rotary valve which was pneumatically activated to load the loop contents onto the GC column. The GC column was the same one used during the EPICS tests.

Results and discussion

EPICS measurements

Henry's Law measurements were made for each study compound at 10, 15, 20, 25, and 30°C and are reported with their COV (Table 1). Generally, the

TABLE 1

Henry's Law constants (H , in atm m³/mol) for 45 organic compounds

Component	10°C		15°C		20°C		25°C		30°C	
	H	COV, %	H	COV, %	H	COV, %	H	COV, %	H	COV, %
nonane	0.400	3.99	0.496	14.8	0.332	18.0	0.414	26.7	0.465	29.6
n-hexane	0.238	40.0	0.413	15.9	0.883	19.2	0.768	16.6	1.56	31.7
2-methylpentane	0.697	23.5	0.694	15.3	0.633	18.0	0.825	16.3	0.848	79.8
cyclohexane	0.103	1.76	0.126	7.03	0.140	11.5	0.177	4.39	0.223	2.61
chlorobenzene	0.00244	7.23	0.00281	1.00	0.00341	1.60	0.00360	0.76	0.00473	0.97
1,2-dichlorobenzene	0.00163	12.2	0.00143	7.63	0.00168	4.29	0.00157	8.56	0.00237	10.6
1,3-dichlorobenzene	0.00221	9.48	0.00231	5.99	0.00294	3.81	0.00285	5.59	0.00422	4.16
1,4-dichlorobenzene	0.00212	5.03	0.00217	5.59	0.00259	4.08	0.00317	8.35	0.00389	9.17
<i>o</i> -xylene	0.00285	5.30	0.00361	5.04	0.00474	5.62	0.00487	2.11	0.00626	1.93
<i>p</i> -xylene	0.00420	5.18	0.00483	4.13	0.00645	2.51	0.00744	1.90	0.00945	2.14
<i>m</i> -xylene	0.00411	4.71	0.00496	2.31	0.00598	3.01	0.00744	4.67	0.00887	2.50
propylbenzene	0.00568	3.45	0.00731	4.82	0.00881	1.24	0.0108	2.62	0.0137	1.38
ethylbenzene	0.00326	0.63	0.00451	5.64	0.00601	3.46	0.00788	2.97	0.0105	2.28
toluene	0.00381	5.25	0.00492	7.83	0.00555	2.61	0.00642	0.60	0.00808	1.34
benzene	0.00330	1.50	0.00388	6.35	0.00452	4.83	0.00528	4.72	0.00720	5.24
methyl ethylbenzene	0.00351	1.66	0.00420	2.38	0.00503	3.61	0.00558	1.97	0.00770	1.12
1,1-dichloroethane	0.00368	2.43	0.00454	2.66	0.00563	1.92	0.00625	1.21	0.00776	2.82
1,2-dichloroethane	0.00117	7.49	0.00130	1.23	0.00147	1.91	0.00141	1.93	0.00174	2.42
1,1,1-trichloroethane	0.00965	2.98	0.0115	5.51	0.0146	0.58	0.0174	1.35	0.0211	2.24
1,1,2-trichloroethane	0.00039	25.8	0.00063	7.41	0.00074	8.64	0.00091	8.82	0.00133	2.55
<i>cis</i> -1,2-dichloroethylene	0.00270	3.86	0.00326	4.26	0.00360	0.17	0.00454	4.00	0.00575	6.32
<i>trans</i> -1,2-dichloroethylene	0.00059	5.24	0.00705	0.79	0.00857	4.48	0.00945	1.30	0.0121	2.82
tetrachloroethylene	0.00846	4.19	0.0111	4.99	0.0141	1.52	0.0171	1.65	0.0245	4.04
trichloroethylene	0.00538	3.85	0.00667	4.41	0.00842	3.72	0.0102	1.25	0.0128	1.84
tetralin	0.00075	38.9	0.00105	30.2	0.00136	17.8	0.00187	10.0	0.00268	3.26
decalin	0.0700	6.96	0.0837	7.74	0.106	4.97	0.117	6.79	0.199	13.9

