Determination of Infinite Dilution Activity Coefficients and 1-Octanol/Water Partition Coefficients of Volatile Organic Pollutants

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The characterization of pollutants is of growing interest as concerns about the environment increase. One parameter useful in predicting the fate of a chemical in the environment, the infinite dilution activity coefficient, has been determined here for several EPA priority pollutants in 1-octanol at 25 °C using a relative gas-liquid chromatographic measurement technique. A simple correlation has been developed relating the limiting activity coefficients of a species in pure water and in pure 1-octanol to its octanol/water partition coefficient. Agreement between the experimental results and published values is very good. The method developed here of computing the octanol/water partition coefficient from gas chromatographic measurements of its infinite dilution activity coefficients is an improvement over traditional partition coefficient determination methods in that it is easier and quicker, without a loss of accuracy. Furthermore, we show that this method is applicable to chemicals covering a large range of hydrophobicities ($1.0 < \log K_{ow} < 5.0$).

Introduction

The study of the fate and transport of volatile halogenated organic compounds in the environment is of interest as these chemicals have been widely used as industrial solvents and because they are appearing in water supplies. Many of these compounds have been classified as EPA priority pollutants because of their demonstrated carcinogenic and/or mutagenic potential.

One property which is useful for analyzing the fate and transport of pollutants in the environment is the activity coefficient, γ_i, of a species i defined as

$$\bar{f}_i^{L}(T,P,x_i) = x_i\gamma_i(T,P,x_i)\, f_i^{L}(T,P) \tag{1}$$

where $\bar{f}_i^{L}$ is the fugacity of the species in a liquid mixture, f_i^{L} is the pure component fugacity, and x_i is the species mole fraction. Since most pollutants found in the environment are in very small concentrations, a more relevant parameter is the infinite dilution activity coefficient, γ_i^{∞}, defined by

$$\lim_{x_i \to 0} \gamma_i = \gamma_i^{\infty} \tag{2}$$

In general, maximum deviations from ideal solution behavior are found at this limiting concentration.

From knowledge of the infinite dilution activity coefficient of a component in a solvent and its vapor pressure, its mole fraction-based Henry's law coefficient can be computed from

$$H_i(T) = \gamma_i^{\infty}(T,P,x_i)\, P_i^{\text{sat}}(T) \tag{3}$$

This parameter is useful for predicting the air/water distribution of a pollutant as well as for designing separation and purification equipment. Infinite dilution activity coefficient measurements made by techniques such as ebulliometry or the static cell are slow. In contrast, by using gas-liquid chromatography, without any loss in the accuracy, measurements may be made rapidly, using very small amounts of the chemical of interest.

Another property useful for the characterization of pollutant behavior in the environment is the octanol/water partition coefficient, K_{ow}, defined for a species i as

$$K_{ow} = C_i^{op}/C_i^{w} \tag{4}$$

where C_i^{op} and C_i^{w} are the concentrations of the species in an octanol-rich phase and in a water-rich phase, respectively, when 1-octanol, water, and a small amount of the species are allowed to come to equilibrium. It should be noted that in octanol/water partitioning at 25 °C, the water-rich phase is essentially pure water (99.99 mol % water) while the octanol-rich phase is a mixture of 1-octanol and water (79.3 mol % 1-octanol) (*1*).

Utilizing liquid molar volumes and liquid-liquid equilibrium relationships at 25 °C, the octanol/water partition coefficient of a species may be related to its infinite dilution activity coefficients in each of the phases by

$$K_{ow} = 0.1508\, \gamma_i^{\infty,w}/\gamma_i^{\infty,op} \tag{5}$$

when species i is at small concentration. Here the factor 0.1508 is the ratio of the total molar concentration of the 1-octanol rich phase (8.378 mol/L) to that of the water-rich phase (55.56 mol/L).

The determination of both Henry's law and octanol/water partition coefficients by traditional methods can be tedious and difficult. In particular, the octanol/water partition coefficient of a hydrophobic compound is usually determined by allowing a long equilibration time with slow stirring (*3*) so that emulsions or microemulsions do not form, followed by a difficult analysis of a hydrophobic chemical that is very dilute and during sampling and analysis may adsorb on surfaces. Therefore, we present here fast, accurate techniques for the determination both the Henry's law and octanol/water partition coefficients based on a relative gas chromatographic method.