vinyl chloride	0.0150	1.27	0.0168	1.63	0.0217	0.62	0.0265	1.24	0.028	2.97
chloroethane	0.00759	3.50	0.00958	1.50	0.0110	0.99	0.0121	1.46	0.0143	0.59
hexachloroethane	0.00593	5.28	0.00559	7.23	0.00591	21.3	0.00835	1.48	0.0103	4.66
carbon tetrachloride	0.0148	1.28	0.0191	3.90	0.0232	3.41	0.0295	2.25	0.0378	5.93
1,3,5-trimethylbenzene	0.00403	4.52	0.00460	1.89	0.00571	4.81	0.00673	2.70	0.00963	0.48
ethylene dibromide	0.00030	33.2	0.00048	49.3	0.00061	52.6	0.00065	5.41	0.00080	7.28
1,1-dichloroethylene	0.0154	3.41	0.203	17.2	0.0218	3.09	0.0259	2.67	0.0318	0.89
methylene chloride	0.00140	6.99	0.00169	1.54	0.00244	4.83	0.00296	2.56	0.00361	1.67
chloroform	0.00172	4.13	0.00233	2.51	0.00332	2.35	0.00421	5.22	0.00554	7.24
1,1,2,2-tetrachloroethane	0.00033	45.6	0.00020	53.0	0.00073	34.6	0.00025	86.1	0.00070	56.6
1,2-dichloropropane	0.00122	1.12	0.00126	9.54	0.00190	6.49	0.00357	26.6	0.00286	15.3
dibromochloromethane	0.00038	33.9	0.00045	37.2	0.00103	6.20	0.00118	2.72	0.00152	4.22
1,2,4-trichlorobenzene	0.00129	39.0	0.00105	51.3	0.00183	7.21	0.00192	8.18	0.00297	22.0
2,4-dimethylphenol	0.00829	22.7	0.00674	13.0	0.0101	19.3	0.00493	10.4	0.00375	8.17
1,1,2-trichlorotrifluoroethane	0.154	5.63	0.215	8.21	0.245	7.40	0.319	5.60	0.321	3.00
methyl ethyl ketone	0.00028	35.5	0.00039	21.4	0.00019	6.32	0.00013	81.8	0.00011	19.8
methyl isobutyl ketone	0.00066	28.5	0.00037	2.80	0.00029	35.4	0.00039	36.1	0.00068	11.6
methyl cellosolve	0.0441	33.2	0.0363	16.1	0.116	32.3	0.0309	16.0	0.03813	15.9
trichlorofluoromethane	0.0536	6.47	0.0680	0.57	0.0804	1.07	0.101	1.75	0.122	3.86

^aPercent coefficient of variation COV = (S.D. × 100)/mean.

COVs were less than 6%, but because several compounds exhibited high COVs, the average COV over the entire temperature range was approximately 10%. Typically, the higher COV values were obtained on measurements with Henry's constant less than $0.0015 \text{ atm m}^3/\text{mol}$ and greater than $0.2 \text{ atm m}^3/\text{mol}$. A detailed discussion of the precision associated with the EPICS procedure is presented by Gossett [3].

Collecting the data over a range of temperatures enabled us to model the temperature dependence of Henry's constant with the van 't Hoff equation [3,4]. Temperature regression equations were generated for each chemical (Table 2). Using this relationship, one assumes the enthalpy of volatilization from solution is constant over the entire temperature range in the regression, even though such a simplification may not always be physically realistic. The simple two-constant fit represented the data well, as evidenced by typical r -squared values in excess of 0.95. However, note that in some cases, the linear correlation of the logarithm of the Henry's Law constant with temperature results in an exceedingly poor correlation coefficient. The Henry's Law constant may be defined in terms of the infinite dilution activity coefficient and the Lewis-Randall reference fugacity (i.e., pure component vapor pressure) Munz and Roberts [5]. Many solutions, particularly aromatics in water, are well known to have an activity coefficient maximum in the range of $10\text{--}25^\circ\text{C}$ [6]. This being the case, it is not surprising that those compounds which have a strong activity coefficient dependence on temperature, might also show a strong non-linear Henry's Law constant behavior.

Batch air stripping measurements

The batch air stripping tests were performed to provide a check with select EPICS results. Because some of the Henry's Law constants were expected to be several orders of magnitude higher than originally studied by Mackay et al. [2], we were concerned whether equilibrium conditions would be achieved in the column system. To reduce this concern, we used a taller column (122 cm) and performed extensive tests with n-hexane and 1,1,1-trichloroethane. n-Hexane was chosen because its high Henry's Law constant might reveal equilibration problems in the column system. Tests were performed at a column temperature of 30°C and the flow rate was varied between tests. The results of several tests performed using n-hexane are shown in Table 3.

At the lower gas flow rates, a smaller bubble size was produced and there appears to be a corresponding improvement in the approach to equilibrium as evidenced by an increase in the observed Henry's Law constant. However, a subsequent test with a liquid depth of 56 cm produced a Henry's Law constant of $7.44 \times 10^{-2} \text{ atm m}^3/\text{mol}$, nearly as high as the value observed at a depth of 119 cm with the same purge gas flow rate. If the changes observed in the Henry's Law constant with changing gas flow rate were entirely due to a lack of equilibrium, one would expect the constant to drop by approximately 50% when

TABLE 2

Component parameters for the temperature regression equation - temperature regression parameters^a

Component	A	B	r ²
nonane	-0.1847	202.1	0.013
n-hexane	25.25	7530	0.917
2-methylpentane	2.959	957.2	0.497
cyclohexane	9.141	3238	0.982
chlorobenzene	3.469	2689	0.965
1,2-dichlorobenzene	-1.518	1422	0.464
1,3-dichlorobenzene	2.882	2564	0.850
1,4-dichlorobenzene	3.373	2720	0.941
<i>o</i> -xylene	5.541	3220	0.966
<i>p</i> -xylene	6.931	3520	0.989
<i>m</i> -xylene	6.280	3337	0.998
propylbenzene	7.835	3681	0.997
ethylbenzene	11.92	4994	0.999
toluene	5.133	3024	0.982
benzene	5.534	3194	0.968
methyl ethylbenzene	5.557	3179	0.968
1,1-dichloroethane	5.484	3137	0.993
1,2-dichloroethane	-1.371	1522	0.878
1,1,1-trichloroethane	7.351	3399	0.998
1,1,2-trichloroethane	9.320	4843	0.968
<i>cis</i> -1,2-dichloroethylene	5.164	3143	0.974
<i>trans</i> -1,2-dichloroethylene	5.333	2964	0.985
tetrachloroethylene	10.65	4368	0.987
trichloroethylene	7.845	3702	0.998
tetralin	11.83	5392	0.996
decalin	11.85	4125	0.919
vinyl chloride	6.138	2931	0.970
chloroethane	4.265	2580	0.984
hexachloroethane	3.744	2550	0.768
carbon tetrachloride	9.739	3951	0.997
1,3,5-trimethylbenzene	7.241	3628	0.962
ethylene dibromide	5.703	3876	0.928
1,1-dichloroethylene	6.123	2907	0.974
methylene chloride	8.483	4268	0.988
chloroform	11.41	5030	0.997
1,1,2,2-tetrachloroethane	1.726	2810	0.194
1,2-dichloropropane	9.843	4708	0.820
dibromochloromethane	14.62	6373	0.914
1,2,4-trichlorobenzene	7.361	4028	0.819
2,4-dimethylphenol	-16.34	-3307	0.555
1,1,2-trichlorotrifluoroethane	9.649	3243	0.932
methyl ethyl ketone	-26.32	-5214	0.797
methyl isobutyl ketone	-7.157	160.6	0.002
methyl cellosolve	-6.050	-873.8	0.023
trichlorofluoromethane	9.480	3513	0.998

^aTemperature regression equation: $H = \exp(A - B/T)$; H in atm m³/mol, and T in K.

TABLE 3

Bubble column test results - n-hexane

Air flow rate, cc/min	Liquid depth, cm	H , atm m^3/mol
91.6	124	5.87×10^{-2}
47.6	121	7.91×10^{-2}
48.4	119	7.51×10^{-2}
21.8	123	1.47×10^{-1}
14.1	128	1.88×10^{-1}

TABLE 4

Bubble column test results - 1,1,1-trichloroethane

Air flow rate, cc/min	Liquid depth, cm	H , atm m^3/mol
24.8	54	2.23×10^{-2}
27.2	120	3.60×10^{-2}
27.3	122	3.47×10^{-2}
104.0	54	2.19×10^{-2}
106.0	75	2.44×10^{-2}
106.0	100	2.73×10^{-2}
108.0	120	2.84×10^{-2}

the liquid depth is decreased by one-half – evidently there were other factors to consider besides equilibrium.

Further tests were performed with 1,1,1-trichloroethane (Table 4). This compound has a much lower Henry's Law constant than n-hexane and thus should be less susceptible to column equilibrium limitations. Tests were performed at a column temperature of 30°C with the liquid depth and gas flow rate varied between tests.

At a given flow rate, increasing the liquid depth increases the Henry's Law constant measured. Variation in the measured Henry's Law constant with changes in flow rate at a particular liquid depth was observed only for the two-section column (54 cm liquid depth tests were conducted with a single column section). Apparently, poor axial mixing created concentration gradients which biased the measurements.