Relative Gas-Liquid Chromatographic Technique

Here we use the relative gas-liquid chromatographic technique discussed by Orbey and Sandler (*3*) for the determination of the infinite dilution activity coefficient of a solute species in a solvent which has been loaded onto a packed column. In this relative method a solute is injected into the column simultaneously with a standard species whose

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infinite dilution activity coefficient in the solvent is known. One then measures the net retention time ratio, α_{BA}, defined by

$$\alpha_{BA} = \frac{t_B - t_{ref}}{t_A - t_{ref}} \tag{6}$$

where t denotes the retention times of the standard (B), the solute (A), and a reference chemical (ref) which does not interact with either the solvent loaded on the column or the column packing. This ratio is related to the infinite dilution activity coefficients of the solute and the standard components in the solvent as follows:

$$\frac{\gamma_A^{\infty}}{\gamma_B^{\infty}} = \left(\frac{P_B^{sat}}{P_A^{sat}}\right)\alpha_{AB}\phi \tag{7}$$

where P_i^{sat} denotes a species saturation pressure at the column operating temperature and ϕ is the correction factor for gas-phase nonidealities as defined in ref 3.

When the column is operated at low pressure, as we do, the gas-phase nonidealities may be neglected and the governing equation simplifies to

$$\frac{\gamma_A^{\infty}}{\gamma_B^{\infty}} = \left(\frac{P_B^{sat}}{P_A^{sat}}\right)\alpha_{AB} \tag{8}$$

Thus, if the infinite dilution activity coefficient of a species in a given solvent is known, the limiting activity coefficient of a second species can be determined on the basis of knowledge of the saturation pressures and the relative net retention times of the substances through a column loaded with the solvent. Further, even if the vapor pressure of the test component A is not known, from eqs 3 and 8 its Henry's Law coefficient can still be found from

$$H_A = \gamma_A^{\infty}P_A^{sat} = \gamma_B^{\infty}P_B^{sat}\alpha_{BA} = H_B\alpha_{BA} \tag{9}$$

In a previous analysis (*4*), this technique was used to determine the aqueous infinite dilution activity coefficients of halogenated aliphatic EPA priority pollutants. The results showed that this relative gas chromatographic technique is very rapid and accurate. In this study, the method is used to study some of the same components in 1-octanol.

Experimental Method

To determine the net retention times of solutes through the column, either a 1 or a 3-ft-long (depending on the retention time) 1/8-in.-diameter Chromosorb GHP stainless steel packed column was loaded with 1-octanol by aspiration. Other packings, as long as they can be coated with 1-octanol, could be used as well. An HP 5890A gas–liquid chromatograph with a flame ionization detector (FID) was used with an HP 33390A integrator. All chemicals were obtained from Aldrich Chemical Co. Ltd., with the exception of 1,1-dichloroethane which was obtained from American Tokyo Kasei, Inc. Methane was employed as the reference gas as it did not interact with the column packing or solvent. The column temperature was held at 25 °C by the combined use of externally supplied cooling and internal heating. Flow rates through the column were maintained at approximately 20 mL/min for the helium carrier gas and 30 and 200 mL/min, respectively, for the hydrogen and compressed air to the FID.

In this work hexane was chosen as the standard chemical; its infinite dilution activity coefficient in 1-octanol was reported by Tiegs et al. (*5*) to be 2.81. Consequently, this substance was injected into the column simultaneously with each of the solutes being studied. The procedure involved first completely loading the column with the solvent. The loaded column was then installed in the chromatograph, and after stable operating conditions were attained, approximately 75 μL of methane was injected to determine the reference retention time, t_{ref}. Then, approximately 0.04 μL samples were injected which consisted of the solute and the hexane standard. Several substances could be studied at the same time by mixing before injection provided that sufficient peak resolution was maintained. Periodically methane reference gas was injected between analyses to check on the stability of the operating conditions and for variations in t_{ref} as a result of the small amount of 1-octanol being continually, but very slowly, stripped off the column. In some cases, the substances under study had a retention time similar to that of the hexane standard. For these chemicals, either pentane or heptane was used as the standard; this is noted in the tables which follow.

Table 1. Infinite Dilution Activity Coefficients in 1-Octanol at 25 °C[a]

substance	vapor pressure (bar)	net retention time ratio	γ_i^{∞}	lit. γ_i^{∞}
CCl_4	0.152	0.486	1.83	1.74 (20 °C) (*5*)
$CHBr_2Cl$	0.0185	0.212	2.13	
$CHCl_3$	0.262	0.465	1.02	0.95 (20 °C) (*5*)
CH_2Br_2	0.0603	0.227	2.15	
CH_2Cl_2	0.584	1.606	1.57	1.56 (20 °C) (*5*)
C_2HCl_3	0.0983	0.276	1.60	
cis-1,2-$Cl_2C_2H_2$	0.270	0.688	1.46	
1,1,1-$Cl_3C_2H_3$	0.165	0.572	1.98	
1,1,2-$Cl_3C_2H_3$	0.0310	0.325	1.94	
1,1-$Cl_2C_2H_4$	0.303	0.345	2.01	
1,2-$Cl_2C_2H_4$	0.105	0.494	2.68	
1,2-$Cl_2C_3H_6$	0.0693	0.313	2.58	
n-C_5H_{12}	0.684	3.085	2.58	2.62 (*5*)
cyclohexane	0.132	0.538	2.34	2.24 (*8*)
n-C_7H_{16}	0.0607	0.325	3.05	3.06 (*5*)

[a] All substances are based on a hexane standard material with the exceptions of 1,1-dichloroethane which used pentane and chlorodibromomethane and 1,1,2-trichloroethane which are relative to heptane.

Infinite Dilution Activity Coefficient in 1-Octanol

The vapor pressures needed for the calculation in eq 8 were obtained from Antoine-like correlations in the Design Institute for Physical Property Data (DIPPR) compilation available on the Scientific and Technical International Network (STN) (*6*). In the case of chlorodibromomethane, however, such data were unavailable. Therefore, the vapor pressure of this substance was estimated using group contribution methods outlined in Reid et al. (*7*). Following the procedure suggested in that reference, the Joback method was employed for critical property and normal boiling point estimation, and the Lee–Kesler correlation for the acentric factor. Then, with propane and octane as references, a two-reference fluid vapor pressure calculation was performed.

The results of the infinite dilution activity coefficient determination in 1-octanol using the relative gas chromatographic technique are listed in Table 1 along with the vapor pressures used for each substance, the measured net retention time ratio α_{BA}, and comparisons with available published infinite dilution activity coefficients.

Agreement between the values found here and those determined by other methods is excellent, and within the error bounds of the various methods used. The relative gas chromatographic method presented here has obvious advantages over traditional equilibrium measurements which take hours or days, compared to the minutes involved in our measurements. Also, the method used here requires only inexpensive equipment, and even though analytical grade chemicals were used in this study, this was not necessary

Table 2. Comparison of the Activity Coefficient Ratio, π, and Octanol/Water Partition Coefficients Found in the Literature

substance	π	$\log \pi$	lit. $\log K_{ow}$
CCl_4	770	2.89	2.64 (*9*)
$CHCl_3$	122	2.09	1.97 (*10*)
CH_2Cl_2	23.3	1.37	1.25 (*11*)
C_2HCl_3	468	2.67	2.29 (*12*)
1,1,1-$Cl_3C_2H_3$	400	2.60	2.49 (*12*)
1,1,2-$Cl_3C_2H_3$	117	2.07	2.42 (*11*)
1,1-$Cl_2C_2H_4$	78.1	1.89	1.79 (*12*)
1,2-$Cl_2C_2H_4$	35.4	1.55	1.48 (*12*)
pentane	5787	3.76	3.39 (*12*)
cyclohexane	5370	3.73	3.44 (*12*)
hexane	19295	4.29	4.11 (*10*)
heptane	98819	4.99	4.66 (*11*)

since impurities will separate from the desired species in the gas chromatograph. The low concentrations of impurities are easily distinguished from the main species by their small peaks, and several components can be studied simultaneously without a loss in accuracy as long as sufficient peak resolution is maintained. Finally, compared to traditional methods, only extremely small sample sizes are necessary; typically, a chemical could be completely studied with less than 1 μL of material, and the substances used are incinerated in the flame ionization detector, thereby minimizing the waste disposal problem.

Octanol/Water Partition Coefficient

To use eq 5 to compute the octanol/water partition coefficient, it is necessary to have the infinite dilution activity coefficient of a species in pure water and in water-saturated octanol. The values of γ^∞ in water for the substances studied here were determined by us previously (*4*). Thus, our first attempt to use eq 5 was to fit the measured infinite dilution activity coefficients in pure water and in pure 1-octanol, and the water + 1-octanol mutual solubility data with an activity coefficient model to determine the infinite dilution activity coefficient in water-saturated 1-octanol, and from that the octanol/water partition coefficient. However, we found that because of the large asymmetry on the system (the solute infinite dilution activity coefficient in water was orders of magnitude larger than in pure octanol), the resulting predictions were very model dependent. Also, because of the mixture asymmetry, there is a large difference between the values of γ^∞ in the water-saturated octanol and pure octanol.