Column mixing efficiency was evaluated by the dispersion of food coloring through the column liquid during operation. Water was added to the column to a depth of 115 cm and air flow was established at nominally 25 cc/min. A

few drops of red food coloring were added to the water at the top of the column section. Approximately 25 min elapsed before the entire column reached the same color intensity.

Two modifications were made to prevent concentration gradients from biasing the results for the remaining batch air stripping tests. First, only the lower 61-cm column section was used because of the considerable mixing problems observed in the taller column. Second, all measurements were performed with a minimum air purge rate of 60 cc/mm. Each test was performed at two different liquid depths to provide an indication of whether the experiment was satisfying equilibrium requirements. The Henry's Law constants were measured at 25 °C for select compounds (column 1 Table 5).

Comparison with other results and estimates

A comparison of selected results of this study and results of previous studies is found in Table 5. Comparisons of Henry's Law constants from EPICS in this study to bubble column results are quite good with the exception of cyclohexane. The difference of over 69% can be attributed to the failure to attain equilibrium in the bubble column tests.

The greatest difference between the results of this study and other reported values occurs in the comparison with Henry's Law constants predicted from vapor pressure and solubility data. The differences, both positive and negative, ranged from 2 to 400%, with no distinct pattern attributable to chemical type or structure. It is not uncommon for reported values of Henry's constants to vary by several orders of magnitude. For example, results for vinyl chloride suggests a Henry's Law constant of approximately 2.65×10^{-2} atm m³/mol at 25 °C, while estimated values of 2.3×10^{-2} to 6.39 atm m³/mol are reported by Mackay and Shiu [7] and Goldstein [8], respectively. Large uncertainties in the absolute aqueous solubility probably contribute most to these discrepancies.

Another method used to estimate Henry's Law constants is UNIFAC or UNIQUAC Functional Activity Coefficient. The UNIFAC model was developed in 1975 to correlate large quantities of data with but a few molecular parameters. The first group contribution technique developed for activity coefficient prediction was that of Wilson and Deal [11]; the subsequent development of UNIFAC by Fredenslund et al. [12] owes much to their early work. By employing the UNIFAC model to calculate activity coefficients for the compounds of interest, we were then able to use pure component vapor pressure data to calculate the Henry's Law constants. The values obtained in this fashion are shown in the last column of Table 5. A limitation of this approach is that the binary interaction parameters as tabulated by Gmehling [13], were not derived from data in the extremely dilute region. As a result, extrapolation to the infinite dilute region may lead to large errors, as seen for cyclohexane or tetrachloroethylene.

The comparison of the EPICS results from this study to those of Gossett

TABLE 5

Comparison of selected results with other reported values – Henry's constant, H , expressed in atm m³/mol at 25 °C