Therefore, we decided instead to look for a direct correlation between the measured infinite dilution activity coefficients and the octanol/water partition coefficient. Consequently, we defined an activity coefficient ratio, π, at 25 °C as

$$\pi = 0.1508\gamma_i^{\infty,w}/\gamma_i^{\infty,o} \qquad (10)$$

where the activity coefficients are those for the solute at infinite dilution in pure water and in pure 1-octanol. This ratio was calculated on the basis of the data obtained here and the aqueous infinite dilution activity coefficients presented earlier (*4*). In the latter case the values at 25 °C were interpolated from the experimental data we obtained over a range of temperatures using the expression

$$\ln \gamma^\infty(T) = \frac{A}{RT} + C \qquad (11)$$

where A and C were obtained by correlating the data. The calculated activity coefficient ratios for the solutes we considered together with their published octanol/water partition coefficients are listed in Table 2 and shown in Figure 1.

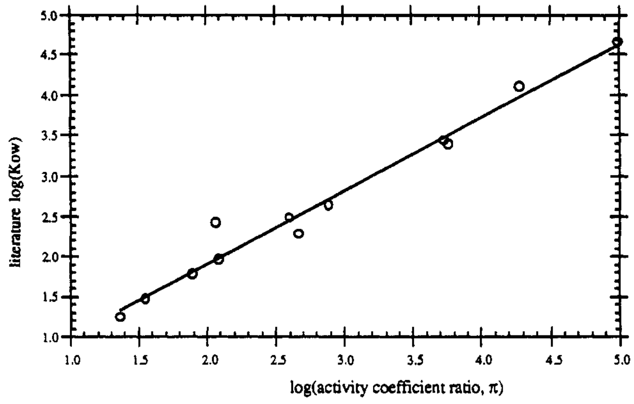

Figure 1. Correlation of the logarithm of the activity coefficient ratio, π, defined in eq 10 to the published values of the octanol/water partition coefficient. The line is the correlation $\log K_{ow} = 0.10 + 0.91 \log \pi$.

Table 3. Test of the Correlation Developed between Pure Solvent Limiting Activity Coefficients and the Octanol/Water Partition Coefficient with Results from the Literature

substance	$\gamma_i^{\infty,w}$	$\gamma_i^{\infty,o}$	$\log \pi$	lit. $\log K_{ow}$	calcd $\log K_{ow}$
benzene	2.48×10^3	2.07	2.26	2.15 (*12*)	2.16
1-hexene	8.43×10^4	2.54	3.70	3.39 (*11*)	3.47
toluene	6.26×10^3	2.18	2.64	2.73 (*12*)	2.50
1,2-dimethylbenzene	3.07×10^4	2.38	3.29	3.12 (*14*)	3.09
1,3-dimethylbenzene	3.38×10^4	2.34	3.34	3.20 (*14*)	3.14
ethylbenzene	3.57×10^4	2.49	3.33	3.15 (*12*)	3.13
1-octene	2.31×10^6	3.00	5.06	4.57 (*13*)	4.70
octane	9.08×10^6	3.36	5.61	5.18 (*10*)	5.21
isopropylbenzene	1.16×10^5	2.66	3.82	3.66 (*12*)	3.58

[a] Aqueous infinite dilution activity coefficients were calculated from solubility data (*1*) while activity coefficients in 1-octanol were obtained from Tiegs et al. (*5*).

Clearly there is a direct correlation between the values of $\log \phi$ and $\log K_{ow}$. In particular, it is possible to determine the octanol/water partition coefficient of a species on the basis of only a knowledge of its infinite dilution activity coefficients in pure water and in pure 1-octanol from the following relationship:

$$\log K_{ow} = 0.10 + 0.91 \log (0.1508\gamma_i^{\infty,w}/\gamma_i^{\infty,o}) \qquad (12)$$

or equivalently

$$\log K_{ow} = -0.65 + 0.91 \log \gamma_i^{\infty,w} - 0.91 \log \gamma_i^{\infty,o} \qquad (13)$$

The infinite dilution activity coefficients are, as we have shown here and in our previous work (*4*), much easier to measure than the octanol/water partition coefficient. It should be emphasized that we have measured the infinite dilution activity coefficient of a chemical in pure water and in pure 1-octanol, while the octanol–water partition coefficient is related to the infinite dilution activity coefficients in water and water-saturated 1-octanol. Since the infinite dilution activity coefficient of a hydrophobic chemical is larger in water-saturated 1-octanol that pure 1-octanol, the coefficient in the correlation of eqs 12 and 13 should be less than unity, and this is what we find (0.91).

To test the validity of this simple correlation for other compounds, aqueous solubility data (*1*) reported for nine aromatic compounds and C_8 alkanes with varying hydrophobicities and their infinite dilution activity coefficients in 1-octanol from Tiegs et al. (*5*) were used to calculate the activity coefficient ratio of eq 10, and these values are given in Table 3. The activity coefficient ratios and the correlation of eq 12 based only on our experimental data are plotted in Figure 2.

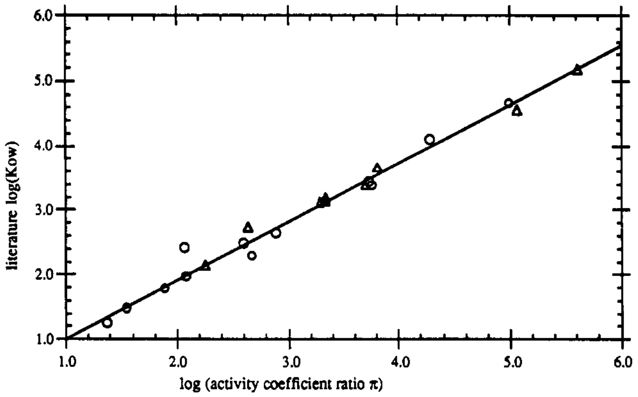

Figure 2. Test of the correlation between the octanol/water partition coefficient and the activity coefficient ratio, π. The circles are from our experimental data which are the basis for the correlation given by the line, while the triangles are data from the literature (see Table 3) not used in developing the correlation.

Table 4. Prediction of Octanol/Water Partition Coefficients Based on the Simple Correlation Developed Here and the Infinite Dilution Activity Coefficients We Have Measured

substance	π	$\log K_{ow}$	substance	π	$\log K_{ow}$
$CHBr_2Cl$	139	2.04	*cis*-1,2-$Cl_2C_2H_2$	84.0	1.85
CH_2Br_2	57.8	1.70	1,2-$Cl_2C_3H_6$	120	1.98

The simple correlation developed here, eq 12, agrees very well with literature values for the octanol/water partition coefficient. Also, we see that this correlation is applicable to solutes covering a wide range of hydrophobicities. Using this simple correlation, the octanol/water partition coefficients were calculated for several chemicals we studied whose values have not previously been reported. The data used for this calculation were the pure solvent infinite dilution activity coefficients determined by the relative gas chromatographic technique in ref 4 and in this study. These are given in Table 4.

Conclusions

A relative gas chromatographic technique for the determination of infinite dilution activity coefficients presented earlier was used here for the case in which the solvent was 1-octanol. Results show good agreement with values previously reported in the literature, and the method was used to obtain infinite dilution activity coefficients for some EPA priority pollutants in 1-octanol. The results of these measurements complement those of a previous study using the same technique in which infinite dilution activity coefficients for the same species in water were measured. A simple, accurate correlation between the ratio of these pure solvent infinite dilution activity coefficients and the octanol/water partition coefficient was then developed. This correlation was then used to compute the octanol/water partition coefficients for four halogenated aliphatic pollutants which had not been previously reported.

The relative gas chromatographic technique has several advantages for the determination of infinite dilution activity coefficients and octanol/water partition coefficients. First, the method is very fast and accurate. Also, several compounds may be studied simultaneously, resulting in an increase in the rate at which data can be obtained. Next, minimal cost is associated with the measurements since very small sample quantities are needed, high analytical grade chemicals are not required, and the substances are incinerated in the measurements so that there is no disposal problem.

Glossary

C_i	concentration (g/L)
f_i^L	pure component liquid fugacity (bar)
$\bar{f}_i^L$	liquid mixture fugacity (bar)
H	Henry's law coefficient (bar)
$\bar{H}_i^{ex}$	partial molar excess enthalpy (J/mol)
K_{ow}	octanol/water partition coefficient
P	total system pressure (bar)
P^{sat}	saturation pressure (bar)
R	universal gas constant [(J/mol)/K]
T	temperature (K)
t	column retention time (min)
x	component mole fraction

Greek Symbols

α_{BA}	retention time ratio
ϕ	nonideality term in the relative gas chromatographic technique
γ	activity coefficient
π	infinite dilution activity coefficient ratio

Superscripts

o	pure 1-octanol
op	octanol-rich phase
w	water phase; pure water
∞	infinite dilution

Subscripts

A	species being investigated
B	standard species whose γ_i^∞ in the solvent is known
i	species i
ref	reference gas which does not interact with the column packing or coating

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