Compound	H^a	H^b	H^c	H^d	H^e	H^f
cyclohexane	5.46×10^{-2g}	1.77×10^{-1}	1.91×10^{-1}			1.43×10^{-2}
chlorobenzene		3.60×10^{-3}	3.58×10^{-3}		3.26×10^{-3}	5.41×10^{-3}
<i>o</i> -xylene		4.87×10^{-3}	4.93×10^{-3}			8.83×10^{-3}
<i>p</i> -xylene	7.52×10^{-3}	7.44×10^{-3}	6.92×10^{-3}			1.17×10^{-2}
<i>m</i> -xylene		7.44×10^{-3}	7.23×10^{-3}			1.10×10^{-2}
propylbenzene		1.08×10^{-2}	7.06×10^{-3}			8.51×10^{-3}
toluene		6.42×10^{-3}	6.45×10^{-3}		6.39×10^{-3}	8.13×10^{-3}
benzene	5.80×10^{-3}	5.28×10^{-3}	5.50×10^{-3}		5.47×10^{-3}	5.45×10^{-3}
methyl ethylbenzene	7.39×10^{-3}	5.58×10^{-3}	4.91×10^{-3}			9.46×10^{-3}
1,1-dichloroethane		6.25×10^{-3}	5.78×10^{-3}	5.62×10^{-3}		4.27×10^{-3}
1,2-dichloroethane	6.28×10^{-4}	1.40×10^{-3}	1.07×10^{-3}		1.72×10^{-3}	2.06×10^{-2}
1,1,1-trichloroethane	1.76×10^{-2}	1.74×10^{-2}	3.02×10^{-2}	1.72×10^{-2}	2.00×10^{-2}	
1,1,2-trichloroethane	1.12×10^{-3}	9.10×10^{-4}	1.20×10^{-3}		8.28×10^{-4}	1.53×10^{-3}
<i>cis</i> -dichloroethylene		4.54×10^{-3}	7.51×10^{-3}	4.09×10^{-3}		
<i>trans</i> -dichloroethylene		9.45×10^{-3}	6.60×10^{-3}	9.38×10^{-3}		
tetrachloroethylene	1.86×10^{-2}	1.71×10^{-2}	2.12×10^{-2}	1.77×10^{-2}	1.60×10^{-2}	1.88×10^{-3}
trichloroethylene		1.02×10^{-2}	1.12×10^{-2}	9.58×10^{-3}	9.72×10^{-3}	2.23×10^{-3}
chloroethane		1.21×10^{-2}	1.13×10^{-2h}	1.11×10^{-2}		4.99×10^{-3}
carbon tetrachloride	2.94×10^{-2}	2.95×10^{-2}	2.21×10^{-2}	3.04×10^{-2}	2.74×10^{-2}	2.76×10^{-2}
1,3,5-trimethylbenzene	8.38×10^{-3}	6.73×10^{-3}	6.04×10^{-3}			1.44×10^{-2}
1,1-dichloroethylene	2.80×10^{-3}	2.59×10^{-2}	1.45×10^{-1}	2.61×10^{-2}	3.68×10^{-2}	
chloroform		4.21×10^{-3}	3.82×10^{-3}	3.67×10^{-3}	3.69×10^{-3}	3.94×10^{-3}
methylene chloride		2.96×10^{-3}	2.53×10^{-3}	2.19×10^{-3}	2.92×10^{-3}	2.54×10^{-3}
vinyl chloride		2.65×10^{-2}	2.32×10^{-2}	2.78×10^{-2}		2.05×10^{-2}

^aBubble column this study.

^bEPICS, this study (raw data).

^cVapor pressure and solubility (average values), Mackay and Shiu [7].

^dEPICS, Gossett [3].

^eDirect ratio, Leighton and Calo [4].

^fPrediction from UNIFAC activity coefficient, VLE database, Gmehling et al. [9]; and vapor pressure data, Reid et al. [10].

^gNon-equilibrium measurement.

^h20 °C.

[3] are quite good; all values agreed within 10%. This close agreement demonstrates reproducibility of the EPICS technique.

Leighton and Calo [4] used an equilibrium cell with continuous gas flow followed by direct analysis of both the air and water phases to determine Henry's constants. Of the twelve compounds common to both studies, results for nine of the compounds agree reasonably well (within 10%). Larger differences (15–42%), both positive and negative, are observed for the other three compounds (1,1,1-trichloroethane, 1,1,2-trichloroethane, and 1,1-dichloroethylene). This difference can be explained by the analytical problems discussed in Leighton's study and is not an artifact of the EPICS procedure.

Conclusions

Experimentally determined Henry's Law constants from this study agreed well with other reported values. However, for many of the compounds there were very few, if any, experimentally determined values with which to compare, and rarely were the values reported over a range of temperatures with confirming statistics. In many cases, agreement between experimentally determined Henry's Law constants and values estimated using the ratio of vapor pressure and aqueous solubility were quite good. However, depending on the intended use of the data (i.e., required accuracy) care should be exercised when using estimated values, as differences of over 400% were noted.

The EPICS procedure proved to be a simple and accurate technique for determining Henry's Law constants for a variety of organic chemicals. The constants reported have numerous environmental applications (fate and transport models, remedial action plans) and are generally within the 10% accuracy suggested by Mackay and Shiu [7].

Batch air stripping is comparable in accuracy to EPICS for dilute aqueous solutions of less volatile compounds. Long bubble retention times, however, may be required to achieve gas-liquid equilibrium for highly volatile constituents, and axial concentration gradients may arise when tall columns or low gas flow rates are employed.

UNIFAC model predictions, based upon calculated activity coefficients and vapor pressure data, were generally quite good, but an order of magnitude difference was noted for a few compounds. Extrapolation of the existing binary interaction database to the infinite dilution region is thought to be the main source of this error. Modifying this database as suggested by Kikic [14] using thermodynamic data taken in the dilute region may yield a significant improvement in the UNIFAC predictions. Such a modified binary interaction database offers a potentially more accurate method of predicting Henry's Law constant in environmental systems.

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